UNIVERSITÀ DEGLI STUDI DI TORINO

SCUOLA DI DOTTORATO

DOTTORATO IN
SCIENZE AGRARIE, FORESTALI E ALIMENTARI

CICLO: XXXIV

AMMONIA AND PARTICULATE MATTER FROM THE AGRICULTURAL SECTOR: ASSESSMENT OF EMISSIONS AND MITIGATION MEASURES

Jacopo Maffia

Docente guida:
Prof. Paolo Balsari

Coordinatore del Ciclo:
Prof.ssa Eleonora Bonifacio

Correlatore:
Prof. Elio Dinuccio

ANNI
2019; 2020; 2021

1. INTRODUCTION

1.1. Particulate Matter

The term Particulate Matter (PM) refers to the solid and liquid particles particles which are suspended in the atmosphere (EEA, 2021; US EPA, 2021; WHO, 2006). Atmospheric particulate is classified based on particles dimension, with the definition of so-called particle fractions. The size classification of particles, as of today use, is based on what is called the aerodynamic diameter, which is the diameter (in μm) of an ideal sphere having the same aerodynamic characteristics of particles in question; therefore, it describes, more than the actual dimension of particles, their behavior in the air and their capacity to follow tortuous air streams, which increases at lower diameter sizes. The main particle fractions which are normally distinguished are Total Solid Particles (TSP), PM_{10} and $PM_{2.5}$, although there are several studies focusing on even smaller fraction ranges such as PM_1 (Polichetti et al., 2009; Vecchi et al., 2004). TSP refers to all particles which are indefinitely suspended in the air (the reference diameter is ranging from <30 to <50 μm). PM_{10}, $PM_{2.5}$ and PM_1 particles, instead, are particles with aerodynamic diameter of <10, <2.5 and <1.0 μm respectively. The rationale behind this distinction is the fact that a particle size is inherently linked with its capacity to penetrate the respiratory system and cause health issues. PM is, in fact, considered one of the main atmospheric pollutants, with negative effects on human health. In particular, small particles (<10 μm) are able to infiltrate human respiratory system and cause health effects (Pope et al., 1992, 1991); coarser particles, instead, are considered less dangerous from a heath perspective especially in terms of long term effects (Brunekreef and Forsberg, 2005). Due to its relevance for health, in the last 20 years, the scholar interest for particulate matter has raised consistently and a raising number of papers has been published each year, with an increasing number of citations (Figure 1). Over the years, the literature has identified a clear relationship among the concentration of PM_{10} and $PM_{2.5}$ in the air we breathe and the incidence of several diseases, such as cancer, respiratory issues and strokes. Periodical reports of the Word Health Organization (WHO) present average figures on the incidence of PM pollution on certain diseases, providing also an estimation of the loss in life expectancy due to PM exposure (WHO, 2006).

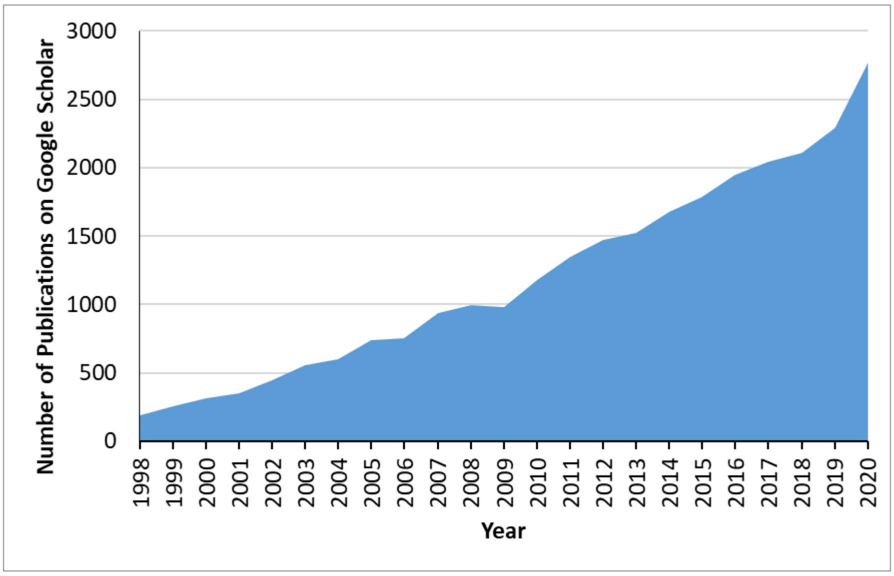


Figure 1. Number of publications on Google Scholar by year (Query: "particulate matter" AND/OR PM10 AND/OR PM AND/OR dust). The database was consulted on the 7th of August 2021.

When considering the health effects of PM particles, it is crucial to acquire knowledge not only on their size (aerodynamic characteristics), but also on their intrinsic chemical and biological properties (Kelly and Fussell, 2012; Womiloju et al., 2003). These properties depend merely on the particle sources and formation processes. In this sense a fundamental distinction must be made among primary and secondary PM. In fact, primary PM is composed by those particles that are generated from direct emission sources, such as chimneys, fires, fuel burning activities or wind erosion. Secondary PM particles are instead formed though chemical reactions happening in the atmosphere, arising from chemical reactions of primary pollutants (Erisman and Schaap, 2004; Feng et al., 2012).

The nature of PM, its origin and chemical composition can vary geographically and also seasonally (Halek et al., 2010; Zhang et al., 2018; ZhiLing et al., 2009). Therefore, the study of PM characteristics and PM emission sources is particularly complex and several questions remain unanswered regarding particulate matter, its formation and transport dynamics and its effects on human health and environment.

1.1.1. Particulate matter emissions and sources

Particulate matter originates from a variety of natural and anthropogenic processes. Natural processes are mostly related to wind erosion, which is particularly relevant in desert regions, volcanic events, sea salt formation, naturally occurring fires and combustions (Sharratt and Auvermann, 2014). Also, the natural disaggregation of vegetal biomass and other phenomena such as pollen transport do contribute to the overall PM count. Moreover, some organic matter degradation processes or other chemical reactions commonly occurring in the atmosphere do contribute to the formation of PM precursors, leading to secondary PM formation. Anthropogenic processes contributing to PM are as many as the natural ones and, due to anthropogenic intervention, some of the natural pathways to PM formation may also be enhanced (Ortega-Rosas et al., 2021; Sousa et al., 2008).

Some of the main types of PM usually find in the air are summarized in Figure 2, which also highlights how particle dimension is dependent from its source. In general, particle deriving from combustion processes, such as fires and exhaust gases, or from secondary formation, such as sulphates, are in PM_1-$PM_{2.5}$ range. Erosion particles and particles from paved and unpaved road dust are instead larger, being mostly in the $PM_{2.5}$-PM_{10} range.

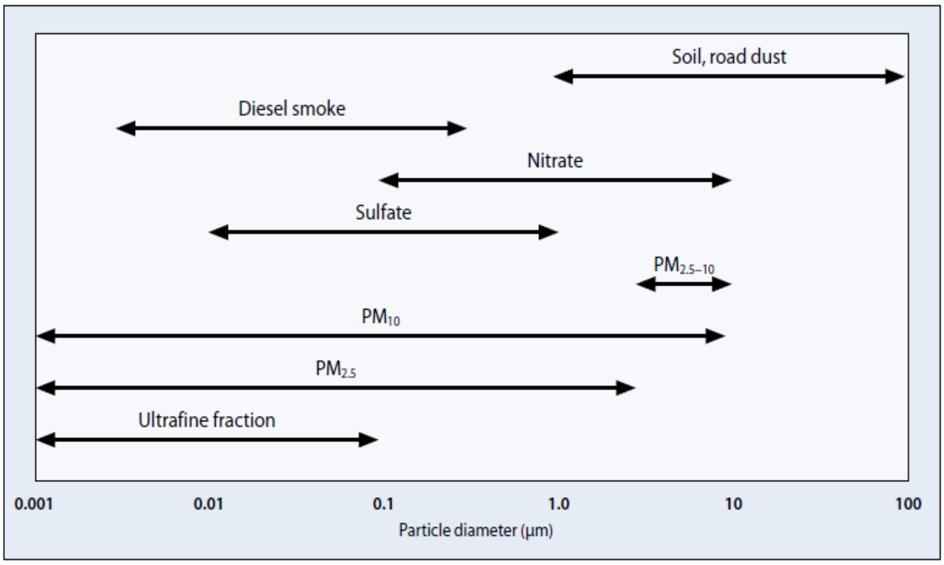


Figure 2. Particle diameter of different types of PM (source: WHO, 2006).

The European Environmental Agency (EEA) provides yearly estimations of total PM_{10} and $PM_{2.5}$ emissions from EU-32 countries (Figure 3). In the years among 1990 and 2010 PM_{10} emissions in the EU dropped significantly from around 2750 kt to less than 2500 kt, with $PM_{2.5}$ constituting the largest share of total emitted particles. The sources of these emissions, accounted for in the year 2010, are several (Figure 4; EEA, 2012). The most emitting sector for both PM_{10} and $PM_{2.5}$ has been the “Commercial, institutional and households” sector, followed by “Road transport” and “Waste” sectors. Agriculture also played a relevant role, contributing for 10.3% to the overall PM_{10} emissions, which is a higher contribution than the “Energy production and distribution” one. Although this may seem counter-intuitive, the small footprint of the energy sector, in terms of PM emissions, is due to the fact that this sector was the one showing the grater improvement and emission reduction in the 1990-2010 period both in terms of energy use from industry (-57.3 and -50.6% of PM_{10} and $PM_{2.5}$ emissions respectively; Figure 5-6) and of energy production and distribution (-65.2 and -67.8% of PM_{10} and $PM_{2.5}$ emissions respectively). Agricultural emissions, instead, remained almost unaltered, with a slight increase in PM_{10} emissions (+9.2 %) and a slight decrease of $PM_{2.5}$ (-8.8%). According to the 2017 inventory by EEA (EEA, 2019), the current situation is still similar, if not worse in relative terms, with agriculture accounting for 15% of total PM_{10} emissions and 5% of total $PM_{2.5}$. Although the relative increase of agricultural contribution is ascribable to the mitigation of emissions from other sectors, it appears evident that the agricultural sector has to limit its contribution to PM emissions.

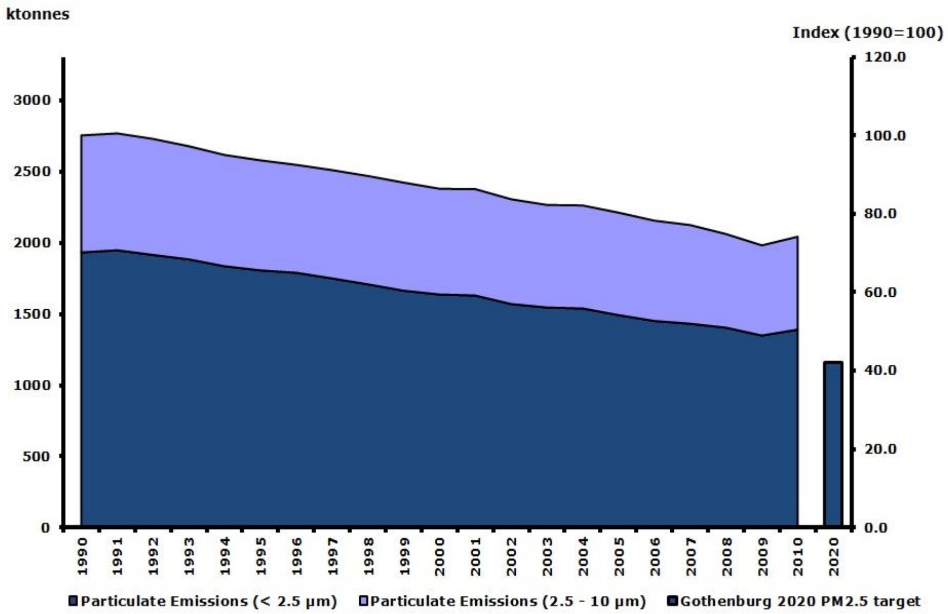


Figure 3. Total $PM_{2.5}$ emissions from European countries in the 1990-2020 period (source: EEA, https://www.eea.europa.eu/data-and-maps).

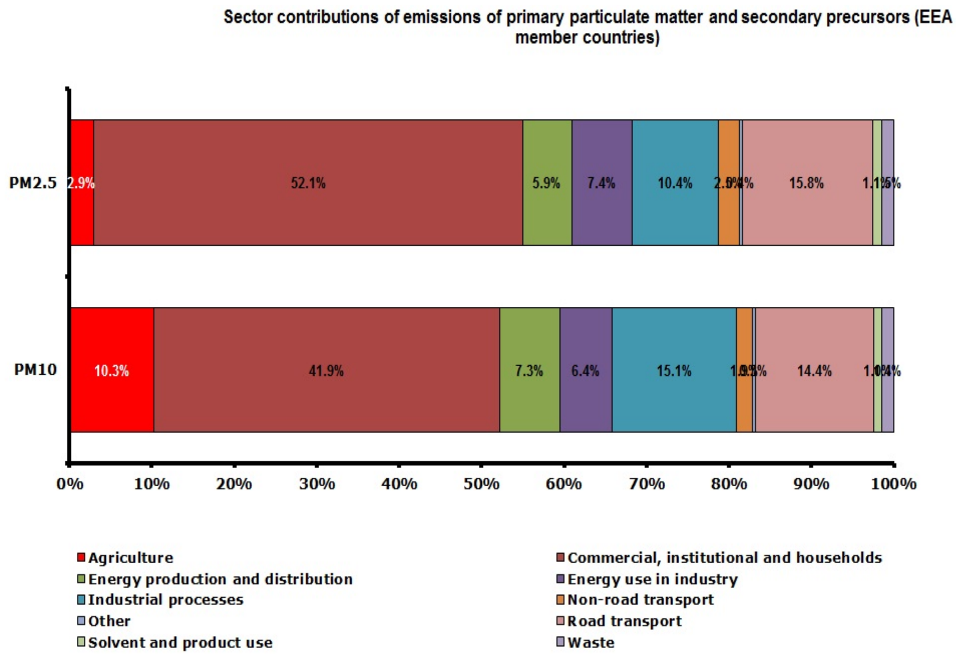


Figure 4. Contribution of different sector to the anthropogenic emissions of PM_{10} and $PM_{2.5}$ during the 1990-2010 period (source: EEA, https://www.eea.europa.eu/data-and-maps).

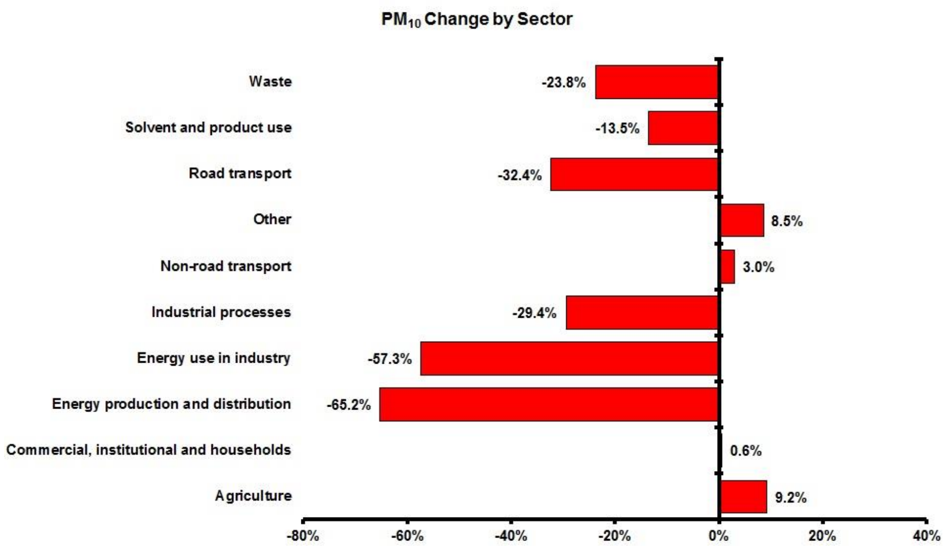


Figure 5. PM_{10} change by sector in the 1990-2010 period (source: EEA, https://www.eea.europa.eu/data-and-maps).

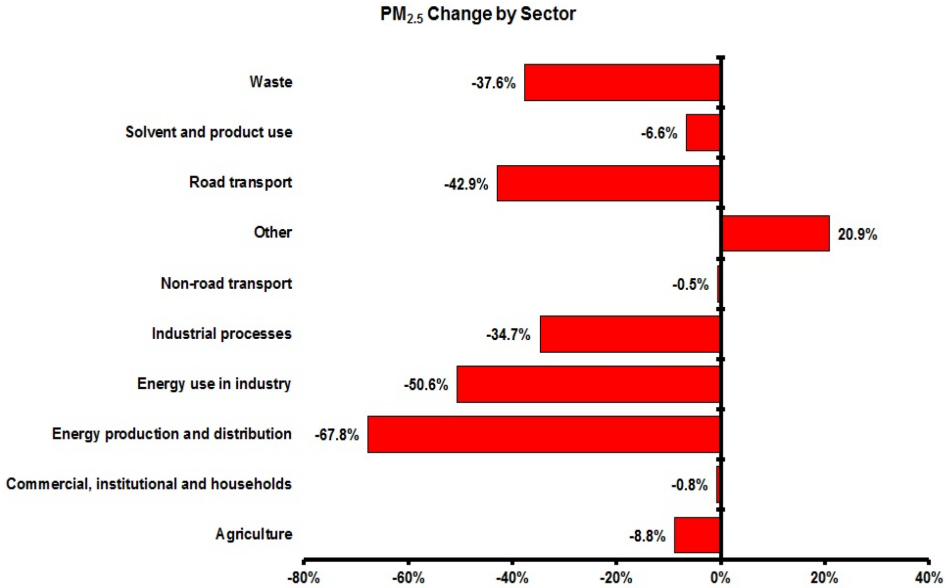


Figure 6. $PM_{2.5}$ change by sector in the 1990-2010 period (source: EEA, https://www.eea.europa.eu/data-and-maps).

1.1.2. Particulate matter related health effects

Particulate matter exposure has been associated with numerous health issues. Health concerns are linked both to short term and long term PM exposure, although clearly the concentration levels triggering short and long term effects are very different, leading to the establishment of different regulatory thresholds on daily and yearly basis (WHO, 2006; Giannadaki et al., 2016). It is also important to highlight that PM exposure does not necessarily lead to immediate or recognizable health effect in the entire population exposed. In fact, most of the exposed people usually present only mild symptoms (Figure 7). The most severe health effects are normally observed in people who are particularly susceptible due to previous medical conditions (WHO, 2006). Moreover, when considering the effect of PM environmental concentration on human health, it is necessary to reason in terms of general exposure and, therefore, to account to lifestyle differences. In fact, in different areas of the world, people may be passing more time indoor or outdoors and, consequently, it will be the exposure to one of these two environments to be most detrimental for their health (Hoek et al., 2008; Williams et al., 2000).

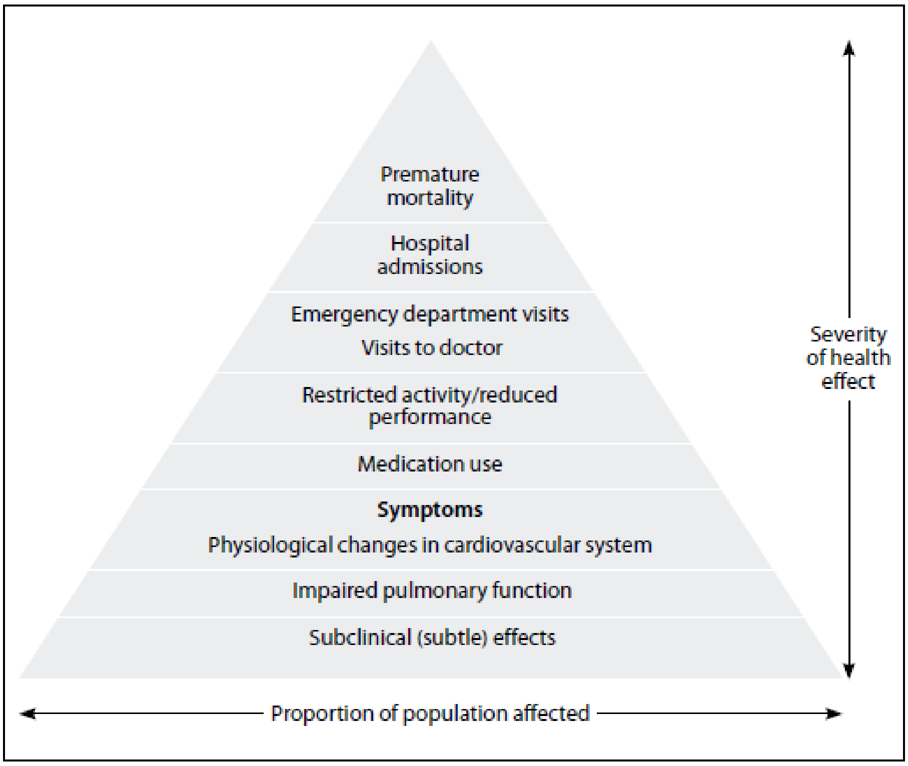


Figure 7. Pyramid representing the relation among severity of health effects from air pollution and the proportion of population affected (source: Aphekom Proceedings, 2011).

There is a high number of studies relating both PM_{10} and $PM_{2.5}$ concentrations to several health consequences, ranging from minor physiological alterations to strokes and even death (Barzeghar et al., 2020; Pope, 2007; Mar et al., 2006; Pope, 1996; Pope et al., 1991; Tong et al., 2020). Increased levels of air pollution for short periods of time were, in fact, shown to cause an increase in morbidity and mortality (Orellano et al., 2020). The regional agency for environmental protection of the Italian region Emilia Romagna (ARPAE) provided a table (Table 1) summarizing air pollution related health issues from both short and long-term air pollution exposure. A more specific figure of mortality increases due to 10 $\mu g\ m^{-3}$ increments of PM_{10} concentration, provided by the Health Effects Institute (HEI; https://www.stateofglobalair.org/) is presented in Figure 8.

Table 1. Short and long-term health effects caused by 10 µg m^{-3} increments in PM_{10} concentration (source: ARPAE, https://arpae.it, consulted in August 2021)

Health effects		**Increment of health effects frequency (%) per 10 µg m^{-3} of PM_{10}**	**Confidence intervals**
Short-term symptoms	Bronchodilators use	3	2 - 4
	Cough	3	3 - 5
	Low respiratory airways symptoms	3	1.8 - 4.6
	Reduction of lung capacity in adults (expiratory peak)	-13	0.17 - 0.09
	Hospitalization for respiratory issues	0.8	0.5 - 1.1
Long-term symptoms	Daily mortality (accidental deaths excluded)	0.7	0.6 - 0.9
	Mortality increase	10	3 - 18
	Bronchitis	29	-
	Reduction of lung capacity in children (expiratory peak)	-1.2	-2.3 - 0.1
	Reduction of lung capacity in adults (expiratory peak)	-1	-

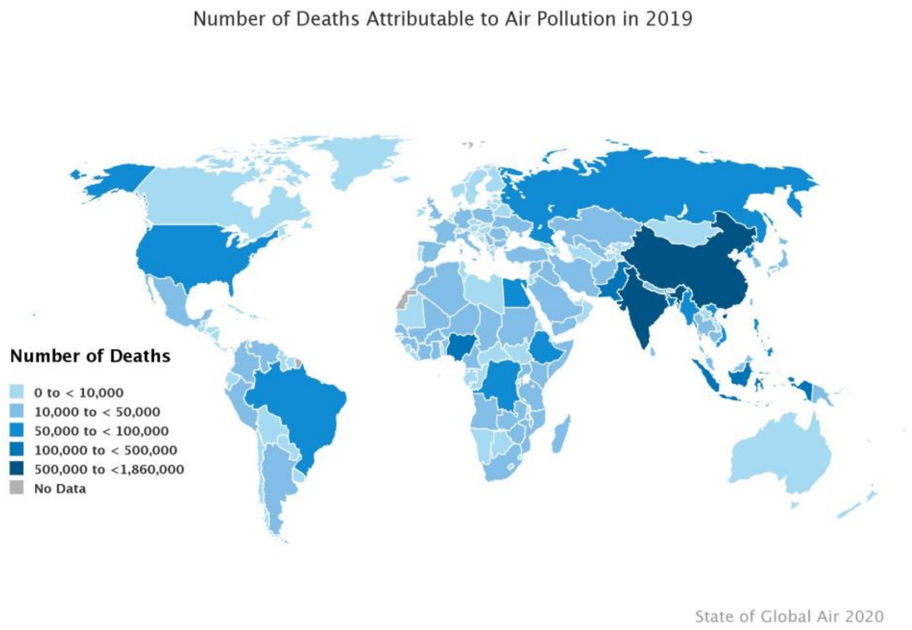


Figure 8. Number of deaths attributable to air pollution in 2019 worldwide (source: HEI, Health Effects Institute).

1.1.3. Particulate matter guidelines: the current situation

The WHO periodically publishes air quality guidelines providing objectives in terms of actual PM_{10} and $PM_{2.5}$ concentration levels to be reached in order to reduce health risks. The guidelines contain three main concentration levels, described as Interim Targets (IT) number 1 (IT-1, ≤35 μg/m^3), 2 (IT-2, ≤25 μg/m^3), 3 (IT-3, ≤15 μg/m^3), scaling down to the guideline level of 10 μg/m^3. The world map presenting average $PM_{2.5}$ concentration in 2017 and compliance with WHO standards is shown in Figure 9. In 2017, around 54% of the world population lived in places where the IT-3 target concentration was exceeded, especially in developing countries.

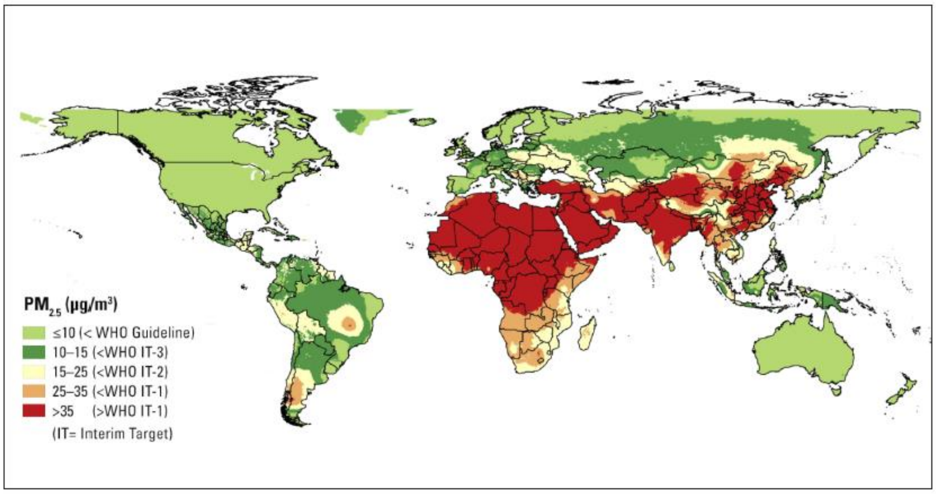


Figure 9. WHO interim targets for PM2.5 concentration worldwide (source: HEI, Health Effects Institute).

1.2. Main particulate emission sources from the Agricultural sector

Particulate matter emissions can be distinguished in primary and secondary particles. Primary particles are generated by physical phenomena such the disaggregation of soil by wind erosion or biomass combustion, Secondary particles are instead originated through chemical reaction occurring in the atmosphere among gaseous and solid compounds. The agricultural sector is responsible for the production of both primary and secondary PM. Primary PM emissions can be ascribed both to crop production activities and to livestock management, while secondary aerosol precursors (compounds that concur in the formation of secondary PM) are mainly derived from livestock management.

1.2.1. Primary PM emission from the Agricultural sector

Agricultural sources of PM are of many different types and can be classified according to different criteria. A first distinction to be made is among primary and secondary PM sources. Primary PM sources can be furtherly distinguished among point sources and area sources. Point sources are characterized by having a specific point of emission, such as a chimney (e.g. in cereal drying facilities) or the outflow opening of a livestock barns. Emissions from this kind of sources are easier to measure and are normally more constant over time. Area source emissions, instead, are characterized by being difficult to assess, due to the open field conditions that characterize these sources. Moreover, open field emissions normally occur in correspondence of specific events, happening once or twice per year and are, therefore, discontinuous and seasonal (Chen et al., 2017; Faulkner, 2013).

PM emissions from cropping operations are mainly due to the resuspension of soil particles due to the passage of heavy machineries, but also to the pulverization of biomass (e.g. crop residues or animal wastes) and to crop residue burning. In particular, the main agricultural operations during which fine particles are released in the atmosphere are soil tillage, harvesting, burning of crop residues, sowing, manure and fertilizer distribution (Sharrat and Auvermann, 2014).
The amount of fine particles produced varies consistently among the different operations. Moreover, there are many parameters, such as environmental conditions (Avecilla et al., 2017), soil and crop type (Madden et al., 2010), soil moisture (Funk et al., 2008; Madden et al., 2010) and mechanical implements (Clausnitzer and Singer, 1996), that can strongly influence the quantity and the physical and chemical characteristics of emitted PM. According to Pattey (2015), who has performed a survey on agricultural PM emissions in Canada, tillage is the operation that contributes the most to the total agricultural emissions. Similarly, Chen et al. (2017) have observed that in Northeastern China tillage and harvesting account for the three fourth of the total agricultural emissions, with tillage being the main pollution source. Also in California, although the environmental conditions are very different from the ones of the above-cited surveys, tillage and land preparation have been considered to be the main agricultural PM_{10} source, accounting for the 65% of total agricultural emissions (Clausnitzer and Singer, 1997). Differently, Amann et al. (2012) have estimated that the main agricultural source of PM emissions in Europe is the burning of residues, which, according to their estimations, contributes to the total PM_{10} and $PM_{2.5}$ emissions for the 7.6% and 9.6% respectively, while ploughing tilling and harvesting altogether account only for the 4.7% (PM_{10}) and 1.5% ($PM_{2.5}$) of total emissions. In the African continent agricultural biomass burning emissions are recognized as the second most important source of PM, following natural mineral dust emissions by wind erosion, and being responsible for half of the premature deaths in Central Africa (Bauer et al., 2019). Similarly, studies carried out in India suggest that also in that continent the main agricultural contributor to PM emissions is biomass burning (Pandey et al., 2014; Guo et al., 2017).

Emissions from agricultural soils caused by wind erosion are also accounted for as agricultural PM emissions. These emissions represent a higher contribution than tillage to the overall soil-derived emissions in most countries.

A consistent amount of PM emissions also derives from animal rearing facilities. These emission sources can be described as point sources which generate an almost continuous emission flux throuthrough the year. A relevant amount of PM produced from livestock systems derives from feeds and bedding materials, but also dried manure and dead skin particles can be found in barn particulate (Cambra-López et al., 2010). The quantity of particles emitted from livestock systems strongly depends on the animal specie and on the rearing system (Winkel, 2016).

Depending on the emitting source, particles differ greatly both for their physical and chemical characteristics. Soil originated particles, for example, are generally in the $PM_{2.5}$-PM_{10} range and are characterized by being mostly inorganic. Particles deriving from livestock rearing facilities are generally smaller (mostly below 2.5 µm Ø) and are composed by larger amounts of organic particles deriving from feed, dry manure and dead skin (Cambra-López et al., 2010). Another type of particles commonly generated in agriculture is represented by those produced through combustion of residues and straws. The composition of residue burning particles can vary greatly depending on the crop being burned, but general traits are the small particle size (PM_1 range) and the presence of black-carbon, organic compounds or even pesticides (Fang et al., 2017; Hafidawati et al., 2018; Zhang et al., 2015), resulting in higher health risks. A more comprehensive overview on PM emissions from open field cropping activities is provided in the review article presented in paragraph 3.1 of this thesis.

1.2.2. Mitigation measures for agricultural Particulate Matter emissions

The literature on mitigation measures for PM emissions from open field cropping operations shows a lack of information. This is partly due to the fact that developing and evaluating PM mitigation measures for open field agricultural operations is particularly difficult. This difficulty is partially due to the fact that emissions factors obtained from open field assessments are related to specific and not repeatable environmental conditions, which makes it difficult to assess the efficiency of mitigation measures through comparative trials. Nonetheless, several studies have tested PM or dust emission mitigation strategies (a table with most of the available mitigation techniques is presented in paragraph 3.1, Table 4).

Most studies verted on mitigation techniques for tillage emissions, assessing the effect of conservation tillage (minimum tillage, MT, no tillage, NT and strip tillage, ST) techniques for reducing PM emissions. Those techniques are able to exert a substantial mitigation of dust (Coates, 1996; Backer, 2005) and PM_{10} (Backer, 2005) emissions during land preparation. The emission reductions achieved with minimum and no tillage are attributed to the reduction of tilling events, while practically no difference has been highlighted for the choice of the tilling implement (Coates, 1996, Backer et al., 2005). Conservation tillage, which appears to be a good solution when it comes to reducing PM_{10} emissions from the operation itself, was originally developed to maintain coverage of the soil, increase fertility and, most of all, contrast wind erosion (Singh et al., 2012). It is important to outline, in fact, that wind erosion of bare soil is the primary soil related source of PM_{10} in countries with relevant winds and unstructured soils (Sharratt and Auvermann, 2014). Northern Italy, in this sense, represents a total exception, since the typical wind speed rarely exceeds 2 m s^{-1} at 2 m from ground level (Fratianni et al., 2007). Reduced tillage practices also have relevant effects from the agronomical point of view, since they may affect crop yields (Irmak et al., 2019) and soil organic matter content (Wulanningtyas et al., 2021).

Some mitigation measures have been assessed also for harvesting operations, especially for certain crops, but most of the studies were performed in the United

States and involve machineries which are not used in Europe. Almond and hazelnut are two of the crops which have been addressed the most and for which harvesters and abatement technology prototypes have been developed (Faulkner, 2013; Pagano et al., 2011). Moreover, the harvester operating parameters, such as airflow and harvester speed, were tested (Faulkner et al., 2009; Ponpesh et al., 2010). The prototypes and abatement technologies tested by previous researches are presented in paragraph 3.1, Table 4.

Post harvesting operations can strongly affect the overall harvest related PM_{10} emissions. Nonetheless, few published articles proposed mitigation measure for post harvesting emissions, such as the one published by Billate et al. (2004), who tested the effect of hopper bins drop heights and grain unloading rate (kg s^{-1}) on PM emissions from grain receiving facilities. In general, very few crops have currently been addressed in terms of mitigation measure proposals for harvesting and post harvesting operations.

For crop burning emissions, the mitigation approach is slightly different as compared to other activities. The main solutions are in fact aiming not to mitigate the emissions but to rather substitute residue burning as a residue management practice, favouring other more sustainable techniques, such as soil incorporation of residues or energy production through biomass or biogas plants (Ravindra et al., 2018).

For sowing operations, different mitigation measures and driller prototypes have been proposed (Biocca et al., 2015; Pochi et al. 2015 Pagano et al., 2011). Those solutions focused on reducing the emission of seed coating particles (abating them up to 100%; Table 4) and the deposition of coating particles to the ground, but did not take into consideration the total PM_{10} emissions from sowing, which also include soil emissions.

For manure and fertilizer spreading, practically no technical solution has been evaluated for its capacity to reduce PM emissions. Future research should address this subject, possibly starting by testing direct injection techniques and comparing them with surface spreading.

Several PM mitigation systems are available also for animal houses emissions. These systems are of two main types: integrated sytems, which reduce the PM concentration inside the building, and end-of-the-pipe systems, which abate the concentraton of PM in the air exiting the building. Integrated solution can be management solution, such as the choice of bedding material or feed type (Cambra-López et al., 2010), or technological solution such as the use of sprinkler syestems spraying water or oil to abate PM concentration and prevent particle resuspension (Winkel et al., 2016; Wood et al., 2014). Another solution is air ionization, which allows PM removal by constituting an electric field and soliciting electrically charged particles to deposit on discharge plate (by following the electric field lines), forming so-called “cakes” that can be washed out or removed in a second moment (Cambra-López et al., 2009). End-of–the-pipe sytems constitute mainly of filters, tourtous barriers (which remove the largest particle fractions) or even barriers placed atat the air outlet of the barn, such as manure belts or three rows (Winkel et al., 2017; Guo & Maghirang, 2012).

1.2.3. Secondary particulate matter sources in agriculture: Ammonia

As for secondary PM, agriculture contributes to the emission of several secondary PM precursors such as ammonia (NH_3), nitrogen dioxide (NO_2), sulfur dioxide (SO_2) and Volatile Organic Compounds (VOC's). The most relevant of those, in terms of agriculture contribution, is ammonia.

Secondary particles can represent up to 50% of the total concentration of particles in the air (Erisman and Schaap, 2004; Gong et al., 2013; Hristov, 2011; Sharma et al., 2007). The three main components of secondary aerosol are sulfur compounds, nitrogen compounds and secondary organic aerosol (SOA). Both nitrogen and sulfur, respectively emitted in form of sulfur and nitrogen dioxide are oxidized in the atmosphere to form nitric and sulfuric acids. In regions where ammonia emissions are relatively high, these acids react with NH_3, forming ammonium sulfate and ammonium nitrate, according to following process:

HNO_3 *(nitric acid)* + NH_3 *(ammonia)* ↔ NH_4NO_3 *(ammonium nitrate)*

This process is the core of the formation of secondary PM of agricultural origin, since anthropogenic NH_3 emissions are almost entirely attributed to the agricultural sector ~92% (EEA, 2019). Agricultural emissions also contribute to SOA formation through the emission of volatile organic compounds (VOC), but SOA formation is a much slower process as compared to nitrate and sulfate formation.

1.3. Ammonia

Ammonia (NH_3) is the most important alkaline gas in the atmosphere and it plays an important role in determining the pH of precipitations and cloud water and in airborne particulate matter formation. Ammonia is also subjected to dry and wet deposition (Aneja et al., 1986). Therefore, it contributes to the abundance of nutrients in terrestrial and aquatic ecosystems, causing euthrophication of soils and water bodies (Behera et al., 2013, Jaworski, 1981). When deposited on soils, ammonia can be oxidized through nitrification/denitrification pathways that can lead to N_2O formation, especially under anoxic conditions, indirectly contributing to climate change (Zhu et al., 2013). Ammonia can also have further impacts on climate change by forming sulfate (SO_4^{2-}) and nitrate (NO_3^-) aerosols, that may have important effects on global radiation exerting a scattering effect on the incoming solar radiation and acting as cloud condensation nuclei, indirectly increasing clouds lifespan (Behera et al., 2013). Moreover, high ammonia concentrations in livestock building cause negative health effects for both farmers and animals, having negative effects on human respiratory systems, on animal wellfare and, over certain concentration, on animals productivity (Wathes et al., 2003; Koerkamp et al., 1998).

1.3.1. Ammonia emission sources

Ammonia is emitted from different sources, including livestock production and manure, agricultural fertizers, human manure, wild animals, biomass burning and industrial emissions (EEA, 2019; Behera et al., 2013). Agricultural activities are the main source of ammonia (92% of anthropogenic emissions; EEA, 2019; Figure 10); most of the ammonia emitted from agriculture derives from the livestock sector and, particularly, from manure management operations, which accounts for ~75% of total ammonia emissions (Webb et al., 2005).

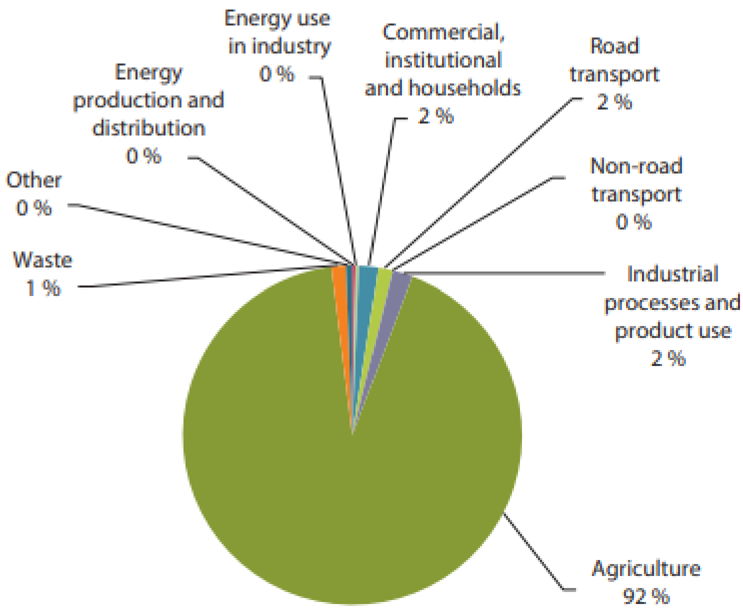


Figure 10. Ammonia emission sources in Europe (source: EEA, 2019).

Ammonia emissions from manure occur due to the degradation of proteins, according to the following equations (1-3; Behera et al., 2013):

$$C_5H_4O_3N_4 + 1.5\ O_2 + 4\ H_2O \rightarrow 5\ CO_2 + 4\ NH_3 \tag{1}$$

$$CO\ (NH_2)_2 + H_2O \rightarrow CO_2 + 2\ NH_3 \tag{2}$$

$$\text{Undigested proteins} \rightarrow NH_3 \tag{3}$$

When formed, the ammonia present in manure is exchanged at the surface between manure and air, with a flux of emission (E, g m^{-2} s^{-1}) that can be modeled as follows:

$$E = k\,(C_{manure} - C_{air}) \quad (4)$$

Where C_{manure} and C_{air} are the concentrations (g m^{-3}) of ammonia in the air above the manure biomass and in the background air respectively and k is the diffusion coefficient (m s^{-1}). Therefore, the ammonia flux is strongly affected by the environmental conditions, such as air temperature, which alters the diffusion coefficient, but also wind speed, since higher wind speeds push the polluted air away from the emitting surface, maintaining a high delta among C_{manure} and C_{air}. Moreover, C_{manure} is affected by the chemical equilibrium between aqueous NH_4^+ and gaseous NH_3 in the manure biomass. This equilibrium is regulated by the manure pH and NH_3/NH_4 content is maximum at pH levels higher than 10, while it drops to almost zero at pH levels lower than 5 (Behera et al., 2013; Arogo et al. 2002).

Ammonia emissions from livestock and manure management occur in three main phases: livestock rearing, manure storage and field spreading. These three processes, their emission potentials and feasible mitigation techniques have been studied over the years (Aarnink et al., 2006; Behera et al., 2013; Dinuccio et al., 2012; Hayes et al., 2006). Nonetheless, although many technical solutions are available to reduce emissions from each main stage and good progress was made in actual emissions reduction (Carozzi et al., 2013; Misselbrook et al., 2016; Philippe et al., 2011), NH_3 releases are still causing great concern for the overall air quality state at both European and global level. Partially, this is simply due to the amount of animal heads which are reared per capita, but it appears evident that there is still room for improvement in NH_3 emission mitigation.

1.3.2. The current situation of ammonia emission in the EU and worldwide

At the European level, NH_3 emissions are one of the major causes of concern, as highlighted by a recent communication (published on June 28th 2019) in the EEA (European Environmental Agency) news feed, which states: "Emissions of Ammonia (NH_3) rose for the fourth year running, increasing by 0.4% across the EU, from 2016 to 2017, according to the annual EEA briefing National Emission Ceilings (NEC) Directive reporting status 2019. Over the 2014-2017 period, the overall increase was about 2.5%. These increases are because of the lack of emission reductions in the agricultural sector." In fact, the data presented in the 2019 EEA report (Figure 11 and 12) show that, although many efforts have been made by the scientific community to develop solutions and mitigation measures, the total emissions did not decrease as much as it was expected and even increased over the last few years. This lack of emission reduction is mainly attributed to the livestock sector. In fact, disaggregated data for manure application on soil and manure management (manure storage) show very shallow reductions of the overall emissions.

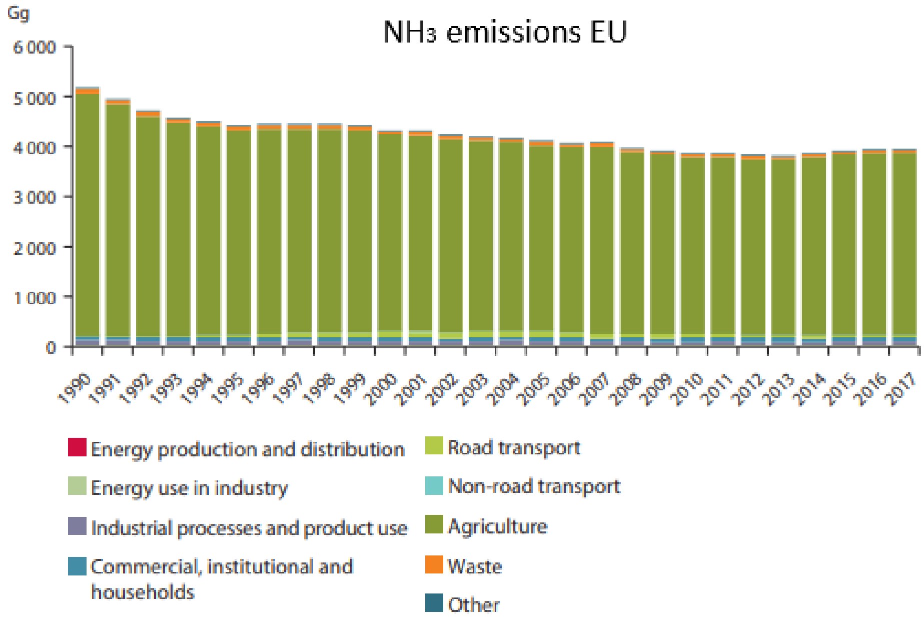


Figure 11. Ammonia emissions (Gg; by sector) in the EU, years 1990-2017 (source: EEA, 2019).

Worldwide the NH_3 emission trend is even less promising. In fact, a linear increase (R^2=0.97) of the total emission has been observed in the 1990-2015 period, with an average yearly increase of 0.95% (Figure 13; JRC, 2020).

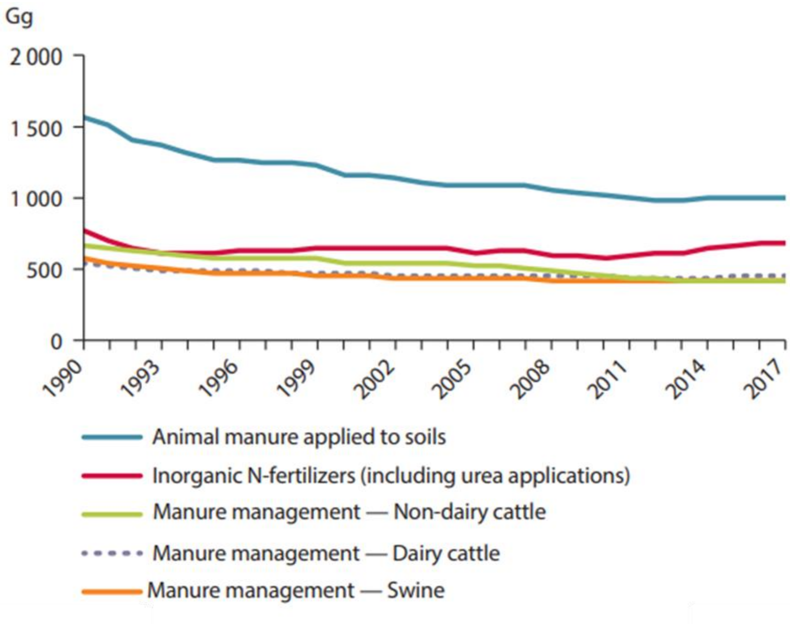


Figure 12. Amonia emissions (Gg) from manure managemet and manure spreading in Europe from 1990 to 2017 (source: EEA, 2019).

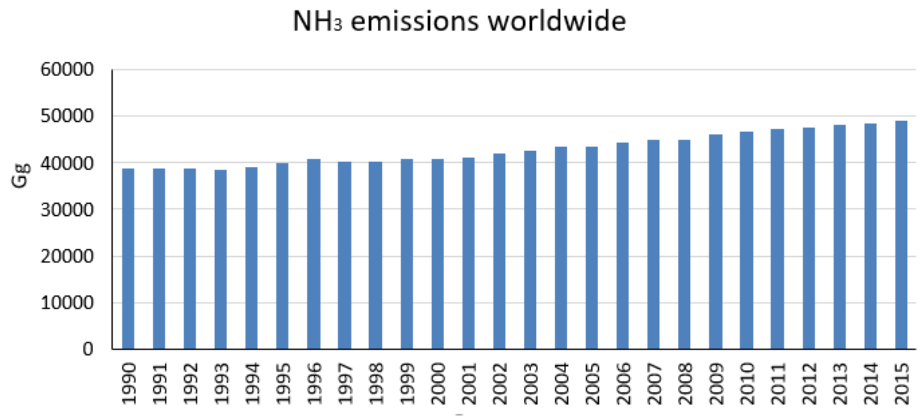


Figure 13. Ammonia emissions (Gg) worldwide, years 1990-2015 (source: JRC, 2020).

1.3.3. *Manure management: main mitigation strategies and future perspectives*

Mitigation measures to reduce ammonia emissions from livestock rearing systems can be applied to the three different steps of the manure management chain (livestock houses, manure storage and land spreading).

Techniques applied to reduce NH_3 emissions from barns can be based on the improvement of the animal diets, aiming to improve nitrogen use efficiency and reduce the nitrogen content of urine and feaces, or on the improvement of structural components of the barns (e.g. flooring, manure removal systems etc.).

Many studies have highlighted the importance of nitrogen intake on ammonia emission and the mitigation effect of reduced protein intake in diets. Examples of strategies based on this principle are diets with improved amino acid ratio and digestibility or phase and separate sex feeding systems (Andretta et al., 2016; Hernández et al., 2012). Moreover, several feed additives have been shown to positively affect the emissions by improving nitrogen use efficiency or enhancing gut health (Jackman et al., 2020; Liu et al., 2018; De Lange et al., 2020). Enzymes, acidifying salts, probiotics and Zeolites are among the many feed additives that have been shown to affect nitrogen use efficiency. Zeolites have been particularly studied for their effects on animal health, productivity, nitrogen use efficiency and ammonia adsorption properties (Mercurio et al., 2016; Papaioannou et al., 2004).

Mitigation of ammonia from livestock houses is also linked with the structural components of the barns and the rearing systems. Manure removal systems and floor types can play a fundamental role in reducing NH_3 emissions, especially through frequent manure removal (e.g. flushing systems; Shepherd et al., 2017; Baldini et al., 2016), reduction of manure surface in contact with air (e.g partially slatted floors; Aarnink et al., 1997) and fouling reduction. Moreover, microclimatic conditions can affect NH_3 emissions from manure. Addition of strong acids in underfloor slurry pits is a further technique that can be adopted; it reduces slurry pH and maintains NH_3 in the NH_4^+ form, providing good emission reduction results (Fangueiro et al., 2015; Kai et al., 2008).

During manure storage, emission can be limited through different solutions, also depending on the manure type (solid or liquid) and on the storage facility (above-ground or ground-level storage tanks, lagoons, windrows etc.). Solutions can be based on physical strategies, such as covering of the emitting surface, on management practices (aiming to reduce stored volumes during critical periods, e.g. summertime) or on chemical additives (e.g. acidifiers).

Covering systems used to reduce emissions from manure storage facilities can be of two main types: fix covers and floating covers. Fix covers can be both rigid and flexible and provide complete covering of the storage tank, obtaining emission reductions of >80% (Santonja et al., 2017); moreover fix covers are effective also for greenhouse gas mitigation. Floating covers are of different shapes and materials; usually these systems are relatively low-cost, as compared to fix covers, and often provide emission reduction for limited amounts of time (e.g. straws, oil or LECA®; Balsari et al., 2006; Pahl et al., 2002; Sommer et al., 1993). Some are made of plastic materials, which are longer-lasting. The efficiency of floating sytems varies a lot in function of different technologies and applications, with figures ranging from 30 to 90 % (Santonja et al., 2017). Slurry acidification can be applied also in this phase (Fangueiro et al., 2015). Another important solution is anaerobic digestion (Massé et al, 2011) which can provide greenhouse gas emission reduction; moreover, covering of the produced digestate, with covers equipped with biogas retrieval systems, can allow for further biogas production, while containig ammonia emissions (Gioelli et al., 2011).

During manure speading in field, N-NH_4 emissions can reach up to 80% (with surface application in summertime) of applied nitrogen (Santonja et al., 2015). To reduce the emissions from this phase, the best solutions are based on direct or delayed incorporation of slurry into soil (Santonja et al., 2015). In case of delayed incorporation, a timelapse of less than 4 hour among manure spreading and soil incorporaration is recommended, since most of the NH_3 emissions occur in the first hours after spreading (Carozzi et al., 2012). The best results in terms of NH_3 emission mitigation are obtained with direct incorporation techniques, although different results are achieved with shallow and deep incorporation (Santonja et al., 2015). Slurry incorporation in soil, although being the best solution for NH_3 emission reduction, may lead to an increase in N_2O emissions from soil, increasing the contribution of agriculture to global warming (Thomsen et al., 2010). A measure that has been proposed to prevent this effect is the use of nitrificatition inhibitors to reduce N_2O emissions, while increasing nitrogen availability for crops (Tao et al., 2021). Moreover, similarly to barn and storage emissions, also for land spreading emissions, acidification techniques can be implemented. Acidification is usually performed using strong acids, which are transported on the tractor with a separate tank and mixed with the slurry at the moment of spreading (Fangueiro et al., 2015).

Acidification techniques are one of the few solutions which are applicable to all steps of the manure management chain, with good mitigation results. Nontheless, the manipulation of strong acids is prone to severe handling risks and regulatory restrictions (especially for on road transport in case of land spreading). Another minor issue is foam formation, that occurs when mixing slurry after acid addition and may cause handling difficulties. Therefore, alternatives to strong acids for slurry acidifications may be beneficial to solve these problems.

Although many different mitigation options are available for NH_3 emissions, many of these fail to meet economical sustainability criteria or are difficult to implement due to difficulties linked with current regulation or structural limits at the farm level. Therefore, it is important to evaluate solutions that can be easily implemented in real world applications, especially ones that imply a contemporary benefit for emission reduction and productivity or nutrient use and byproducts valorization. In this thesis some viable mitigation measures were tested, which aimed to overcome the limits to real world application.

2. RESEARCH ACTIVITIES: OBJECTIVES AND THESIS STRUCTURE

The aim of the research works performed was to address the issue of particulate matter emissions from agriculture, focusing both on primary and, indirectly, on secondary particulate matter, by dealing with primary PM and NH_3 emissions. The thesis has been thus arranged in two sections (section 3 and 4) focusing on PM and NH_3 emissions respectively.

Considering that the subject of PM emission is a less explored at international level when compared to the ammonia ones, the PhD research activity was initially focused on primary PM emission from outdoor agricultural activities, trying to cover , at least partially, the present following gaps in knowledge:

1) Relatively few studies assessing the emissions from open field cropping have been carried out so far (very few in Europe and almost none in Italy);

2) The environmental variability is crucial in determining the emissions and, therefore, local emission estimation studies need to be performed;

3) The physical and chemical characteristics of soil and crop derived particles are poorly known;

4) Very few studies focused on the effect of the management practices and mechanical implements used on PM emissions from fields;

5) There is poor knowledge about the actual health risks associated with agricultural PM and its contribution to air pollution on the local scale;

6) Very few mitigation measures have been developed and tested.

For what concerns NH_3 emissions, the current literature is way richer in terms of basic research, and both emission dynamics and entity in agricultural environments have been addressed in count-less studies (Aarnink et al., 2006; Carozzi et al., 2013; Misselbrook et al., 2005; Philippe et al., 2011). Nonetheless, there is still work to do to find, test and improve the mitigation measures/solutions aimed to reduce NH_3 emissions. Moreover, even if the emissions have been quantified in many situations and under many climatic conditions, the scientific community agrees on the necessity of developing and employing low-cost tools to provide constant monitoring of the emissions, especially in open space environments, where emission quantification is more complex (Misselbrook et al., 2005; Pacholski, 2016). Moreover, the is still room for improvement in the development of efficient mitigation measures to limit NH_3 emissions (Carozzi et al., 2013; Philippe et al., 2011).

This thesis was organized as a collection of articles, divided in two main sections, one focusing on PM emissions and one on NH_3 emissions. The research on PM was more focused on developing measurement methods for outdoor PM emissions quantification and on learning more about the emission dynamics, in order to be able, in a further step, to address mitigation tools. As for the second section, on NH_3 emissions, the efforts were mainly focused on assessing the efficacy of different mitigation measures on reducing the emissions from barns, storage and fields.

The research work on PM emissions from agriculture was focused on emissions from outdoor sources. The decision to focus all efforts on this niche was due to the large knowledge gap that was identified thanks to the literature review presented in paragraph 3.1. In fact, at the European level, very few emission factors (EFs) were developed for mechanical field operation (e.g. tillage, harvesting etc.) and for outdoor animal husbandry. At the Italian level the absence of information on the topic is even greater, with only a handful of published studies to note.
The section focusing on PM emissions is composed by five articles, entitled as follows:

I. PM emissions from open field crop management: emission factors, assessment methods and mitigation measures–a review;
II. Evaluation of particulate matter (PM_{10}) emissions and its chemical characteristics during rotary harrowing operations at different forward speeds and levelling bar heights;
III. Soil PM_{10} emission potential under specific mechanical stress and particles characteristics;
IV. Assessing particulate matter (PM_{10}) emissions from outdoor runs in laying hen houses by integrating wind tunnel and lab-scale measurements;
V. Particulate Matter Emissions from Soil Preparation Activities as Influenced by Minimum and Strip Tillage Practices.

Article I is a review article addressing PM emissions from open field cropping activities, which served to acquire an in-depth knowledge of the research subject and to investigate the main knowledge gaps and measurement methodologies, allowing to strategically plan the following researches. Article II represented the first experience in assessing PM emissions from open field cropping operations, it focused on soil emissions and, particularly, on rotary harrowing. It aimed to test the measurement equipment and methods acquired for emission assessments and also to provide first insights on the emission potential of rotary harrowing and on the influence of tractor speed and implement settings on the emissions. Both the literature review (Article I) and the field experience acquired during the research that led to Article II, pointed out the importance of soil characteristics and humidity in determining the magnitude of emissions from soil. To acquire a deeper understanding of these dynamics, a laboratory system (presented in Article III) was developed, aiming to investigate soil emission potential at varying humidity contents and also to serve as a tool to scale the emission factors measured during field trials in function of soil humidity. Article IV was realized as the result of research carried out during an abroad period at Wageningen University, and it focused on the emissions of PM from outdoor runs in laying hen houses. This work aims to develop a measurement system for this specific emission source, which had never been studied before, and to provide a first emission figure. Article V represents a first assessment of PM emission from land preparation activities, following the entire process from tilling to sowing. It also aimed to provide an evaluation of the effect of three different tilling systems on the emissions.

The section focusing on NH_3 emissions is also composed by five articles, entitled as follows:

VI. Application of nitrification inhibitor on soil to reduce NH_3 and N_2O emission after slurry spreading;

VII. Addition of powdery sulfur to pig slurry to reduce NH_3 and GHG emissions after mechanical separation;

VIII. Development and Testing of an Innovative System to Acidify Animal Slurry with Powdery Sulphur before Mechanical Separation;

IX. Testing the Efficiency of a Passive Sampler for Ammonia Monitoring and Comparison with Alpha-Samplers;

X. Clinoptilolite (E567), a natural zeolite, inclusion in heavy-pig diets: effect on the productive performance and gaseous emissions during fattening and manure storage.

Article VI aimed to assess the mitigation effect of a commercial nitrification inhibitor on NH_3 emissions occurring during slurry spreading. Article VII focused on the NH_3 emission reduction during slurry spreading, achieved through implementing acidification with powdery sulfur. The assessment made in article VII led to the development of an automated slurry acidification system, presented in article VIII, allowing full scale implementation of powdery sulfur as an acidifier. Article IX is the only article which does not not focus on a mitigation measure; the research aimed to assess the efficiency of a passive sampler for ammonia monitoring and to develop laboratory testing system to investigate the sampler efficiency. Article X presents research aiming to assess the effects of clinoptilolite implementation in pig diets on NH_3 emissions form barn and slurry storage facilities.

3. RESEARCH WORKS ON PARTICULATE MATTER EMISSIONS

The research works presented in this section are deeply interlinked. In fact, the work performed on particulate matter emissions during the PhD experience coincided with the start of a new research stream for the Waste Management Research Group of the University of Torino. Therefore, the following articles follow a path starting from a first investigation in the available knowledge on the subject (Article I; Paragraph 3.1), on to the first field trial experience (Article II; Paragraph 3.2), to the improvement of the overall methodology by implementing a laboratory scale assessment system for soil emission potential (Article III; Paragraph 3.3) and to the evaluation of mitigation measures (Article V; Paragraph 3.5). Articles I, II, III and V are part of the work performed in a project, funded by the CRT foundation, which is called *"Valutazione delle emissioni di materiale particolato dalle operazioni colturali e di trasformazione aziendale del mais"* (Evaluation of PM emission from cropping operation and first transformation of Maize) and aims to address the issue of PM emission from Maize cropping system, which is the major cropping system in Piedmont region.
Article IV (Paragraph 3.4), is a standalone work, which is the outcome of an abroad semester spent working at the Wageningen University and Research center.

3.1. ARTICLE I: *"PM emissions from open field crop management: Emission factors, assessment methods and mitigation measures – A review"*

The field of Particulate Matter emissions was an almost completely new field of study for the Agricultural engineering research group of the University of Torino. Therefore, it was necessary to perform an in-depth review of the literature to understand what was the information provided by current literature and which were the possible niches to fill with new studies and research projects. Moreover, it was necessary to gain a perspective of the field methodologies for emission assessment, in order to identify the ones that better fit our working conditions and master them. Therefore, writing a review article on PM emissions from field cropping operations has been a way to capitalize on a necessary work of in depth studying and understanding of emission sources, emission dynamics, measurement methodologies and mitigation methods.
The only review previously available on the topic was the one published by Sharratt and Auvermann (2014), which addressed agricultural PM emissions more generally and did not provide details on measurement methods and mitigation measures.

Atmospheric Environment (2020), Volume 226, 117381, ISSN 1352-2310

Authors: Jacopo Maffia, Elio Dinuccio, Barbara Amon, Paolo Balsari

Atmospheric Environment 226 (2020) 117381

Contents lists available at ScienceDirect

Atmospheric Environment

journal homepage: http://www.elsevier.com/locate/atmosenv

ELSEVIER

Review article

PM emissions from open field crop management: Emission factors, assessment methods and mitigation measures – A review

Jacopo Maffia [a,*], Elio Dinuccio [a], Barbara Amon [b,c], Paolo Balsari [a]

[a] Dipartimento di Scienze Agrarie, Forestali e Alimentari, Università di Torino, Largo Paolo Braccini 2, 10095, Grugliasco, Italy
[b] Leibniz Institute for Agricultural Engineering and Bioeconomy (ATB), Max-Eyth-Allee 100, 14469, Potsdam, Germany
[c] University of Zielona Góra, Faculty of Civil Engineering, Architecture and Environmental Engineering, Poland

HIGHLIGHTS

- Summary of PM_{10} and $PM_{2.5}$ Emission Factors from cropping operations.
- Some operations are poorly addressed by previous researches.
- Need of assessing emission from whole cropping systems.
- Effective mitigation measures need to be developed and tested.

Abstract
Globally, particulate matter (PM) emissions are a growing cause of concern due to the potential impact on human health and environment. The agricultural sector is responsible of the 17% of the total anthropogenic emission of PM_{10} and the agricultural operations (tilling, harvesting, residue burning etc.) have been recognized as one of the main drivers of this contribution. This topic has been addressed in many articles, focusing on the impacts coming from different steps of the agricultural production system and using different assessment methods. The aim of this review is to identify the main agricultural operations producing particulate emission, providing a collection of the Emission Factors (EF) available in literature. The most used EFs determination methods have also been described, by focusing on pros and cons of each method. Issues and lacks of information to be addressed by future research have been highlighted. It has been observed that very few PM emission assessment have been done by taking into consideration whole cropping systems and the information available is fragmented onto single cropping activities. In addition, very few mitigation measures have been developed so far.

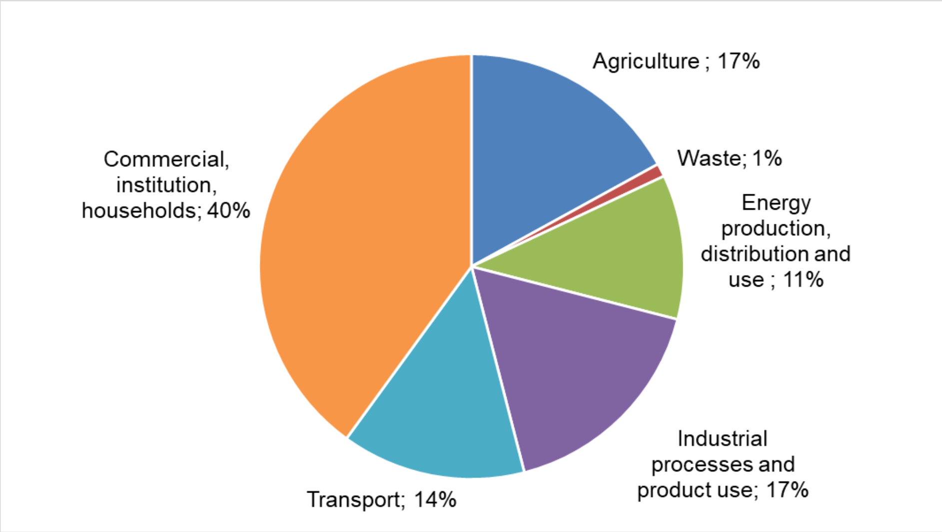
1. Introduction

Particulate matter (PM), is considered, both in urban and rural area, as one of the most concerning air pollutants due to its effect on human health and environment (Douglas et al., 2018; Giannadaki et al., 2018; Giannakis et al., 2019). The agricultural sector largely contributes to the emissions of PM_{10} and $PM_{2.5}$, being responsible of the 17% and 5% of the total anthropogenic emissions respectively (EEA, 2016). The contribution of different sectors to the total PM_{10} emissions is summarized in Figure 1. Among the main agricultural activities contributing to the emissions are livestock rearing and open field crop management. The contribution of open field activities is particularly difficult to estimate, due to the wide variety of field operations and crops and to the importance of climatic factors as drivers of PM emissions.

This literature review focuses on primary particulate matter (PM_{10} and $PM_{2.5}$ fractions) emissions from open field agricultural operations. The main objective is to identify the agricultural operations producing particulate emission and to highlight, for each of those practices, the main health concerns, as induced by emission magnitude, particle size and particle characteristics. To fulfill this goal, information for each agricultural operation was gathered from literature, focusing primarily on available Emission Factors (EFs). A further aim of this review work was to identify the most common EFs determination methods used in current literature and to highlight their pros and cons. Moreover, the main PM mitigation measures were reported along with their target operation and the expected mitigation effect.

The gaps of information on the subject were highlighted on the base of the review made and some of the niches that could be filled by future research were outlined.

Figure 1. Contribution of the main sectors to total anthropogenic PM_{10} emissions (adapted from EEA, 2016).



2. Main agricultural operations contributing to PM emissions

Farmers enter the field several times per year for many different purposes and, each time, they potentially produce dust emissions. Those emissions are mainly due to the raising of soil particles due to the passage of heavy machineries, but also to the pulverization of biomass (e.g. crop residues or animal wastes). In particular, the main agricultural operations during which fine particles are released in the atmosphere are soil tillage, harvesting, burning of crop residues, sowing, manure and fertilizer distribution (Sharrat and Auvermann, 2014). Also spraying operations can contribute to PM emissions, both through primary drift of droplets (Carlsen et al., 2006a; Grella et al., 2019) and secondary drift of evaporating compounds (Carlsen et al., 2006b). It was decided not to include spraying operations in the current review because this subject constitutes a research field of his own.

The amount of fine particles produced varies consistently among the different operations. Moreover, there are many parameters, such as environmental conditions (Avecilla et al., 2017), soil and crop type (Madden et al., 2010), soil moisture (Funk et al., 2008; Madden et al., 2010) and mechanical implements (Clausnitzer and Singer, 1996), that can strongly influence the entity and the physical and chemical characteristics of emitted PM.

Despite the variability of those parameters and of estimation methods applied to calculate PM emission factors, most of the authors tend to agree on which operations are mostly contributing to total particulate matter emissions. According to Pattey (2015), who has performed a survey on agricultural PM emissions in Canada, tillage is the operation that contributes the most to the total agricultural emissions. Similarly, Chen et al. (2017) have observed that in Northeastern China tillage and harvesting account for the three fourth of the total agricultural emissions, with tillage being the main pollution source. Also in California, although the environmental conditions are very different from the ones of the above-cited surveys, tillage and land preparation have been considered to be the main agricultural PM_{10} source, accounting for the 65% of total agricultural emissions (Clausnitzer and Singer, 1997). Differently, Amann et al. (2012) have estimated that the main agricultural source of PM emissions in Europe is the burning of residues, which, according to their estimations, contributes to the total PM_{10} and $PM_{2.5}$ emissions for the 7.6% and 9.6% respectively, while ploughing tilling and harvesting altogether account only for the 4.7% (PM_{10}) and 1.5% ($PM_{2.5}$) of total emissions. In the African continent agricultural biomass burning emissions are recognized as the second most important source of PM, following natural mineral dust emissions by wind erosion, and being responsible for half of the premature deaths in Central Africa (Bauer et al., 2019). Similarly, studies carried out in India suggest that also in that continent the main agricultural contributor to PM emissions is biomass burning (Pandey et al., 2014; Guo et al., 2017).

In the following paragraphs, the main agricultural operations involved in PM emissions will be addressed, collecting information about the origin and the characteristics of emitted particles, available emission factors and parameters affecting emissions.

2.1. Tillage and soil preparation

Tillage and soil preparation techniques are responsible of producing a significant amount of primary PM emissions. The exact amount of PM_{10} emissions produced can vary a lot according to environmental conditions, especially soil moisture (Chen et al., 2017; Öttl and Funk, 2007; Flocchini et al., 2001) and to the specific tilling implement used (Moore et al., 2013). This implies a strong variability in the emission factors obtained during different measurement campaigns, even if done in the same area and applying the same cultivation practices (Table 1; Wang et al., 2010). The European guidelines, in fact, set a wide reference range of emission factor values for tilling operations, going from 25 to 225 mg m^{-2} (for PM_{10}) and from 1.5 to 10 mg m^{-2} (for $PM_{2.5}$), where the two values are obtained by measuring the emissions during tillage of wet and dry soil, respectively (Funk et al., 2008).

Table 1. PM_{10} and $PM_{2.5}$ EFs for different land preparation techniques as determined by different authors.

Operation	PM_{10} EFs (mg m^{-2})	$PM_{2.5}$ EFs (mg m^{-2})	Region/country	Reference	EF estimation method
Tilling (plowing+disking+land planning)	31 - 119	3 - 33	Northeasthern China	Chen et al., 2017	Vertical profile method
Rolling	12.1±2.4	-	USA, New mexico	Wang et al., 2010	Vertical profile method
Listing	210±29.8	-			
Disking	44.8±6.4 – 202.8±13.5	-			
Plowing	120 - 1045	5	Europe	Oettl et al., 2007	Lagrangian dispersion modeling
Harrowing	82	29			
Disking	137	12			
Cultivating	186	6			

Root cutting	33.6	-		WRAP, 2006	Various methods
Disking, tilling, chiseling	134.5	-			
Ripping, subsoiling	515.6	-			
Land planing, floating	1401.1	-			
Weeding	89.7	-			
Disking (1st passage)	99.7±12.5	20.4±2.6	USA, California	Moore et al., 2013	LIDAR
Disking (2nd passage)	80.7±20.5	39.5±5.9			
Chiseling	79.5±13.1	35.8±5.9			
Land planning	281.9±28	13.8±3.9			
Disking (1st passage)	125.6 ± 57.9	-	USA, California	Moore et al., 2013	Gaussian dispersion modeling
Disking (2st passage)	149.2 ± 91.8	23.3 ± 7.4			

Chiseling	167.5	34.5 ± 115.1			
Land planning	41.3 ± 10.6	18.4			
Disking	78±6 – 1375±91	-	USA, California	Cassel et al., 2003	Vertical profile method
Floating	119±8 – 2322±145	-			
Land planning	1229±98 – 1704±128	-			
Ripping	507±292	-	USA, California	Holmén et al., 2001	Vertical profile method
Disking	91.2±104	-			

The particulate matter blown away from the fields, during and after soil preparation activities, is mainly composed of mineral particles with a lower amount of organic particles (Goossens and Riksen, 2004), thus being coarser as compared to those emitted during harvesting and straw burning (Chen et al., 2017, 2015). Nonetheless, according to Bogmann et al. (2005), who did a total solid particles (TSP) emission assessment in a European environment, 50% of the particles emitted during tillage have a diameter of less than 20 µm.

Concerning the emissions of particles in the smaller size fractions ($PM_{2.5}$), Moore et al. (2013) found practically no $PM_{2.5}$ emissions during soil tillage operations. On the contrary, (Chen et al., 2017) observed a $PM_{2.5}/PM_{10}$ ratio during tillage equal to 28%. This contradiction can be explained by the findings of Carvacho et al. (2004), who observed that the $PM_{2.5}$ soil emission potentials are higher in soils containing more silt, while they tend to be lower in sandy soils.

Table 1 summarizes EFs estimations for tillage operations, referring to different tilling implements. The implements used for soil preparation can induce different PM emissions as compared one to another (Table 1). Some authors observed that comparisons between emission factors related to the use of different tools could be unreliable because of the impossibility of standardizing the environmental conditions among trials (Holmén 2001, Cassel et al., 2003; Wang et al., 2010). However, the emission factors reported in Table 1, which are related to different operations, can be used for gathering general indications. The emission factors reported are divided by tilling operation type, although some authors (Holmén et al., 2001, Cassel et al., 2003) stated that, as crop calendars may affect the period in which certain operations are performed, it should be better to further categorize EFs per crop type or per month. A further consideration to be done is that the methods used to estimate the emission factors vary considerably according to different authors, increasing the uncertainty of possible comparisons.

Among the main primary tillage operations, the most polluting one, in terms of PM emissions, appears to be ripping, followed by conventional plowing and disking (Clausnitzer and Singer, 1997, 1996; Holmén et al., 2001). As for secondary operations, it was highlighted, from a study conducted by Moore et al. (2013), that during a second passage performed on a field with the same implement the generated emission rates of the finer ($PM_{2.5}$) tend to be higher. Similarly, other studies have shown that the final operations, such as land planning and floating, tend to produce higher emission rates than the primary ones (Cassel et al., 2003; Clausnitzer and Singer, 1997, 1996). This effect is probably due to the progressive disaggregation of soil aggregates that have been proven to affect PM_{10} emissions (Madden et al., 2010). The effect of tillage on windblown dust and PM emissions was also shown to be affected by the implement choice (Lopez et al., 1998; Pi et al., 2018; Singh et al., 2012), being for example higher with disking that with under cutter tillage (Pi et al., 2018).

Moreover, tillage does not only contribute directly to PM emissions, but it can also affect the dust dispersion events caused by wind events or other disturbances. This is due to the effect of tillage on soil physical properties (especially aggregate stability and overall soil structure) and to the removal of soil cover with the incorporation of crop residues into soil (Gao et al., 2014; Sharratt et al., 2010). Particularly, Sharratt et al. (2010) observed that intense tillage practices could affect wind erosion in the after copping period (especially in case of summer fallows), leading to higher sediment fluxes during strong wind events.

Another aspect to be considered is that tillage practices can possibly lead to the emission of pesticide particles, previously deposited onto the soil trough pesticide spraying (Grella et al., 2017) or sowing or coated seeds (Forero et al., 2017).

2.2. Harvest and post-harvest operations

Harvesting operations are recognized to be among the major sources of PM in agriculture (Chen et al., 2017; Clausnitzer and Singer, 1996; Pattey, 2015). As compared to dust particles emitted during soil tillage, those produced by harvesters tend to be finer and to have a higher content of organic particles (Telloli et al., 2014). Chen et al. (2017b) conducted a study in which they observed a dramatic increase of $PM_{2.5}$ concentrations in the air during harvesting periods both in urban and rural areas (in the Changchun region in Northeastern China), confirming the potential importance of harvesting practices in determining the raising of $PM_{2.5}$ environmental levels. Moreover, harvest generated dusts are also recognized for carrying bioactive components. For example, wheat dust can contain endotoxins and mycotoxins that induce negative health effects (de Rooij et al., 2017; Douglas et al., 2018; Halstensen et al., 2013; Traversi et al., 2011).

Table 2 shows some of the EF estimations that were made for harvesting operations, classified per crop type. As can be seen in Table 2, harvesting related EFs are characterized by a great variability, mainly due to the variety of harvesting implements adopted for different crops and, in some cases, even for the same crop. In addition, for several crops, such as forage crops, the harvesting procedure consists of many different steps, each having its own emission potential. The EF assessments available in literature focus on few main crops, while the actual contribution of several others remains practically unknown. In fact, even the environmental agency guidelines (USEPA, 1995) propose emission factors only for few crops, such as wheat and cotton.

Another important aspect to consider is that the crop originated dusts, and grain dust especially, are not only those released during the harvester's passage. In fact, further emissions occur during post-harvest activities, such as yield transport, storage and drying. Those operations can be attributed to the agricultural sector because they are usually performed at farm level (even grain drying is often performed by farmers). In the USEPA gas emission inventory (USEPA, 2003) the EFs reported for truck loading and transport of grains, both for wheat and sorghum, are equal to 12 g m^{-2} (wheat loading), 22 g m^{-2} (sorghum loading), 110 g m^{-2} (wheat transport) and 200 g m^{-2} (sorghum transport). Comparing those EFs with the ones proposed by EPA for the actual harvest of those two crops, it appears that the first post-harvest steps account for 41.8% (transport) and 16.7% (loading) of the total (harvest + loading + transport) emissions, which is more than half of the total emissions. Considering that, if also grain drying and cleaning operations were considered, the post-harvest contribution would be even greater, it is important to include those steps in emission inventory databases to obtain a reliable representation of total harvest related emissions.

Table 2. PM_{10} and $PM_{2.5}$ EFs for harvesting of different crops as defined by various authors.

Crop type	PM_{10} emission factor (mg m^{-2})	$PM_{2.5}$ emission factor (mg m^{-2})	Region/country	Reference	EF estimation method
Spring wheat	74±12	-	Canada	Qiu and Pattey, 2008	Atmospheric tracer technique
Cotton (picking)	107±13	-	USA, California	Cassel et al., 2003	Vertical profile method
Cotton (stalk cutting)	42±7	-			
Wheat	665±40	-			
Tomato	785±48	-			
Wheat	270	-	Europe	van der Hoek and Hinz, 2007	Adaptation of EFs from literature

rye	200	-			
barley	203	-			
oat	340	-			
halmond	275 - 381	18 - 26	USA, California	Faulkner et al., 2009	Gaussian dispersion model
wheat	170	-	USA	US-EPA AP 42	Various methods
sorghum	1110	-			
Corn	190.5			Wrap, 2006	Various methods
cotton	381.1				
fruit trees	9.5				
onions	190.5				
potatoes	190.5				
sugar beets	190.5				
Tomatoes	19.5				
vine crops	190.5				
wheat	650.1				

2.3. Crop residue burning

The burning of agricultural residues is recognized to generate high emission of GHG (Arai et al., 2015; Murali et al., 2010) and particulate matter (Dennis et al., 2002; Hays et al., 2005) and to strongly affect rainwater composition (Coelho et al., 2011). Furthermore, as pointed out by Kumar et al. (2019) straw burning affects the overall environment, causing a loss of ecosystem services. Nonetheless, agricultural residue crop burning is still a widespread management practice, partially due also to its effect on pest and weed control at very low costs.

In Europe, the burning of crop residue is not allowed according to the directive 2008/98/EC, due to its effects on human health. However, in many less developed regions and countries this management practice is still common in most of the main cropping systems, such as in rice, wheat and maize cropping (Gupta et al., 2004), while in sugarcane cropping system it is often a step of the harvesting process (Franca et al., 2014). This makes it a very complex subject to address, being the crop type itself one of the parameters affecting both the chemical characteristics and the amount of the emitted particles. Table 3 summarizes some of the main EFs estimation for crop residue burning of different crops, measured both through laboratory, field and aircraft measurements. As can be seen in Table 3, the reported EFs for different crops range between 21.5 and 1.8 g kg^{-1} for PM_{10}, and the $PM_{2.5}/PM_{10}$ also ranges between 0.52 and 0.98. The EFs vary a lot also for the same crop. This could be partially due to the fact that many different methods are used to estimate EFs. Therefore, although many EFs have been published, it is difficult to select a reference EF, due to the wide range of proposed values. Moreover, many measurements were performed under laboratory conditions (Santiago-De la Rosa et al., 2018; Mugica-Álvarez et al., 2018; Li et al., 2017) and the results can not directly be transferred to EFs under field conditions. Laboratory determinations of EFs, although they do not examine actual fire, have the advantage of allowing more strict comparisons among different crop biomasses as compared to field measurements, due to the standardization of environmental conditions.

The size and composition of particles generated from biomass burning are different from those from other agricultural operations. These particles are in fact finer and most of them are in the $PM_{2.5}$ of even in the PM_1 fraction range (Le Canut et al., 1996, Yokelson et al., 2009, Oanh et al, 2011). This is of particular importance since the concentration of finer particles ($PM_{2.5}$ range) has been associated with an increase in mortality risk (Pope III, 2002). Moreover, Oanh et al. (2011) observed the presence of organochlorine pesticides in particles generated from rice straw burning. The presence of these and other organic compounds could lead to an increase toxicity of the emitted particles. The main parameters affecting the emissions, other than the crop type are the moisture content (Hayashi et al., 2014), the meteorological conditions and fire control activities (Oanh et al, 2011).

Table 3. PM_{10} and PM2.5 EFs for residue burning of different crops as determined by various authors.

Crop type	PM_{10} emission factor (g kg-1)	$PM_{2.5}$ emission factor (g kg-1)	Reference	EF estimation method
Alfalfa	11.11 ± 0.91	9.98±0.71	Santiago -De la Rosa et al. (2018)	Open combustion chamber
Barley	1.77 ± 0.19	1.19±0.10	Santiago -De la Rosa et al. (2018)	Open combustion chamber
Bean	2.75 ± 0.18	2.24±0.19	Santiago -De la Rosa et al. (2018)	Open combustion chamber
Bluegrass	7.48	-	Boubel et al. (1969)	Open combustion chamber
Corn	-	5.9 ± 0.7	Li et al. (2017)	Combustion stove
Cotton	13.37 ± 1.90	8.22±0.54	Santiago -De la Rosa et al. (2018)	Open combustion chamber
Cotton	-	15.2 ± 2.1	Li et al. (2017)	Combustion stove
Fescue	5.90	-	Boubel et al. (1969)	Open combustion chamber
Maize	3.3 ± 0.42	2.7±0.28	Santiago -De la Rosa et al. (2018)	Open combustion chamber

Rapeseed	-	16.9 ± 2.6	Zhang (2015)	Carbon mass balance method
Rapeseed	-	5.8 ± 1.3	Zhang (2015)	Carbon mass balance method
Rice	4.95 ± 0.52	3.04±0.24	Santiago -De la Rosa et al. (2018)	Open combustion chamber
Rice	-	14.7 ± 2.4	Li et al. (2017)	Combustion stove
Rice	-	20.3 ± 1.5	Zhang (2015)	Carbon mass balance method
Rice	-	9.6 ± 4.3	Zhang (2015)	Carbon mass balance method
Rice	9.4 ± 3.5	8.3±2.7	Oanh et al. (2011)	Carbon mass balance method
Rice	-	12±0.3	Hays et al. (2005)	Enclosure system
Rye (annual)	4.76	-	Boubel et al. (1969)	Open combustion chamber
Rye (perennial)	5.44	-	Boubel et al. (1969)	Open combustion chamber
Sorghum	21.56 ± 2.26	11.30±1.05	Santiago -De la Rosa et al. (2018)	Open combustion chamber
Soybean	-	3.2 ± 0.3	Li et al. (2017)	Combustion stove
Sugarcane	1.81 ± 0.14	1.19 ± 0.08	Mugica-Alvarez (2018)	Open combustion chamber
Sugarcane[a]	-	3.9	Andreae et al. (1998)	Carbon mass balance method coupled with

				aircraft measurements
Sugarcane	-	2.6 ± 1.6	França et al. (2012)	Open combustion chamber
Wheat	-	4.7±0.04	Hays et al. (2005)	Enclosure system
Wheat	4.07 ± 0.51	2.54±0.39	Santiago-De la Rosa et al. (2018)	Open combustion chamber
Wheat	-	5.8 ± 0.4	Li et al. (2017)	Combustion stove
Wheat	-	10.0 ± 1.2	Zhang (2015)	Carbon mass balance method
Wheat	-	6.1 ± 1.3	Zhang (2015)	Carbon mass balance method

2.4. Sowing

Seed drilling machines, operating on agricultural fields, also produce particulate matter emissions. The emitted particles generate mainly from soil, but a small portion comes from the seeds, which are abraded during sowing activity. There are few available experimental data on the entity of total PM_{10} emissions during sowing. Air aerosol concentrations measured during corn sowing were reported to be equal to 1.02 mg m^{-3} (Clausnitzer and Singer, 1996), being approximately equal to those induced by tooth harrowing and other soil preparation practices, as reported by the same authors. During seeding, which is usually performed after several land preparation activities, land particles may raise with more ease than during previous tillage passes, due to the progressive loss of soil structure, as described by Madden et al. (2010).

A further aspect regarding dust emissions during sowing is the potential drift of dressed seed particles, containing pesticides that could be spread in the surrounding environment. This particular issue is a cause of concern due to its potential effects on wildlife, and especially on pollinators, and led the European Food Safety Authority to produce a specific risk assessment guidance book (EFSA, 2013). The amount of seed abraded dust emitted during sowing vary among different crop seeds, being higher for maize and lower for rapeseed and oilseed (Nuyttens et al., 2013). Seed coating particles do not only spread onto the soil or in the surrounding environment, but can also contaminate the seed drilling machine, leading to further health risks (Manzone et al., 2016).

Tapparo et al. (2012) conducted an essay with three different types of drilling machines while sowing seeds treated with Clothianidin (1.25 mg/seed), Thiamethoxam (0.6 mg/seed) and Fipronil (0.5 mg/seed) and calculated the emissions factors (on TSP) that were equal to 0.043 – 0.153 mg m^{-2}, 0.074 mg m^{-2} and 0.045 mg m^{-2} , respectively, of emitted insecticides. They also observed that only a small amount of those particles was associated with the PM_{10} fraction of the emitted dust. Though the PM_{10} associated compounds may travel further distances from the field as compared to the ones linked to coarser particles (Tapparo et al, 2012).

As for soil particles emitted during sowing and planting, other than having a direct environmental impact, they can also affect the drift of seed coating pesticides by exerting an abrasive effect on seeds. This effect was confirmed by the findings of Schaafsma et al. (2018) who observed that, while sowing with a vacuum seeder machine, 15 mg m^{-2} of soil dust passed through the planter, inducing the loss of 0.24 mg m^{-2} of Clothianidin active ingredient.

Moreover, the emission of seed coating compounds from agricultural fields does not occur only because of seed abrasion during seed drilling, but it can happen as a consequence of further disturbances such as soil tillage and high wind events which can induce the removal of soil bounded residues from fields. Forero et al. (2017) were able to detect neonicotinoids in fugitive dust during tillage (the concentration ranged from traces to 4.48 ng m^{-3}) and high wind events. This kind of effect highlights how different operations (like sowing and tilling) can influence each other. Because of these interactions, it could be better to consider the emissions crop-wise, by evaluating the emission factors and the environmental risks of the sequence of activities needed for growing a specific crop as a whole.

2.5. Manure and fertilizer spreading

Manure spreading is recognized to be one of the contributors to primary PM emissions in the agricultural sector (Sharrat and Auvermann, 2014). Nonetheless, there are practically no measured emission factors available in literature regarding this operation.

The importance of PM emission from land application of manure is strongly linked to the composition of the generated particles. Manure generated dust, in fact, includes bioaerosol emissions, which implies pathogen exposure risks both for agricultural operators and for inhabitants of near field residential areas. This effect has been described by Jahne et al. (2015b), who demonstrated that infection risks for certain pathogens are higher for people living near manure application sites. A further aspect to be considered is that bioaerosol from manure spreading could contaminate the nearby crops (especially in case of leafy vegetables), causing the contamination risk to rise above acceptable levels in the first 160 m from the application point (Jahne et al., 2016).

Manure is not the only biomass applied to agricultural soils nowadays, since many other organic materials are frequently used as soil fertilizer or amendments. Among those biomasses some of the most controversial ones, due to their potential load of pathogens and pollutants (Akbar-Khanzadeh et al., 2012), are sewage sludges. In their paper, Paez-Rubio et al. (2007) determined the quantity of dust particles emitted during the spreading of biosolids, being equal to 7.6 ± 6.3 mg of PM_{10} per kg of dry biomass applied (the spreading was performed from a stationary position and thus all the measured emissions derived from the biomass, since the soil was not disturbed).

Recent researches (Jahne et al., 2016; Jahne et al., 2015a; Jahne et al., 2015b; Kang et al., 2014) focused mainly on the aspect of bio-aerosol and bacteria emissions during manure spreading, while few of them report also the total PM_{10} emissions. Furthermore, very few information is available on the effects of spreading implements and tractor speed on the emissions, although those aspects could affect the emissions.

Similarly to manure spreading, also chemical fertilizer application can lead to PM emissions. In fact, abraded fertilizer particles can be released during land application. Pattey and Qiu (2012) reported an estimation of the PM emitted per ton of applied fertilizer, being equal to 1.09 kg t^{-1} for PM_{10} and 0.31 kg t^{-1}.

A further aspect to be considered is that, both manure and fertilizer spreading operations do not only contribute to primary PM emissions, but those are also considered as some of the main sources of ammonia (NH_3) emissions in the atmosphere (Plautz, 2018). Thus, due to the reactions between of NH_3 with sulfur and nitrogen oxides in the atmosphere, leading to secondary aerosol formation (particularly in the $PM_{2.5}$ fraction), those operations can account for both a direct and indirect contribution to dust pollution (Backes et al., 2016; Plautz, 2018).

3. Emission factors assessment methods

The PM Emission Factors for agricultural operations currently available in literature were obtained by using several different methods, some being more common than others. The six main methods used in recently published papers are the following:

- Vertical profiling method;
- Dispersion modeling;
- Atmospheric tracer technique;
- Carbon mass balance method;
- LiDAR technology;
- Laboratory measurement methods.

3.1. Vertical profiling method

The vertical profile method is a micrometeorological method which relies on field measurements of wind speed and PM_{10} concentration to infer the wind speed and

PM concentration profiles. The method is well described by several authors (Holmén et al., 2008, 2001; Wang et al., 2010) and it is similar to the method used to estimate ammonia emission rates (IHF method, Ryden and McNeill, 1984). The wind speed profile can be obtained, using the logarithmic wind profile equation (Stull, 1988), by measuring the wind speed with a 3D sonic anemometer or by measuring the wind speed at two different heights.

The concentration profile is obtained by measuring the PM concentration at four different heights, with optical PM monitors (particle counters) placed on a vertical array. The chosen heights depend on the distance of the array from the emission area.

The EFs are then obtained by fitting the two profiles into the following equation (Holmén et al., 2001):

Where EF is the emission factor (mg/m^2), z is the height above ground (m), z_0 is the surface roughness length (Stull, 2001), u(z) is the average wind speed at height z (meters per second) during the treatment (calculated from u_* and ζ based on the Similarity theory in Stull, 2001), c(z) is the mean concentration at height z (meters), t is the length of time of the treatment, θ is the angle between the measured wind direction and the direction that is perpendicular to the tractor path, w is the upwind width of soil worked during the test period, and z_{max} is the height at which the concentration is esteemed equal to 0.00.

This method allows calculating EFs relying exclusively on field measurements, but it has some drawbacks:

- A high number of instruments is needed to perform concentration and wind speed measurements at different heights;

- The estimation of the vertical concentration profile, the plume height and the wind speed profile implies a certain level of uncertainty as it is based on punctual measurements;

- The distance of the PM monitors from the operation path strongly affects both the magnitude of estimated EFs and the particle size distribution detected downwind.

As for the distance in which to measure the PM concentration downwind, Holmén et al. (2008) noted a difference in the $PM_{2.5}/PM_{10}$ ratio between a near source emission measurement ($PM_{2.5}/PM_{10}$ of about 50%) and a far from source measurement ($PM_{2.5}/PM_{10}$ of about 10%). According to the authors, this difference could be due to the fact that the finer PM fraction ($PM_{2.5}$) tends to be dispersed more vertically, which makes detection in long range concentration measurements more difficult.

3.2. Definition of the EFs through dispersion modeling

Atmospheric dispersion models can be utilized to perform EF estimations for agricultural field operations. The most commonly used models are designed primarily to predict concentration of pollutants downwind of a source with a known emission rate, ER ($\mu g\ s^{-1}$). Nonetheless, models are often used inversely to predict Emission Factor (EF) of a source of pollution starting from downwind concentration measurements (Faulkner et al., 2009).

The ERs, and thus the EFs, calculated through this procedure correspond to those that would have generated the measured concentration in the exact measuring spot under simulated conditions. As a consequence, the reliability of the EF estimation does not only rely on the concentration measurement, but also on the characteristics of the chosen model and on its capability of taking into consideration as many influencing parameters as possible (e.g. meteorological variables).

Several dispersion models have been used to estimate EFs from agricultural fields up to now, and they can be distinguished in three main categories:

- Gaussian models (e.g. ISC3, AERMOD);
- Eulerian models;
- Lagrangian models.

The intrinsic differences between these models has been discussed in several works dealing with dispersion modeling in general (Holmes and Morawska, 2006; Leelőssy et al., 2014). Some authors performed direct comparison between models, as done by Faulkner et al. (2009), who compared the actual reference EPA model (AERMOD) and the former one (ISC3-ST) for assessing harvesting PM_{10} EFs and found no statistical difference between them. Other authors (Wang et al., 2010, 2009), preferred to compare modeled EFs with data obtained by different methods, with techniques such as the use of LiDAR technology (treated in paragraph 3.3).

Lagrangian models have been also developed as “backward models” (models which are properly designed calculate EFs starting from measured concentration values and meteorological data). A model featuring this kind of analytical procedure, known as BLS (Backward Lagrangian Stochastic) model (Flesch et al., 1995, 2004), has been specifically developed for agricultural open field applications and, until now, it has been mainly used to estimate emissions of ammonia and other gases. The BLS model has been used to estimate PM emission rates from cattle feedlots (Bonifacio et al., 2013; Mcginn et al., 2010) and has been reported to have several advantages, like the possibility to manage multi-plot sources (Gericke et al., 2011) and to calculate emission for short time periods (e.g. a few hours; Mcginn et al., 2010). Those characteristics could allow the BLS model to be a useful tool for EF estimation from open field operations, which are usually occurring over short time periods.

3.3. Atmospheric tracer technique

The atmospheric tracer technique has been included in this list although it has been sparely used for EF estimations in the agricultural environment. In fact, it has been proposed by (Qiu and Pattey 2008), who used it to estimate EFs for wheat harvesting. The method measures simultaneously the concentration of PM (using a tapered element oscillating microbalance, TEOM 1400a, Thermo Scientific,Waltham, MA, USA) and a tracer gas both upwind and downwind of the tractor path. By placing a tracer emitting device on the tractor, with a known ER, it is possible to infer the PM emission rate through a simple proportion, as follows:

Where $ER_{(PM10)}$ and $ER_{(tracer\ gas)}$ are the emission rates of the pollutant and of the tracer respectively, while [PM_{10}] and [tracer gas] are the two concentrations as measured downwind.

The so obtained ER can then be transformed to an EF by multiplying it for the duration or the operation and dividing it for the treated surface. As for the choice of the tracer gas Qiu and Pattey (2008) chose the Dinitrogenoxide (N_2O, measured with a closed-path tunable diode laser, TGA-100, Campbell Scientific, Logan, Utah, USA) because of its low background level variability and because, although it can be emitted from soils, the emission levels are low. Other tracer gases may be tested in the future.

The main drawback of the atmospheric tracer technique is the assumption of equal transportation dynamic (through convective fluxes) of fine particulate and of the tracer gas. Nonetheless, considering that similar determination methods have been used to estimate gas emissions in agriculture and in other environments, especially in source apportionment studies (Jordan et al., 2006; Lamb et al., 1986; Viana et al., 2008), the tracer method can be considered as an established methodology.

Qiu and Pattey (2008) also performed a comparison between the EFs obtained with the tracer technique and those calculated by using the AERMOD model (on the same experiment) and found no significant difference. It appeared though, that the EFs obtained with the tracer method had a lower variability as compared with the modeled ones.

Thus, this technique seems to be a viable alternative to the other methods described, being potentially capable to give equally good results with a lower level of measurement efforts. Further evaluation of the method should be performed in the future to study its performances with different atmospheric stability and wind speed conditions.

3.4. Carbon mass balance method

The carbon mass balance method is one of the most diffuse methods for assessing emissions from crop residue burning events. The methods uses an approach wich is somehow similar to the atmospheric tracer technique. EFs for PM emissions are estimated by referring the overall emission of organic carbon to the total initial carbon content of the burnt biomass. This is made possible by the fact that crop biomass is a carbonaceous fuel and the pollutant are substantially organic compound. It is therefore possible to relate the emission of PM to that of a reference specie (R_{specie}), usually CO or CO_2 (Andreae, 2019). This is done by first relating the measured mixing ratios of PM and R_{specie}, to obtain the so called emission ratios, which are more correctly referred to as normalized excess mixing ratios (NEMRs; Akagi et al., 2011). NEMRs are obtained according to the following formula:

Where ΔPM is the difference between the PM concentration in the plume and its background concentration and ΔR_{specie} is the difference between the plume concentration of R_{specie} and its background concentration.

A further step is then required to assess EFs starting from NEMRs, by implementing the following formula (Andreae, 2019):

where EF_{PM} is the PM emission factor, MW_{PM} and $MW_{Rspecie}$ are the molecular weights of the species the investigated PM fraction and the reference specie respectively, and $EF_{Rspecie}$ is the known or assumed emission factor of the reference species (often CO or CO_2).

Although the procedure to estimate the emission is quite simple and reliable, some complication can be encountered. Sometimes, for example, the estimation of Background concentrations can pose some issue, especially with reference gases such a CO_2, which is characterized by having many sources and sinks in the surrounding environment, that can easily lead to under or overestimations. Moreover, to adopt this technique, it must be assumed that PM and R_{specie} are equally dispersed from the source to the sampling point, which is not forcefully true. Phenomena such as PM dry deposition and aggregation could in fact lead to an underestimation of the emission.

Another important aspect in determining the reliability of the method is the actual sampling strategy used. In fact, the mass balance technique can be coupled both with ground based (Akagi et al., 2014) and aircraft sampling data (Andreae et al., 1998, Le Canut et al., 1996), while in certain occasions both sampling strategies can be used (Burling et al., 2011). The main advantages of aircraft measurements are the possibility of assessing emissions coming from large areas and the capability of measuring the concentration inside the plume, better estimating the concentration of the more volatile particles. In fact, as highlighted by Holmén et al. (2008), finer particles ($PM_{2.5}$) tend to disperse more vertically than coarser ones. This is crucial in case of crop burning emissions, since most of the produced particle are in finest PM fractions (Yokelson et al., 2009). The main disadvantage of aircraft measurements, on the other hand, is the higher cost implied by the use of aircrafts.

3.5. Use of LiDAR technology for EFs and plume parameter estimation

The LiDAR (Laser Imaging Detection and Ranging) technology has often been used, in recent years, to study particle emissions from agricultural operations and especially to derive plume dispersion parameters. The first applications, such as the one carried out by Holmén et al (2001, 1998), pointed out that LiDAR measurement could be used to estimate vertical and horizontal dispersion coefficients of field dust plumes and proposed an ER estimation method through LiDAR calibration with filter samplers. This applications also allow to evaluate the uncertainty of plume height estimations with the vertical profile method (Holmén et al., 2001). Similarly, LiDARs have also been used to evaluate the uncertainty of plume parameter estimation performed with models. Wang et al. (2010) compared EFs estimated with LiDAR and with the AERMOD model and found that, although similar, the results obtained with LiDAR had smaller uncertainty intervals.

In a more recent study (Holmén et al., 2008), involving the use of a backscatter LiDAR, plume size and plume movement were studied through LiDAR images and this information allowed to observe that, under convective conditions, the plume tends to move more vertically than laterally. This kind of information could be useful to answer some methodological questions, like if the PM concentration measurements are better done near or far from the emitting source (Holmén et al., 2008). A further advantage of the more recent LiDAR application is that it is possible to differentiate aerosols of different origins (Gregorio et al., 2018; Holmén et al., 2008), such as the engine exhaust plume and the soil dust plume coming from a single area source. Willis et al. (2017), by coupling LiDAR measurements with PSD quantification through stationary sampler and micrometeorological measurements, were further able to calculate ER, at a whole facility scale, from LiDAR measurements.

In recent years, the LiDAR technology has become an important tool for EF estimation, especially during experimental trials, being often used as reference method to evaluate models (Moore et al., 2015; Wang et al., 2009). The main negative aspects of this evaluation technique are linked to its costs and to its complexity in terms of instrument use and calibration requirements. On the other hand, this technique is the most informative one in terms of plume shape and plume dynamics.

3.6. Laboratory measurement methods

Although the environmental conditions are of crucial importance in determining PM emissions from cropping operations and cannot be simulated under laboratory conditions, several laboratory assessment methods have been applied to this specific field. Particularly, laboratory methods are used to assess the PM Emission Potential (EP, mg kg^{-1}), which is the potential capacity of a substrate to emit fine particles in a certain fraction range, of agricultural soils and crop biomass. Moreover, laboratory techniques have often been used to assess crop specific EFs for residue burning activities. The main methods are:

- Wind tunnels;
- Soil resuspension chambers;
- Open combustion chambers.

Wind tunnels are tunnel shaped dynamic enclosure systems, in which an air flow is forced over or through a certain volume of soil, causing it to re-suspend. Wind tunnels are generally more suited to assess wind blown PM emissions from fields (in wind erosion studies) than tillage induced ones, since they do not allow to simulate the active soil disturbance as generated by tilling implements (Funk et al., 2008). Nonetheless, in studies such as those by Funk et al. (2008), a wind tunnel has been used to assess emissions from soil under different moisture conditions, retrieving information very relevant to estimate tilling EFs variation with different soil moisture contents.

Soil resuspension chambers are built with the aim of actively re-suspending fine particles in a soil sample by mechanically agitating it. The most common soil resuspension mechanisms consist either of rotating drums, in which the soil sample is mechanically re-suspended (such as in Madden et al., 2009), or of abrader systems, in which the soil particles are propelled through a path allowing the abrasion action to cause the emission (such as in Chandler et al., 2002). After particle resuspension has been achieved, the polluted air stream is usually pulled or blown at a known rate (using pumps) toward a further sedimentation/sampling chamber, where PM_{10} is selected through an impactor and deposited on a filter (Chandler et al., 2002; Madden et al., 2009). The soil EP is then calculated dividing the mass of PM_{10} (mg) deposited on the filter after a certain sampling time, by the total volume of soil sample used (kg). A more comprehensive review of soil resuspension chamber designs and experimental methodologies has been provided by Gill et al. (2006).

Soil resuspension chambers have been used to study the effects of moisture, soil texture and soil structure on PM emissions from tillage (Madden et al., 2010; Madden et al., 2009; Carvacho et al., 2004; Chandler et al., 2002).

Open combustion chambers are the most common laboratory equipment used to simulate crop residue burning under laboratory conditions. Combustion chambers are normally constituted by a burning plate, on which the crop material is burned, and of a chimney, inside which the air is sampled to analy

se PM concentration. To calculate crop specific EFs (g kg^{-1}), the air concentration of PM (g m^{-3}) inside the chimney is multiplied by total volume (m^3) of combustion gases passed through it and divided by the mass (kg) of the crop material. Although most open combustion chambers have similar designs (schemes can be found in Mugica-Álvarez, 2018; França et al., 2012), some alternative designs have been proposed, such as that described by Jenkins et al. (1990), who adopted a chamber shaped similarly to a wind tunnel, which was developed to simulate agricultural biomass burning emissions from wide surfaces. Another design option is the one adopted by Li et al. (2017), who used a chamber of small dimension (0.23 m^3), which was characterized by having a HEPA filter placed at the air inlet and by being equipped with a second chamber in which polluted air is mixed before sampling. As in the case of soil resuspension devices, also combustion chambers have been used to assess the effect of substrate moisture on PM emission (Hayashi et al., 2014), other than assessing fuels of different types and origins (Christian et al., 2003).

In conclusion, laboratory trials are of crucial importance to acquire information on the effects that specific factors (such as substrate characteristics and moisture) have on the out coming emissions and allow to better comprehend the dynamics that are at the base of open field emission events.

4. Mitigation measures

The development and evaluation of PM mitigation measures for open field agricultural operations is not an easy task. This difficulty is partially due to the fact that EFs obtained from open field assessments are related to specific and not repeatable environmental conditions, which makes it difficult to assess the efficiency of mitigation measures through comparative trials. Nonetheless, several studies have tested PM or dust emission mitigation strategies. Table 4 shows some of the main mitigation measures proposed for reducing PM emissions during agricultural operations.

Table 4. Brief description and emission abatement rates of the main dust emission mitigation measures for agricultural operations as reported by various authors.

Reference	**Operation**	**Mitigation measure**	**Emission abatement**
Coates et al. (1996)	Conventional land preparation	Minimum tillage	45% (of TSP)
Backer et al. (2005)	Conventional land preparation	Conservation tillage system	up to 100% (of PM_{10})
Billate et al., (2004)	Corn receiving facilitilty (hopper bin - pit conveyor)	increasing grain flow rate + lowering drop height	92% (of total PM_{10})

Biocca et al. (2015)	Maize sowing	filtering-recycling system	95-71% (of insecticide particles at ground level)
Pagano (2011)	Hazelnut harvesting	Harvester prototype	18% (of total PM_{10})
Pochi et al. (2015)	Maize sowing	Modified driller	up to 100% (of active ingredient concentration in the air)
Chapple et al. (2014)	Maize sowing	SweepAir® system	>99% (of seed coating particles)
Faulkner (2013)	Almond harvesting	3 different harvester prototypes	76 - 41 - 9% (of total PM_{10})
Faulkner (2013)	Almond harvesting	cyclone abatement technology	79% (of total PM_{10})
Ponpesh et al. (2010)	Almond harvesting	Decreasing airflow	77% (of total PM_{10})
Faulkner et al. (2009b)	Almond harvesting	reduction of harvester speed	no significant abatement

Conservation tillage techniques are widely proposed as valid alternatives to traditional tilling for reducing PM emissions. Those techniques are able to exert a substantial mitigation of dust (Coates, 1996; Backer, 2005) and PM_{10} (Backer, 2005) emissions during land preparation. The emission reductions achieved with minimum and no tillage are mainly attributed to the reduction of tilling events, while practically no difference has been highlighted for the choice of the tilling implement (Coates, 1996, Backer et al., 2005). Although conservation tillage is indubitably a good solution when it comes to reducing PM_{10} emissions, it can affect crop yields (Irmak et al., 2019) and cannot always be applied. Therefore, it would be valuable to explore the possibility of lowering the emission potential of implements used in conventional tillage for PM emission mitigation.

Several mitigation measures are proposed for harvesting operations, especially for certain crops, which are known for producing high PM_{10} emissions during harvest. Almond and hazelnut are two of the crops which have been addressed the most and for which harvester and abatement technology prototypes have been developed (Faulkner, 2013; Pagano et al., 2011). Moreover, the harvester operating parameters, such as airflow and harvester speed, were tested (Faulkner et al., 2009; Ponpesh et al., 2010). The prototypes and abatement technologies were successful in reducing PM_{10} emissions, reaching up to 79% and 18% of emission reduction respectively for almond and hazelnut harvesting (Table 4). The regulation of the harvester airflow gave good results as well, while no effect was obtained by lowering the harvester speed (Table 4).

As previously reported, post harvesting operations can strongly affect the overall harvest related PM_{10} emissions. Nonetheless, few published articles proposed mitigation measure for post harvesting emissions, such as the one published by Billate et al. (2004), who highlighted that in corn receiving operations reducing the drop height from the hopper bin and grain unloading rate (kg s^{-1}) can result in lower PM_{10} emissions.

From the literature review made, it appears that few crops have currently been addressed in terms of mitigation measure proposals for harvesting operations. Thus, more research is required, aiming to find solutions to reduce harvesting PM_{10} emissions from the main crops (e.g. maize, wheat etc.). Further mitigation measures should also be developed for immediate post harvesting operations.

For crop burning emissions, the mitigation approach is slightly different as compared to other activities. The main solutions are in fact aiming not to mitigate the emissions but to rather substitute residue burning as a residue management practice, favoring other more sustainable techniques. Ravindra et al. (2018) summarized these sustainable alternatives, going from soil incorporation of residues to their use for energy production through biomass or biogas plants. Other alternatives are the implementation of cattle feed with crop residues or the production of compost and biochar.

For sowing operations, different mitigation measures and driller prototypes have been proposed (Biocca et al., 2015; Pochi et al. 2015 Pagano et al., 2011). Those solutions focused on reducing the emission of seed coating particles (abating them up to 100%; Table 4) and the deposition of coating particles to the ground, but did not take into consideration the total PM_{10} emissions from sowing. Thus, there could be room for further studies adopting a broader approach and considering the soil particles emitted during seed drilling passages.

For manure and fertilizer spreading practically no technical solution has been evaluated for its capacity to reduce PM emissions. Future research should address this subject, possibly starting by testing the technology that has been developed to reduce the emission of ammonia emissions from field manure spreading.

5. Results of the review

In this section, collected data and information were summarized in order to:

a) Identify operations/crops with most crucial environmental impacts /EFs;

b) identify the main emission factor estimation methods and highlight their pros and cons;

c) review mitigation measures proposed for PM_{10} emission reductions in field emissions;

d) identify gaps in of knowledge on this specific topic and highlight future research opportunities.

5.1 Main agricultural operations contributing to PM emission

The EF determination is the first step to take in order to find feasible solutions to an environmental issue, such as PM emissions, and it also allows decision makers to produce regulations based on sound scientific data.

By reviewing the literature on PM emissions from agricultural activities it was evident that some activities such as tillage, residue burning and harvesting have been addressed more often than others, such as manure and fertilizer spreading or sowing. Moreover, these last two operations have been mainly studied from a very specific perspective, focusing only on a fraction of the total PM produced (namely the bio-aerosol component for manure spreading and the seed coating for sowing). Moreover, it was observed that for many countries in the world, such as Africa, India and South America, few or any specific EFs are available in scientific literature.

The EFs gathered in Tables 1 and 2 are summarized in Figures 2, 3 and 4, in order to have an overall impression of the PM_{10} both crop-wise (for wheat, cotton, and maize) and operation-wise (tillage, harvest, sowing and fertilizer spreading). The graphs were made by averaging the EFs summarized in Tables 1 and 2 for tillage (the tillage comprehends three passages: plowing/disking, harrowing and land planning/floating) and harvest. The contribution of sowing operations was set equal for the three crops, in the absence of specific investigations, and was assumed to be equal to a tooth harrowing passage (82 mg m^{-2}), in agreement with the findings of Clausnitzer and Singer (1996). The contribution of fertilizer application was considered to be equal to 1.09 kg t^{-1} of applied fertilizer (as in Pattey and Qiu, 2012), with an application rate of 0.3 t ha^{-1} (the same application rate was used for the three crops, although a better approximation should be made for more precise applications).

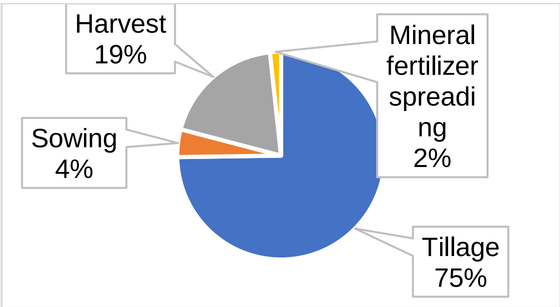


Figure 2. Summary of the contribution of tillage practices, harvesting, sowing and fertilizer spreading to the total PM_{10} emitted from wheat cropping operations.

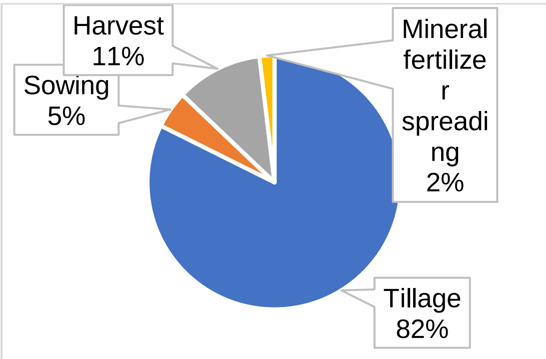


Figure 3. Summary of the contribution of tillage practices, harvesting, sowing and fertilizer spreading to the total PM_{10} emitted from maize cropping operations.

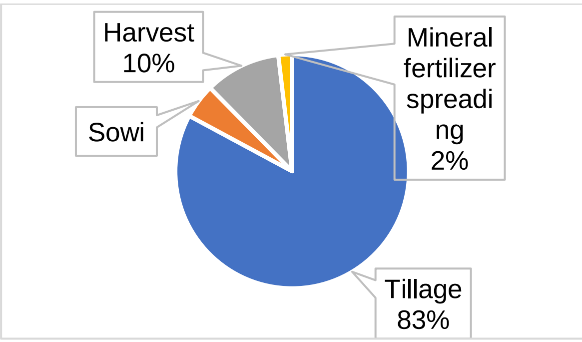


Figure 4. Summary of the contribution of tillage practices, harvesting, sowing and fertilizer spreading to the total PM_{10} emitted from cotton cropping operations.

Figures 2, 3 and 4 suggest that tillage practices are the most polluting operations in terms of PM_{10} emissions for all three crops represented here (among 75 and 83% of the overall emissions), as they consist of three or more passages, each one with his own emission potential. Harvesting follows as the second most emitting practice, being the one that varies the most among crops (from 10 to 19% of total emissions). Sowing and mineral fertilizer application have a lower impact (among 2 and 5 % of total emissions). Also, the total emission potential varies between crops, being higher for wheat (1,904 mg m^{-2}) and lower for cotton (1,718 mg m^{-2}) and maize (1,538 mg m^{-2}). This brief summary of the total emission for each is not a precise estimation, since it is based on data acquired under varying conditions and it does not consider all the steps of the cropping system. Still, it can be useful to provide a rough estimation of the emission magnitude and of the contributions of various crops and operations on total PM emissions.

5.2. Evolution of EF estimation methods

The EFs available in the literature were obtained through a large variety of estimation methods. This variety of methods makes it difficult to carry out comparisons between EFs, especially considering that it is not clear which method can be considered as the reference one.

One of the main objectives of this review was to list the main methods for open-field EF estimation and to understand the current research trends, since some methods are becoming obsolete and less used while some others are getting used more often and could eventually be considered as reference methods in the future. In fact, the vertical profile method, which has long been considered as a reference technique for EF estimation, has been abandoned by most researchers, mainly due to its high instrumentation costs, but also because it entails a certain uncertainty of results. Thus, some other methods tend to be preferred.

Particularly, the most common estimation methods appear to be those implementing dispersion models inversely to estimate emissions. Among dispersion models, Lagrangian models are considered more precise as compared to Gaussian models. Nonetheless, Gaussian models are still suggested as reference models by some regulatory agencies (such as the US-EPA with the AERMOD model) due to their simplicity of use. The use of models, in general, seems to be the preferred way to obtain EFs and emission inventories for regulatory purposes and the most common models have been used as reference to validate other EF estimation methods.

The main advantage in the use of LiDAR technology for EF estimation reside in the fact that it allows to study the plume dynamics and dispersion, being so more informative as compared to other methods. This method has the advantage of not relying on modeled environmental conditions, leading to estimates that can be more legitimately used to evaluate the efficacy of dispersion models, which are based on wind modelling.

The atmospheric tracer method, which was used by Qiu and Pattey (2008), and is worth to be mentioned, because it shares with the LiDAR technique the advantage of being independent from wind modeling.

In general, the current trend in EF estimation for agricultural field operation is moving toward the use of models as main estimation tools. Besides, for the evaluation of models reliability, it could be better to use field based methods, such as the LiDAR or the atmospheric tracer technique, that don't rely on modeled environmental conditions, but on actual measurements.

5.3. Mitigation measures and development trends

The development of feasible mitigation measure for PM emissions is to be seen as the final aim of the process that starts with the evaluation of the emission factors. Although there are several articles dealing with PM mitigation measures, most of them focus on few operations. In fact, there are some operations, such as manure spreading, that were unaddressed in terms of solutions to reduce emissions. Also for tillage practices there were few articles focusing on mitigating the emission of PM, proposing mainly a reduction of tilling passages as main solution. Also for harvesting, the research focused on few crops. Differently, sowing operations have been widely discussed although the main focus has been on seed coating particle reduction more than on total PM_{10}. In conclusion, there are many gaps of knowledge in the field of agricultural PM emissions, where proposals for mitigation measures are still required, leaving open opportunities for future research and technology development.

Generally, a more intensive effort should be put into the development and testing of mitigation measures, especially for those operations that are majorly contributing to field derived PM_{10} emissions.

Future perspectives and research needed

The literature review highlighted that there is more information available on PM_{10} emission factors (EFs) from certain agricultural operations, such as tillage, harvesting and residue burning than from others, such as sowing and manure and fertilizer spreading. Moreover, emission assessment studies were usually conducted with an operation-wise approach, while it appears from literature that a crop-wise approach would lead to more precise estimations (being less influenced by seasonal variation). The lack of an overall view of the emissions, as they take place in each step of a productive system, could potentially lead to substantial underestimation of the overall emissions. To avoid this, all the operations that have not be taken into consideration for their overall PM_{10} emissions (such as sowing and manure spreading), but mainly for a particular kind of particle (namely seed coating or bio-aerosol) should be assessed.

As for the emission factor estimation methods, the most utilized ones in current research are those applying inverse dispersion models to estimate emissions rates from field, also thanks to their cost-effectiveness and adaptability. Other techniques that provide good results are LIDAR measurements and the atmospheric tracer techniques. Those two techniques are particularly interesting, because they do not rely on modeled atmospheric conditions, and could thus be used as basis for comparison for dispersion models.

The mitigation measures developed for in field PM_{10} emissions from agricultural operations are quite few. For tilling practices the main proposed solutions to abate emissions are the implementation of minimum or no tillage systems, while few efforts have been put into the estimation of the emission potential of tilling implements. For harvesting, adequate measures have been developed for a few crops, while many other are still to be addressed. The emission abatement measures proposed for sowing operations are focused on seed coating particles, while few information is even available on the total PM_{10} particles emitted. As for manure and fertilizer spreading no PM_{10} mitigation measure has been proposed or assessed.

Future research in the field of PM emissions from agricultural operations should aim to fill the current gaps of knowledge. Aspects for future work include:

- the emissions deriving from whole cropping systems, through step by step measurement and evaluation;
- the influence of implement choice and operation parameters on tillage induced PM_{10} emission with possible development of implements with low emission potential;
- the assessment of harvesting induced PM_{10} emissions for crops not yet assessed and the development of mitigation measures (e.g. harvester prototypes development and operation parameters management);
- the assessment of total PM_{10} emissions for solid and liquid manure application and the evaluation of mitigation measures.

Acknowledgements

This work has been realized within the project "Valutazione delle emissioni di materiale particolato dalle operazioni colturali e di trasformazione aziendale del mais" (Evaluation of PM emission from cropping operation and first transformation of Maize), funded by Cassa di Risparmio di Torino (CRT foundation) [grant numbers 2018.2273].

References

Akagi, S. K., Burling, I. R., Mendoza, A., Johnson, T. J., Cameron, M., Griffith, D. W. T., Paton-Walsh, C., Weise, D. R., Reardon, J., and Yokelson, R. J., 2014. Field measurements of trace gases emitted by prescribed fires in southeastern US pine forests using an open-path FTIR system, Atmos. Chem. Phys., 14, 199–215, https://doi.org/10.5194/acp-14-199-2014

Akbar-Khanzadeh, F., Ames, A., Bisesi, M., Milz, S., Czajkowski, K., Kumar, A., 2012. Particulate Matter (PM) Exposure Assessment—Horizontal and Vertical PM Profiles in Relation to Agricultural Activities and Environmental Factors in Farm Fields. Journal of Occupational and

Environmental Hygiene 9, 502–516. https://doi.org/10.1080/15459624.2012.695216
Amann, M., Klimont, Z., Winiwarter, W., 2012. Emissions from agriculture and their control potentials [WWW Document]. URL http://gains.iiasa.ac.at/images/stories/reports/TSAP/TSAP-AGRI-20120612.pdf (accessed 1.30.19).
Andreae, M., 2019. Emission of trace gases and aerosols from biomass burning – An updated assessment. Atmospheric Chemistry and Physics Discussions. 1-27. 10.5194/acp-2019-303.
Andreae, M., Andreae, T., Annegarn, H., Beer, F., Cachier, H., Elbert, W., Harris, G.W., Maenhaut, W., Salma, I., Swap, R., Wienhold, F., Zenker, T., 1998. Airborne studies of aerosol emissions from savanna fires in southern Africa: 2. Aerosol chemical composition. Journal of Geophysical Research, v.103, 32,119-32,128 (1998). 103. 10.1029/98JD02280.
Arai, H., Hosen, Y., Hong, V.N.P., Thi, N.T., Huu, C.N., Inubushi, K., 2015. Greenhouse gas emissions from rice straw burning and straw-mushroom cultivation in a triple rice cropping system in the Mekong Delta. Soil Science and Plant Nutrition 61, 719–735. https://doi.org/10.1080/00380768.2015.1041862
Avecilla, F., Panebianco, J.E., Buschiazzo, D.E., 2017. Meteorological conditions during dust (PM 10) emission from a tilled loam soil: Identifying variables and thresholds. Agricultural and Forest Meteorology 244–245, 21–32. https://doi.org/10.1016/j.agrformet.2017.05.016
Backes, A.M., Aulinger, A., Bieser, J., Matthias, V., Quante, M., 2016. Ammonia emissions in Europe, part II: How ammonia emission abatement strategies affect secondary aerosols. Atmospheric Environment 126, 153–161. https://doi.org/10.1016/j.atmosenv.2015.11.039
Baker, B.J., Southard, R., Mitchell, J., 2005. Agricultural Dust Production in Standard and Conservation Tillage Systems in the San Joaquin Valley. Journal of environmental quality. 34. 1260-9. 10.2134/jeq2003.0348.
Bauer, S. E., Im, U., Mezuman, K., Gao, C. Y., 2019. Desert Dust, Industrialization, and Agricultural Fires: Health Impacts of Outdoor Air Pollution in Africa. Journal of Geophysical Research: Atmospheres, 124(7), 4104-4120.
Billate, R.D., Maghirang, R.G., Casada, M.E., 2004. Measurement of particulate matter emissions from corn receiving operations with simulated hopper-bottom trucks. Transactions of the ASAE 47, 521–529. https://doi.org/10.13031/2013.16021
Biocca, M., Pochi, D., Fanigliulo, R., Gallo, P., 2015. Dust emissions during the sowing of maize dressed seeds and drift reducing devices. Open Agriculture Journal 9, 42–47. https://doi.org/10.2174/1874331501509010042
Bogman, P., Cornelis, W., Rolle, H., Gabriels, D., 2005. Prediction of TSP and PM10 emissions from agricultural operations in Flanders, Belgium.
Bonifacio, H.F., Maghirang, R.G., Auvermann, B.W., Razote, E.B., Murphy, J.P., Harner, J.P., 2012. Particulate matter emission rates from beef cattle

feedlots in Kansas—Reverse dispersion modeling. Journal of the Air & Waste Management Association 62, 350–361. https://doi.org/10.1080/10473289.2011.651557

Boubel, R., W., Darley, E., F., Schuck E. A., 1969. Emissions from Burning Grass Stubble and Straw, Journal of the Air Pollution Control Association, 19:7, 497-500, DOI: 10.1080/00022470.1969.10466517

Burling, I. R., Yokelson, R. J., Akagi, S. K., Urbanski, S. P., Wold, C. E., Griffith, D. W. T., Johnson, T. J., Reardon, J., and Weise, D. R., 2011. Airborne and ground-based measurements of the trace gases and particles emitted by prescribed fires in the United States, Atmos. Chem. Phys., 11, 12197–12216, https://doi.org/10.5194/acp-11-12197-2011

Carlsen, S.C.K., Spliid, N.H., Svensmark, B., 2006a. Drift of 10 herbicides after tractor spray application. 2. Primary drift (droplet drift). Chemosphere 64, 778–786. https://doi.org/10.1016/j.chemosphere.2005.10.060

Carlsen, S.C.K., Spliid, N.H., Svensmark, B., 2006b. Drift of 10 herbicides after tractor spray application. 1. Secondary drift (evaporation). Chemosphere 64, 787–794. https://doi.org/10.1016/j.chemosphere.2005.10.061

Carvacho, O.F., Ashbaugh, L.L., Brown, M.S., Flocchini, R.G., 2004. Measurement of PM2.5 emission potential from soil using the UC Davis resuspension test chamber. Geomorphology 59, 75–80. https://doi.org/10.1016/j.geomorph.2003.09.007

Cassel, T., K. Trzepla-Nabaglo, and R. Flocchini. 2003. PM10 Emission Factors for Harvest and Tillage of Row Crops. 12th International Emission Inventory Conference-BEmission Inventories-Applying New Technologies,[San Diego, CA, April 29YMay 1, 2003.

Chandler, D. G., Saxton, K. E., Kjelgaard, J., Busacca, A. J., 2002. A technique to measure fine-dust emission potentials during wind erosion. Soil Science Society of America Journal, 66(4), 1127-1133.

Chapple, A.C., Vrbka, L., Friessleben, R., Schnier, H.F., Cantoni, A., Arnold, A.C., 2014. A novel technical solution to minimize seed dust during the sowing process of maize using vacuum based equipment: principles and an estimate of efficiency. Aspects of Applied Biology 119–124.

Chen, W., Tong, D., Zhang, S., Dan, M., Zhang, X., Zhao, H., 2015. Temporal variability of atmospheric particulate matter and chemical composition during a growing season at an agricultural site in northeastern China. Journal of Environmental Sciences 38, 133–141. https://doi.org/10.1016/j.jes.2015.05.023

Chen, W., Tong, D.Q., Zhang, S., Zhang, X., Zhao, H., 2017. Local PM10 and PM2.5 emission inventories from agricultural tillage and harvest in northeastern China. Journal of Environmental Sciences 57, 15–23. https://doi.org/10.1016/j.jes.2016.02.024

Christian, T. J., Kleiss, B., Yokelson, R. J., Holzinger, R., Crutzen, P. J., Hao, W. M., ... & Ward, D. E., 2003. Comprehensive laboratory measurements of biomass-burning emissions: 1. Emissions from Indonesian, African, and other fuels. Journal of Geophysical Research: Atmospheres, 108(D23).

Clausnitzer, H., Singer, M.J., 1996. Respirable-Dust Production from Agricultural Operations in the Sacramento Valley, California. Journal of Environment Quality 25, 877. https://doi.org/10.2134/jeq1996.00472425002500040032x

Clausnitzer, H., Singer, M.J., 1997. Intensive land preparation emits respirable dust. California Agriculture 51, 27–30. https://doi.org/10.3733/ca.v051n02p27

Coates, W., 1996. Particulates Generated by Five Cotton Tillage Systems. Transactions of the ASAE. 39. 1593-1598. 10.13031/2013.27673.

Coelho, C.H., Allen, A.G., Fornaro, A., Orlando, E.A., Grigoletto, T.L.B., Campos, M.L.A.M., 2011. Wet deposition of major ions in a rural area impacted by biomass burning emissions. Atmospheric Environment 45, 5260–5265. https://doi.org/10.1016/j.atmosenv.2011.06.063

Council directive 2008/98/EC On waste and repealing certain Directives (2008). Official journal L312/3

de Rooij, M.M.T., Heederik, D.J.J., Borlée, F., Hoek, G., Wouters, I.M., 2017. Spatial and temporal variation in endotoxin and PM10 concentrations in ambient air in a livestock dense area. Environmental Research 153, 161–170. https://doi.org/10.1016/j.envres.2016.12.004

Dennis, A., Fraser, M., Anderson, S., Allen, D., 2002. Air pollutant emissions associated with forest, grassland, and agricultural burning in Texas. Atmospheric Environment 36, 3779–3792. https://doi.org/10.1016/S1352-2310(02)00219-4

Douglas, P., Robertson, S., Gay, R., Hansell, A.L., Gant, T.W., 2018. A systematic review of the public health risks of bioaerosols from intensive farming. International Journal of Hygiene and Environmental Health 221, 134–173. https://doi.org/10.1016/j.ijheh.2017.10.019

EEA, 2016. European Union emission inventory report 1990–2012 under the UNECE Convention on Long-range Transboundary Air Pollution (LRTAP), EEA Report No 16/2016, European Environment Agency.

EFSA, 2013. European Food Safety Authority (EFSA) Guidance on the risk assessment of plant protection products on bees (Apis mellifera, Bombus spp. and solitary bees): guidance on risk assessment on bees. EFSA J., 11 (2013), p. 3295. https://doi.org/10.2903/j.efsa.2013.3295

Faulkner, W.B., 2013. Harvesting equipment to reduce particulate matter emissions from almond harvest. Journal of the Air & Waste Management Association 63, 70–79. https://doi.org/10.1080/10962247.2012.738625

Faulkner, W.B., Downey, D., Giles, D.K., Capareda, S.C., 2011. Evaluation of Particulate Matter Abatement Strategies for Almond Harvest. Journal of the Air & Waste Management Association 61, 409–417. https://doi.org/10.3155/1047-3289.61.4.409

Faulkner, W.B., Goodrich, L.B., Botlaguduru, V.S.V., Capareda, S.C., Parnell, C.B., 2009. Particulate Matter Emission Factors for Almond Harvest as a Function of Harvester Speed. Journal of the Air & Waste Management Association 59, 943–949. https://doi.org/10.3155/1047-3289.59.8.943

Flesch, T.K., Wilson, J.D., Harper, L.A., Crenna, B.P., Sharpe, R.R., 2004. Deducing Ground-to-Air Emissions from Observed Trace Gas Concentrations: A Field Trial. J. Appl. Meteor. 43, 487–502. https://doi.org/10.1175/1520-0450(2004)043<0487:DGEFOT>2.0.CO;2

Flesch, T.K., Wilson, J.D., Yee, E., 1995. Backward-Time Lagrangian Stochastic Dispersion Models and Their Application to Estimate Gaseous Emissions. J. Appl. Meteor. 34, 1320–1332. https://doi.org/10.1175/1520-0450(1995)034<1320:BTLSDM>2.0.CO;2

Flocchini, R.G., James, T.A., Ashbaugh, L.L., Brown, M.S., Carvacho, O.F., Matsumura, R.T., 2001. Sources and Sinks of PM10 in the San Joaquin Valley 207.

Forero, L.G., Limay-Rios, V., Xue, Y., Schaafsma, A., 2017. Concentration and movement of neonicotinoids as particulate matter downwind during agricultural practices using air samplers in southwestern Ontario, Canada. Chemosphere 188, 130–138. https://doi.org/10.1016/j.chemosphere.2017.08.126

França, D., Longo, K., Rudorff, B., Aguiar, D., Freitas, S., Stockler, R., & Pereira, G., 2014. Pre-harvest sugarcane burning emission inventories based on remote sensing data in the state of Sao Paulo, Brazil. Atmospheric Environment, 99, 446-456.

França, D.A., Longo, K.M., Neto, T.G.S., Santos, J.C., Freitas, S.R., Rudorff, B.F.T., Cortez, E.V., Anselmo, E., Carvalho, J.A., Jr., 2012. Pre-Harvest Sugarcane Burning: Determination of Emission Factors through Laboratory Measurements. Atmosphere 3, no. 1, 164-180. https://doi.org/10.3390/atmos3010164

Funk, R., Reuter, H.I., Hoffmann, C., Engel, W., Öttl, D., 2008. Effect of moisture on fine dust emission from tillage operations on agricultural soils. Earth Surface Processes and Landforms 33, 1851–1863. https://doi.org/10.1002/esp.1737

Gao, F., Feng, G., Sharratt, B., Zhang, M., 2014. Tillage and straw management affect PM10 emission potential in subarctic Alaska. Soil and Tillage Research 144, 1–7. https://doi.org/10.1016/j.still.2014.07.001

Gericke, D., Pacholski, A., Kage, H., 2011. Measurement of ammonia emissions in multi-plot field experiments. Biosystems Engineering 108, 164–173. https://doi.org/10.1016/j.biosystemseng.2010.11.009

Giannadaki, D., Giannakis, E., Pozzer, A., Lelieveld, J., 2018. Estimating health and economic benefits of reductions in air pollution from agriculture. Science of The Total Environment 622–623, 1304–1316. https://doi.org/10.1016/j.scitotenv.2017.12.064

Giannakis, E., Kushta, J., Giannadaki, D., Georgiou, G.K., Bruggeman, A., Lelieveld, J., 2019. Exploring the economy-wide effects of agriculture on air quality and health: Evidence from Europe. Science of The Total Environment 663, 889–900. https://doi.org/10.1016/j.scitotenv.2019.01.410

Gill, T. E., Zobeck, T. M. Stout, J. E., 2006. Technologies for laboratory generation of dust from geological materials. Journal of hazardous materials, 132(1), 1-13.

Goossens, D., Riksen, M. (Eds.), 2004. Wind erosion and dust dynamics: observations, simulations, modelling. Wageningen University and Research Centre, Wageningen.

Gregorio, E., Gené, J., Sanz, R., Rocadenbosch, F., Chueca, P., Arnó, J., Solanelles, F., Rosell-Polo, J.R., 2018. Polarization Lidar Detection of Agricultural Aerosol Emissions [WWW Document]. Journal of Sensors. https://doi.org/10.1155/2018/1864106

Grella, M., Gallart, M., Marucco, P., Balsari, P., Gil, E., 2017. Ground Deposition and Airborne Spray Drift Assessment in Vineyard and Orchard: The Influence of Environmental Variables and Sprayer Settings. Sustainability 9, 728. https://doi.org/10.3390/su9050728

Grella, M., Marucco, P., Balsari, P., 2019. Toward a new method to classify the airblast sprayers according to their potential drift reduction: comparison of direct and new indirect measurement methods. Pest. Manag. Sci. ps.5354. https://doi.org/10.1002/ps.5354

Guo, H., Kota, S.H., Sahu, S.K., Hu, J., Ying, Q., Gao, A. and Zhang, H., 2017. Source apportionment of PM2. 5 in North India using source-oriented air quality models. Environmental pollution, 231, pp.426-436.

Gupta, P.K., Sahai, S., Singh, N., Dixit, C.K., Singh, D.P., Sharma, C., Tiwari, M.K., Gupta, R.K., Garg, S.C., 2004. Residue burning in rice–wheat cropping system: Causes and implications. Current Science 87, 1713–1717.

Halstensen, A.S., Heldal, K.K., Wouters, I.M., Skogstad, M., Ellingsen, D.G., Eduard, W., 2013. Exposure to Grain Dust and Microbial Components in the Norwegian Grain and Compound Feed Industry. Ann Occup Hyg 57, 1105–1114. https://doi.org/10.1093/annhyg/met036

Hayashi, K., Ono, K., Kajiura, M., Sudo, S., Yonemura, S., Fushimi, A., Saitoh, K., Fujitani, Y., Tanabe, K., 2014. Trace gas and particle emissions from open burning of three cereal crop residues: Increase in residue moistness enhances emissions of carbon monoxide, methane, and particulate organic carbon. Atmospheric Environment 95, 36–44. https://doi.org/10.1016/j.atmosenv.2014.06.023

Hays, M.D., Fine, P.M., Geron, C.D., Kleeman, M.J., Gullett, B.K., 2005. Open burning of agricultural biomass: Physical and chemical properties of particle-phase emissions. Atmospheric Environment 39, 6747–6764. https://doi.org/10.1016/j.atmosenv.2005.07.072

Hinz, T., 2002, *Particulate matter in and from agriculture*, Landbauforschung Völkenrode, Special Issue 235, Bundesforschungsanstalt für Landwirtschaft.

Holmén, B., Miller, D., Hiscox, A., Yang, W., Wang, J., Sammis, T., Bottoms, R., 2008. Near-source particulate emissions and plume dynamics from agricultural field operations. Journal of Atmospheric Chemistry 59, 117–134. https://doi.org/10.1007/s10874-007-9086-6

Holmén, B.A., Eichinger, W.E., Flocchini, R.G., 1998. Application of Elastic Lidar to PM10 Emissions from Agricultural Nonpoint Sources. Environ. Sci. Technol. 32, 3068–3076. https://doi.org/10.1021/es980176p

Holmén, B.A., James, T.A., Ashbaugh, L.L., Flocchini, R.G., 2001. Lidar-assisted measurement of PM10 emissions from agricultural tilling in California's San Joaquin Valley – Part II: emission factors. Atmospheric Environment 35, 3265–3277. https://doi.org/10.1016/S1352-2310(00)00519-7

Holmes, N.S., Morawska, L., 2006. A review of dispersion modelling and its application to the dispersion of particles: An overview of different dispersion models available. Atmospheric Environment 40, 5902–5928. https://doi.org/10.1016/j.atmosenv.2006.06.003

Irmak, S., Kukal, M.S., Mohammed, A.T., Djaman, K., 2019. Disk-till vs. no-till maize evapotranspiration, microclimate, grain yield, production functions and water productivity. Agricultural Water Management 216, 177–195. https://doi.org/10.1016/j.agwat.2019.02.006

Jahne, M.A., Rogers, S.W., Holsen, T.M., Grimberg, S.J., 2015a. Quantitative microbial risk assessment of bioaerosols from a manure application site. Aerobiologia 31, 73–87. https://doi.org/10.1007/s10453-014-9348-0

Jahne, M.A., Rogers, S.W., Holsen, T.M., Grimberg, S.J., Ramler, I.P., Kim, S., 2016. Bioaerosol Deposition to Food Crops near Manure Application: Quantitative Microbial Risk Assessment. Journal of Environmental Quality 45, 666–674. https://doi.org/10.2134/jeq2015.04.0187

Jahne, Michael A., Rogers, S.W., Holsen, T.M., Grimberg, S.J., Ramler, I.P., 2015b. Emission and Dispersion of Bioaerosols from Dairy Manure Application Sites: Human Health Risk Assessment. Environmental Science & Technology 49, 9842–9849. https://doi.org/10.1021/acs.est.5b01981

Jenkins, B. M., Chang, D. P. Y., Raabe, O. G., 1990. Development of test procedures to determine emissions from open burning of agricultural and forestry wastes. Final report on Phase 1 (No. PB-90-172305/XAB). California Univ., Davis, CA (USA).

Jordan, T.B., Seen, A.J., Jacobsen, G.E., 2006. Levoglucosan as an atmospheric tracer for woodsmoke. Atmospheric Environment 40, 5316–5321. https://doi.org/10.1016/j.atmosenv.2006.03.023

Kang, W., Kim, I., Lee, T., Kim, K., Kim, D., 2014. Effect of temperature on bacterial emissions in composting of swine manure. Waste Management, Waste Management on Asia 34, 1006–1011. https://doi.org/10.1016/j.wasman.2013.10.039

Kasumba, J., Holmén, B.A., Hiscox, A., Wang, J., Miller, D., 2011. Agricultural PM10 emissions from cotton field disking in Las Cruces, NM. Atmospheric Environment 45, 1668–1674. https://doi.org/10.1016/j.atmosenv.2011.01.004

Kumar, S., Sharma, D.K., Singh, D.R., Biswas, H., Praveen, K.V., Sharma, V., 2019. Estimating loss of ecosystem services due to paddy straw burning

in North-west India. International Journal of Agricultural Sustainability 17, 146–157. https://doi.org/10.1080/14735903.2019.1581474
Lamb, B., Westberg, H., Allwine, G., 1986. Isoprene emission fluxes determined by an atmospheric tracer techniquE. Atmospheric Environment (1967) 20, 1–8. https://doi.org/10.1016/0004-6981(86)90201-5
Le Canut, P., Andreae, M. O., Harris, G. W., Wienhold, F. G., Zenker, T., 1996. Airborne studies of emissions from savanna fires in southern Africa: 1. Aerosol emissions measured with a laser optical particle counter. Journal of Geophysical Research: Atmospheres, 101(D19), 23615-23630.
Leelőssy, Á., Molnár, F., Izsák, F., Havasi, Á., Lagzi, I., Mészáros, R., 2014. Dispersion modeling of air pollutants in the atmosphere: a review. Open Geosciences 6. https://doi.org/10.2478/s13533-012-0188-6
Li, C., Hu, Y., Zhang, F., Chen, J., Ma, Z., Ye, X., Yang, X., Wang, L., Tang, X., Zhang, R., Mu, M., Wang, G., Kan, H., Wang, X., Mellouki, A., 2017. Multi-pollutant emissions from the burning of major agricultural residues in China and the related health-economic effects. Atmospheric Chemistry and Physics 17, 4957–4988. https://doi.org/10.5194/acp-17-4957-2017
Lopez, M.V., Sabre, M., Gracia, R., 1998. Tillage effects on soil surface conditions and dust emission by wind erosion in semiarid Arago´n ž NE Spain/ 15.
Madden, N. M., Southard, R. J., Mitchell, J. P., 2009. Soil water content and soil disaggregation by disking affects Pm 10 emissions. Journal of environmental quality, 38(1), 36-43.
Madden, N.M., Southard, R.J., Mitchell, J.P., 2010. Soil water and particle size distribution influence laboratory-generated PM10. Atmospheric Environment 44, 745–752. https://doi.org/10.1016/j.atmosenv.2009.11.044
Manzone, M., Balsari, P., Marucco, P., Tamagnone, M., 2016. Potential external contamination of pneumatic seed drills during sowing of dressed maize seeds. Pest Manag. Sci. 72, 1302–1308. https://doi.org/10.1002/ps.4148
McGinn, S.M., Flesch, T.K., Chen, D., Crenna, B., Denmead, O. T., Naylor, T., Rowell, D.. 2010. Coarse Particulate Matter Emissions from Cattle Feedlots in Australia. *J ENVIRON QUAL , 39:3, 791-798.*
Moore, K.D., Wojcik, M.D., Martin, R.S., Marchant, C.C., Bingham, G.E., Pfeiffer, R.L., Prueger, J.H., Hatfield, J.L., 2013. Particulate Emissions Calculations from Fall Tillage Operations Using Point and Remote Sensors. Journal of Environment Quality 42, 1029. https://doi.org/10.2134/jeq2013.01.0009
Moore, K.D., Wojcik, M.D., Martin, R.S., Marchant, C.C., Jones, D.S., Bradford, W.J., Bingham, G.E., Pfeiffer, R.L., Prueger, J.H., Hatfield, J.L., 2015. Particulate-matter emission estimates from agricultural spring-tillage operations using LIDAR and inverse modeling. JARS 9, 096066. https://doi.org/10.1117/1.JRS.9.096066
Mugica-Álvarez, V., Hernández-Rosas, F., Magaña-Reyes, M., Herrera-Murillo, J., Santiago-De La Rosa, N., Gutiérrez-Arzaluz, M., de Jesús Figueroa-Lara, J., González-Cardoso, G., 2018. Sugarcane burning emissions:

Characterization and emission factors. Atmospheric Environment 193, 262–272. https://doi.org/10.1016/j.atmosenv.2018.09.013
Murali, S., Shrivastava, R., Saxena, M., 2010. Green house gas emissions from open field burning of agricultural residues in India. J Environ Sci Eng 52, 277–284.
Nuyttens, D., Devarrewaere, W., Verboven, P., Foqué, D., 2013. Pesticide-laden dust emission and drift from treated seeds during seed drilling: a review: Pesticide-laden dust emission from treated seeds during sowing. Pest Management Science 69, 564–575. https://doi.org/10.1002/ps.3485
Oanh, N.T.K., Ly, B.T., Tipayarom, D., Manandhar, B.R., Prapat, P., Simpson, C.D., Sally Liu, L.-J., 2011. Characterization of particulate matter emission from open burning of rice straw. Atmospheric Environment 45, 493–502. https://doi.org/10.1016/j.atmosenv.2010.09.023
Öttl, D., Funk, R., 2007. PM emission factors for farming activities by means of dispersion modeling. Landbauforsch Völkenrode SH 308:173-177
Paez-Rubio, T., Ramarui, A., Sommer, J., Xin, H., Anderson, J., Peccia, J., 2007. Emission rates and characterization of aerosols produced during the spreading of dewatered class B biosolids. Environmental science & technology 41, 3537–3544.
Pagano, M., Fanigliulo, R., Tomasone, R., Cedrola, C., Recchi, P.F., Colorio, G., 2011. Mechanical hazelnut harvesting: First results of a pickup prototype for a low environmental impact. Acta Horticulturae 919, 139–146. https://doi.org/10.17660/ActaHortic.2011.919.17
Pandey, A., Sadavarte, P., Rao, A. B., & Venkataraman, C., 2014. Trends in multi-pollutant emissions from a technology-linked inventory for India: II. Residential, agricultural and informal industry sectors. Atmospheric environment, 99, 341-352.
Pattey, E., 2015. Primary particulate matter emissions and trends from Canadian agriculture, in: Qiu, G., Fiset, S., Ho, E., MacDonald, D., Liang, C. (Eds.), . Presented at the AIR POLLUTION 2015, València, Spain, pp. 143–154. https://doi.org/10.2495/AIR150121
Pattey, E., Qiu, G., 2012. Trends in primary particulate matter emissions from Canadian agriculture. Journal of the Air & Waste Management Association 62, 737–747. https://doi.org/10.1080/10962247.2012.672058
Pi, H., Sharratt, B., Schillinger, W.F., Bary, A.I., Cogger, C.G., 2018. Wind erosion potential of a winter wheat–summer fallow rotation after land application of biosolids. Aeolian Research 32, 53–59. https://doi.org/10.1016/j.aeolia.2018.01.009
Plautz, J., 2018. Piercing the haze. Science 361, 1060–1063. https://doi.org/10.1126/science.361.6407.1060
Pochi, D., Biocca, M., Fanigliulo, R., Gallo, P., Pulcini, P., n.d. Sowing of seed dressed with thiacloprid using a pneumatic drill modified for reducing abrasion dust emissions 8.

Ponpesh, P., Giles, D.K., Downey, D., 2010. Mitigation of in-orchard dust through modified harvester operation. Transactions of the ASABE 53, 1037–1044.
Pope III, C. A., Burnett, R. T., Thun, M. J., Calle, E. E., Krewski, D., Ito, K., & Thurston, G. D., 2002. Lung cancer, cardiopulmonary mortality, and long-term exposure to fine particulate air pollution. Jama, 287(9), 1132-1141.
Qiu, G., Pattey, E., 2008. Estimating PM10 emissions from spring wheat harvest using an atmospheric tracer technique. Atmospheric Environment 42, 8315–8321. https://doi.org/10.1016/j.atmosenv.2008.07.022
Ravindra, K., & Singh, T. & Mor, S., 2018. Emissions of air pollutants from primary crop residue burning in India and their mitigation strategies for cleaner emissions. Journal of Cleaner Production. 208. 10.1016/j.jclepro.2018.10.031.
Ryden, J.C., McNeill, J.E., 1984. Application of the micrometeorological mass balance method to the determination of ammonia loss from a grazed sward. Journal of the Science of Food and Agriculture 35, 1297–1310. https://doi.org/10.1002/jsfa.2740351206
Santiago-De La Rosa, N., González-Cardoso, G., Figueroa-Lara, J. D. J., Gutiérrez-Arzaluz, M., Octaviano-Villasana, C., Ramírez-Hernández, I. F., & Mugica-Álvarez, V, 2018. Emission factors of atmospheric and climatic pollutants from crop residues burning. Journal of the Air & Waste Management Association, 68(8), 849-865.
Schaafsma, A.W., Limay-Rios, V., Forero, L.G., 2018. The role of field dust in pesticide drift when pesticide-treated maize seeds are planted with vacuum-type planters: Field dust and seed pesticide drift. Pest Management Science 74, 323–331. https://doi.org/10.1002/ps.4696
Sharratt, B., Auvermann, B. 2014. Dust pollution from agriculture. In: Van Alfen, N.K., editor. Encyclopedia of Agriculture and Food Systems. Volume 2. Cambridge, MA:Elsevier Academic Press. p. 487-504.
Sharratt, B., Wendling, L., Feng, G., 2010. Windblown dust affected by tillage intensity during summer fallow. Aeolian Research 2, 129–134. https://doi.org/10.1016/j.aeolia.2010.03.003
Singh, P., Sharratt, B., Schillinger, W.F., 2012. Wind erosion and PM10 emission affected by tillage systems in the world's driest rainfed wheat region. Soil and Tillage Research 124, 219–225. https://doi.org/10.1016/j.still.2012.06.009
Stull, R. B., 1988. An Introduction to Boundary Layer Meteorology. Kluwer Academic Publishers.
Tapparo, A., Marton, D., Giorio, C., Zanella, A., Soldà, L., Marzaro, M., Vivan, L., Girolami, V., 2012. Assessment of the Environmental Exposure of Honeybees to Particulate Matter Containing Neonicotinoid Insecticides Coming from Corn Coated Seeds. Environmental Science & Technology 46, 2592–2599. https://doi.org/10.1021/es2035152
Telloli, C., Malaguti, A., Mircea, M., Tassinari, R., Vaccaro, C., Berico, M., 2014. Properties of agricultural aerosol released during wheat harvest threshing,

plowing and sowing. Journal of Environmental Sciences 26, 1903–1912. https://doi.org/10.1016/j.jes.2014.07.004

Traversi, D., Alessandria, L., Schilirò, T., Gilli, G., 2011. Size-fractionated PM10 monitoring in relation to the contribution of endotoxins in different polluted areas. Atmospheric Environment 45, 3515–3521. https://doi.org/10.1016/j.atmosenv.2011.04.020

USEPA, 1995. *Compilation of Air Pollution Emission factors. AP-42*. Fifth edition, VOLUME I. Environmental Protection Agency, Research Triangle Park, N.C.

USEPA, 2003. *Compilation of Air Pollution Emission factors. AP-42*. Fifth edition, VOLUME I, supplement A (May, 2003).Environmental Protection Agency, Research Triangle Park, N.C.

van der Hoek, K.W., and Hinz, T., 2007. Particulate matter emissions from arable production - a guide for UNECE emission inventories. Landbauforschung Völkenrode Special Issue 308. FAL Agricultural Research Bundesforschungsanstalt für Landwirtschaft (FAL) Bundesallee 50, 38116 Braunschweig, Germany

Viana, M., López, J.M., Querol, X., Alastuey, A., García-Gacio, D., Blanco-Heras, G., López-Mahía, P., Piñeiro-Iglesias, M., Sanz, M.J., Sanz, F., Chi, X., Maenhaut, W., 2008. Tracers and impact of open burning of rice straw residues on PM in Eastern Spain. Atmospheric Environment 42, 1941–1957. https://doi.org/10.1016/j.atmosenv.2007.11.012

Wang, J., Hiscox, A.L., Miller, D.R., Meyer, T.H., Sammis, T.W., 2009. A comparison of Lagrangian model estimates to light detection and ranging (LIDAR) measurements of dust plumes from field tilling. Journal of the Air & Waste Management Association 59, 1370–1378.

Wang, J., Miller, D.R., Sammis, T.W., Hiscox, A.L., Yang, W., Holmén, B.A., 2010. Local Dust Emission Factors for Agricultural Tilling Operations: Soil Science 175, 194–200. https://doi.org/10.1097/SS.0b013e3181dae283

Willis, W.B., Eichinger, W.E., Prueger, J.H., Hapeman, C.J., Li, H., Buser, M.D., Hatfield, J.L., Wanjura, J.D., Holt, G.A., Torrents, A., Plenner, S.J., Clarida, W., Browne, S.D., Downey, P.M., Yao, Q., 2017. Lidar Method to Estimate Emission Rates from Extended Sources. Journal of Atmospheric and Oceanic Technology 34, 335–345. https://doi.org/10.1175/JTECH-D-16-0130.1

WRAP (Western Regional Air Partnership's), 2006. Fugitive Dust Handbook. Countess Environmental 4001 Whitesail Circle Westlake Village, CA 91361 (WGA Contract No. 30204-111). September 7, 2006.

Yokelson, R. J., Crounse, J. D., DeCarlo, P. F., Karl, T., Urbanski, S. P., Atlas, E., Campos, T., Shinozuka, Y., Kasputin, V., Clarke, A. D., Weinheimer, A., Knapp, D. J., Montzka, D. D., Holloway, J., Weibring, P., Flocke, F., Zheng, W., Toohey, D., Wennberg, P. O., Wiedinmyer, C., Mauldin, L., Fried, A., Richter, D., Walega, J., Jimenez, J. L., Adachi, K., Buseck, P. R., Hall, S. R., and Shetter, R., 2009. Emissions from Biomass Burning in the Yucatan. Chemistry and Biochemistry Faculty Publications, 15. https://scholarworks.umt.edu/chem_pubs/15

Zhang, T., Wooster, M.J., Green, D.C., Main, B., 2015. New field-based agricultural biomass burning trace gas, PM2.5, and black carbon emission ratios and factors measured in situ at crop residue fires in Eastern China. Atmospheric Environment, Interdisciplinary Research Aspects of Open Biomass Burning and its Impact on the Atmosphere 121, 22–34. https://doi.org/10.1016/j.atmosenv.2015.05.010

3.2. ARTICLE II: *"Evaluation of particulate matter (PM_{10}) emissions and its chemical characteristics during rotary harrowing operations at different forward speeds and levelling bar heights"*

The literature review article on PM emissions from land preparation activities (Paragraph 3.1) allowed to identify the Backward dispersion modelling technique as the best method for emission assessment. The coupling of this technique with Optical Particle Counters (OPC) and 3D sonic anemometers, which allow continuous PM concentration and wind measurements, appeared to allow for robust emission estimation. Moreover, the literature did provide information only on emissions from certain tilling implements, while others remained unstudied, and very few studies actually performed in field comparison among different implements or machinery setups. A further lack of knowledge lied in the chemical characteristics of soil emitted PM. This first field study aimed to cover some of these knowledge gaps, while allowing to test the possibility of using the chosen field test methodology for comparative studies. This step was also fundamental to ensure the validity of the utilized field setup for assessment of proper mitigation measures.

Environmental Pollution (2020), Volume 265, Part A, 115041, ISSN 0269-7491

__Authors__: Jacopo Maffia, Paolo Balsari, Elio Padoan, Franco Ajmone-Marsan, Davide Ricauda Aimonino, Elio Dinuccio

Environmental Pollution 265 (2020) 115041

Contents lists available at ScienceDirect

Environmental Pollution

journal homepage: www.elsevier.com/locate/envpol

Evaluation of particulate matter (PM_{10}) emissions and its chemical characteristics during rotary harrowing operations at different forward speeds and levelling bar heights

Jacopo Maffia [*], Paolo Balsari , Elio Padoan , Franco Ajmone-Marsan , Davide Ricauda Aimonino , Elio Dinuccio

Dipartimento di Scienze Agrarie, Forestali e Alimentari, Università di Torino, Largo Paolo Braccini 2, 10095, Grugliasco, Italy

Abstract

Particulate matter (PM) is an air pollutant which poses a considerable risk to human health. The agricultural sector is responsible of the 15% of the total anthropogenic emissions of PM_{10} (PM fraction with aerodynamic diameter below 10 µm) and soil preparation activities have been recognized as one of the main drivers of this contribution. The emission factors (EF) proposed by European environmental agency (EEA) for tilling operations are based on very few studies, none of which has been made in Italy. Moreover, few studies have considered the influence of operative parameters on PM_{10} emissions during tilling. The aim of this work was to assess PM_{10} emission and dispersion during rotary harrowing and to understand how operative parameters, such as forward speed and implement choice may affect PM release. A further objective was to assess the near field dispersion of PM_{10} to address exposure risks. Emission factors (EFs) were determined during two different trials (T1 and T2). During T1, the effect of tractor speeds (0.6, 1.1 and 1.7 m s^{-1}) on PM^{10} emissions was investigated, while in T2 a comparative essay was made to study the influence of levelling bar height on emissions. The average ground level downwind concentrations of PM_{10} during harrowing operation was estimated through dispersion modelling. The observed PM_{10} EFs for rotary harrowing were 8.9 ± 2.0 mg m^{-2} and 9.5 ± 2.5 mg m^{-2} on T1 and T2, respectively. The heavy metal content of soil-generated PM_{10} was also assessed. In the generated PM, the elemental concentrations were higher than ones in soil. As, Cd and Ni concentration levels, determined in PM_{10} near to the tractor path, were also high, being several times higher than the annual average regulatory threshold levels in ambient air, as defined by the European regulation.

1. Introduction

The increase in atmospheric concentrations of particulate matter (PM) is a major cause of concern, having been associated with acute and chronic health effects and even with the rise in mortality and morbidity rates (WHO, 2006; Tonne et al., 2016). Many emission sources contribute to PM_{10} (PM fraction with aerodynamic diameter below 10 µm), among which agriculture may play a significant role, being held responsible for the 15% of total anthropogenic PM_{10} emissions in Europe (EEA, 2019). Agricultural emissions of primary particulate mainly derive from wind erosion of agricultural soils, livestock farming activities and crop management (Maffia et al., 2020). Crop management activities have been recognized to be a substantial contributor to the overall emissions (Sharratt and Auvermann, 2014). Currently, the emission factors (EF) used by the European Environmental Agency (EEA) for crop management operations are based on a limited number of studies and did not take into account the different tilling implements used by farmers. Moreover, few studies have considered the influence of operative parameters on PM_{10} emissions during tilling (Maffia et al., 2020).

Issues related to PM emissions and atmospheric concentrations have recently been at the centre of public attention in Northern Italy due to the associated health risks. In fact, the latest report of the Italian institute for environment protection and research has highlighted exceedances of the recommended daily PM_{10} concentration threshold (50 µg m^{-3}) for more than 35 days per year in most monitoring stations of the Po Valley (Cattani et al., 2019).

The northwest part of this area, where the present trials took place, is characterized by a low average annual wind speeds, which fall often below 1 m s^{-1} (Fratianni et al. 2007), and by being intensively exploited, both by industrial and farming activities, and densely populated. To face the high PM pollution of the area (Cattani et al., 2019) it is important to acknowledge its specific climatic conditions and to start assessing local emission factors for the main emission sources, to provide the policy makers with up to date information to address the air quality issue.

Health risks linked to PM are not only due to the size of the particles or to the concentration, but also to its elemental composition (Kendall et al., 2004). Particularly, many studies have focused on the potentially toxic effects due to Trace Elements (TE) adsorbed on PM_{10} in urban and roadside environments (Padoan et al., 2016; Zhang et al., 2019; Wu et al., 2020).

Agricultural soils are well known for being both sources of PM_{10} and, at least in certain areas, enriched in TE due to both anthropogenic and natural sources (Li et al., 2019). In fact, the application of pest control products and organic fertilizers, such as pig manure, has been shown to increase the soil reserves of TE such as Cu, Zn and Mn (Brun et al., 2001; Guo et al., 2018). Nevertheless, few information is available on the concentrations of these elements in the airborne PM_{10} emitted during tilling or wind erosion events. A recent investigation (Wang et al., 2016) has shown that the TE concentrations in PM_{10} of 4 different agricultural regions in China were higher than the expected, with carcinogenic risk above the acceptable limits due mostly to Pb, Co, Ni and Cd concentrations. It is therefore important to consider particle composition when assessing PM emissions from agricultural sources.

The main aim of this study was to improve the knowledge on PM_{10} emissions during soil preparation operations and, in particular, on those due to rotary harrowing. Emissions from rotary harrowing (coupled with packer roller and with levelling bar) were assessed in low wind conditions, to provide a local EF for this operation, which has been poorly studied before. Further objectives were to assess the effect of operative parameters, such as tractor speed and levelling settings on the emission value. In addition, the characteristics of the emitted PM_{10} and their near field dispersion were assessed to obtain a broader picture of the impact that harrowing operations can have on human health.

The field experiments presented hereafter are the first assessments of PM emission from land preparation activities performed in Northern Italy. In this specific area, the environmental, topographic, and demographic conditions could heavily influence both the amount of emission related to soil cultivation and their potential contribution to the total PM exposure levels.

2. Materials and methods

2.1. Experimental layout and Field measurements

Two different trials, T1 and T2, were performed in July and October 2019, respectively, in two different locations of the Piemonte region, Italy (44°50'27.9" N, 7°21'32.2" for T1; 44°54'52.9" N, 7° 23' 45.9" E for T2) in two fields with a sandy-loam soil for T1 trials and a loamy soil for T2 trials. In both trials, measurements of PM_{10} were carried out at each tractor passage using an optical PM monitor (TSI, DustTrackTM II model 8530), with a sampling frequency of 1 Hz. The PM monitor was placed alongside the area tilled by the tractor at 4 m (Figure 1). The instrument was moved to the next passage line after each pass and placed either east or west of the line according to wind direction. The DustTrack monitor was placed in the field 1 hour before the start of the trial and continued sampling until 1 hour after the trial, to assess the background PM_{10} concentration.

The positioning of the instrument was arranged similarly to what done in previous studies (Faulkner, 2013; Kasumba et al., 2011), with the sampler inlet placed at 1 m aboveground and with a fixed distance between the sampler and the tractor path of 4 m. According to the results of Holmén et al. (2008) and Kasumba et al. (2011), obtained in New Mexico, sampling at higher distances from the source could lead to underestimate the concentration of finer PM fractions due to vertical dispersion of the plume and to the increased distance between the sampler inlet and the plume center.

Meteorological data were collected using a weather station mounted in a corner area of the field, with every side free from obstacles. The weather station has two 3D anemometers (Campbell scientific, 3D Metek uSonic-Omni), mounted at 2 and 4 m above ground respectively, and a temperature probe (HOBO, U12). The anemometers data were sampled at a rate of 5 Hz.

Field trials were carried out with a 12 rotors, 3 m working width, rotary power harrow (Frandent Eternum R303-19, Frandent Group s.r.l., Italy). The harrow was equipped with a packer roller (0.55 m diameter) on T1, whereas a levelling bar was installed in T2 in order to evaluate EF in different implement configurations. In T2, the roller was replaced with a couple of wheels mounted on the same tillage depth adjustment system.

The rotary harrow was hooked up to the three point hitch of a four-wheel-drive row crop tractor (Fendt 718 Vario, AGCO GmbH, Germany) having a 132 kW maximum engine power and an unladen mass of 7155 kg (OECD, 2010). A ballast of 1200 kg was also linked to the front three point hitch in order to reduce wheels slip.

During harrowing PTO rotation speed was maintained at about 1000 rpm achieving a rotor angular speed of 285 rpm, while the tillage depth was set to 10 cm.

In T1, 36 passages were performed, although some of those had to be later excluded from the analyses due to sudden changes in wind direction that resulted in imprecise EF estimations (the final number of calculated passages was 32). The length of each harrower passage has been, in both cases, of 40 m. The experimental layout was designed in order to test the effect of three different tractor speeds (S1 = 0.6 m s^{-1}, S2 = 1.1 m s^{-1} and S3 = 1.7 m s^{-1}), where S2 is the one normally implied by farmers, on PM_{10} emissions. S1, S2 and S3 passages were randomized inside large plots (3 m wide and 120 m long), that were considered as blocks for the statistical analysis and served to the purpose of limiting the variability linked with soil heterogeneity and wind speed. The scheme of a large plot layout and of PM sensor positioning is represented in Figure 1.

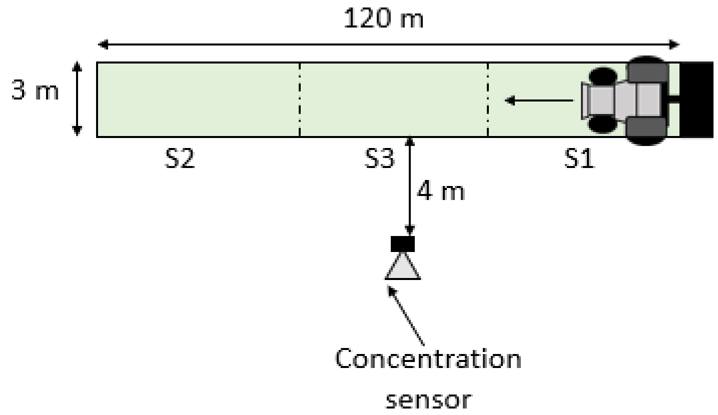


Figure 1. Scheme of T1 experimental units (S1, S2 and S3 passages randomised in a large plot) and positioning of the concentration (DustTrack) sensor.

In T2, 24 tractor passages were performed (two of those were lost due to sudden wind direction changes). The experimental layout was designed in order to test the effect of levelling bar height on PM_{10} emissions. The bar attachment height was alternatively adjusted to two different levels, a lower, L, and a higher one, H. The attachment height of the bar was tested both with the bar perpendicular to the ground (S) and inclined of a 45° angle (I). In addition, the distance of the bar from the harrower was varied during the trial among D1 (23 cm from the harrower) and D2 (28 cm from the harrower). The combinations of bar attachments heights and orientations resulted in different distances between the bar and the point of the harrower teeth, being of 14, 16.5, 17 and 20 cm for L-S, L-I, H-S and H-I respectively. The different configurations and the split plot experimental layout are graphically represented in Figure 2. The plot was organized so as to reduce the time-lapse among passages involved in direct comparison, limiting the variability linked with changing environmental conditions (such as wind speed). The levelling bar is commonly installed on rotary harrows to improve soil fragmentation during harrowing by keeping the soil closer to the harrow rotors for a longer period. The variation of the vertical position and of the distance of the bar from rotors will change soil interaction with rotors tines, modifying aggregates size and affecting PM emissions (Madden et al., 2010). Bar inclination, instead, was an experimental solution aimed to reduce draught and, therefore, fuel consumption.

Soil conditions in T1 and T2 were different. In T1 harrowing was performed on bare soil after tillage, while on T2 only a superficial incorporation of crop residues (maize stalks) had been performed, leaving a rougher surface with some residues still on the surface. In both cases soil samples were taken at 0-15 cm depth. At each sampling site, sub-samples were collected in the center of each parcel (36 sub-samples in T1 and 24 in T2), mixed into one sample and quartered in field. Soils were dried at room temperature and sieved with a 2-mm sieve prior to laboratory analyses.

2.2. Elaboration of meteorological data

Start and end times of each tractor passage were recorded during field measurements. The passage time intervals were used to clip the output file of the anemometer, to obtain the average wind components (u, v, w) at the time of each peak. Wind components were then used to assess main wind speed (WS) and wind direction (WD) according to Stull (2012).

The Pasquill Guifford class (PGclass) was estimated for each passage by first calculating the Monin Obhukov Length (Llenght) and then estimating the stability class according to the table in Smith et al. (1995). The Llenght was estimated using the Bigleaf R package (Knauer et al., 2018), according to the method described in Foken (2008). The input parameters required by Bigleaf were air temperature (Tair), atmospheric pressure (p), friction velocity (u*) and sensible heat flux (H). Tair was retrieved by field measurements; p was assessed from elevation using Bigleaf package (Knauer et al., 2018); u* was calculated from wind data according to the method in Stull (2012); H was assessed on the base of the estimation procedure proposed by Hanna and Chang (1992).

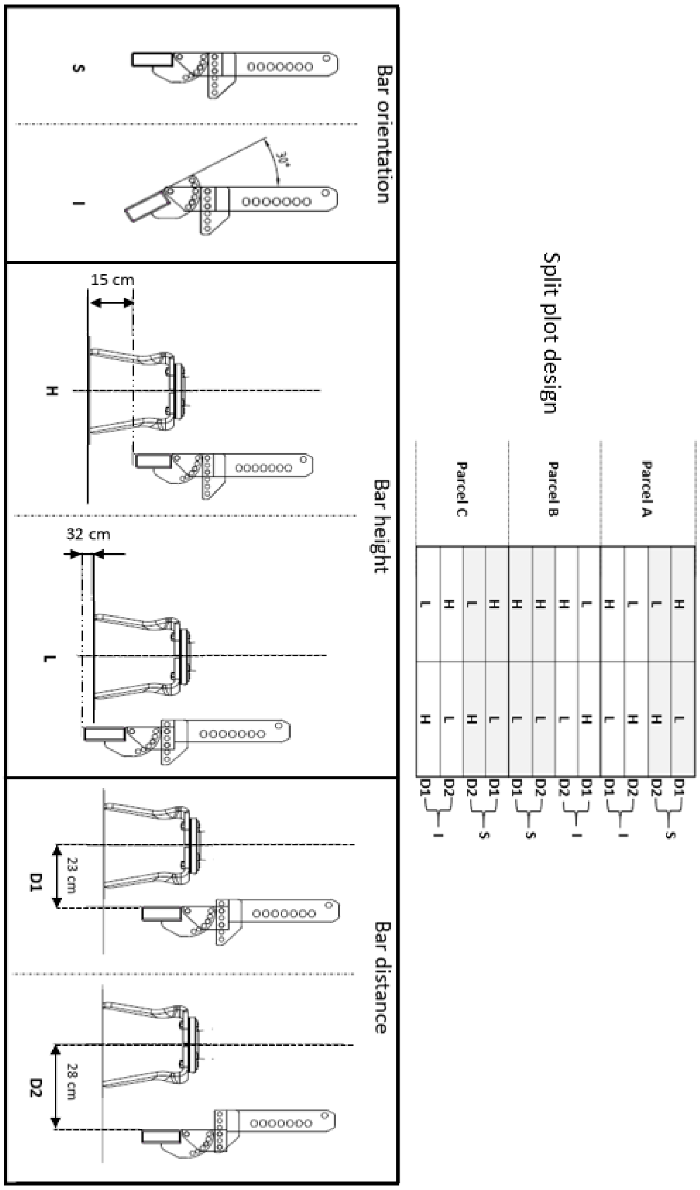


Figure 2. Experimental settings of the harrower and split plot design adopted in T2.

2.3. *Dispersion modelling to estimate EFs and downwind concentration increases*

EFs were estimated using a backward lagrangian model (WindTrax). The input parameters to the model were WS (at 2 and 4 m of height), WD (at 2 and 4 m of height), PGclass, Tair, average PM_{10} concentration (at four meters from the source) and average background PM_{10} concentration. The model was set to simulate the dispersion of 106 particles and the surface roughness (Z0) was set to the reference value (1 cm), parameterized for “bare soil” conditions. The emission source was modelled as an area source having the same dimension of the plot tilled at each harrower passage. Modelling tilling sources as areas rather than moving point sources is the most common solution for EFs estimation through backward modelling (Faulkner, 2013; Funk et al., 2008; Jahne et al., 2015).

A simulation was ran per each tractor passage performed on the two field days. The output given by the model was an Emission Rate (ER, mg m-2 s-1) referred to the modelled area source. The ER was later converted in EF (mg m-2) according to the following formula:

Where tpass is the elapsed time (s) between the start and the end of each passage. The above equation follows the principle presented by Faulkner et al. (2009).

Near source concentration increases during harrowing have been estimated and plotted using the GRAL model (using its open source graphical user interface, GUI), which is a high resolution lagrangian model and has previously been used to assess PM dispersion from tilling (Funk et al., 2008). Moreover, the model has been proved to be particularly suited for modelling under low wind speed conditions (Öttl et al., 2005; Öttl et al., 2002). Two dispersion simulations (one for T1 and one for T2) were realised considering for both an equal area source, with a surface of 1 ha and a squared shape, so that the concentration increases can be related to a known area source of regular size and properly compared. The main inputs to the model were WS, WD, PGclass and the PM_{10} emission rate (kg h^{-1}). The average WS and the prevalent WD observed during D1 and D2 passages were used to run two different simulations. The stability classes used were B and D for T1 and T2, respectively. The ER was obtain converting the estimated EFs on both days into kg ha-1 and considering that harrowing a surface of 1 ha at an average speed of 3 km h^{-1} requires 1 h of time. Downwind concentration was estimated at a height of 1 m (over the ground level) and the horizontal grid resolution was of 1 m.

2.4. *Soil analysis*

All samples were analysed for pH (1:2.5 soil:water), total carbon and nitrogen (TC, TN) (UNICUBE, Elementar), carbonates (volumetric method), bulk density and field humidity according to the official Italian methods (Colombo & Miano, 2015). The particle-size distribution (PSD) was measured via the sieve-pipette method (Gee and Bauder, 1986).

To determine the pseudo-total metal content in soil, aqua regia (HCl:HNO3 3:1 v/v) microwave extraction was performed (Ethos D, Milestone). The elemental pseudo-total contents of 22 elements (listed in Table 3) were determined in all samples using ICP-MS (NexION 350D, Perkin Elmer). All analyses were performed in duplicate. Accuracy was verified using a Certified Reference Material for aqua regia soluble contents (CRM 141R, Community Bureau of Reference, Geel, Belgium). Recoveries were between 95 – 105 % for all elements. All reagents were of ultrapure or analytical grade.

2.5. Soil resuspension in laboratory and PM_{10} filter analyses

The soils collected in the field, after being dried as for chemical analyses, were re-suspended under laboratory condition to simulate PM_{10} emission during tilling. Soil was re-suspended using a soil resuspension chamber, which was assembled using a rotating plastic (PET) drum (Madden et al., 2010), having a cylindrical form, a total volume of 25 L and a circular opening of 15 cm of diameter. The drum was moved by an electric engine (0.75 kW) at an average speed of 26 rpm. A filter based high volume sampler (TCR Tecora®, Echo Hi-Vol), working with a 220 L min^{-1} flow rate, was placed in front of the drum opening to sample the out coming PM_{10} particles. The scheme of the resuspension system is illustrated in Figure 3.

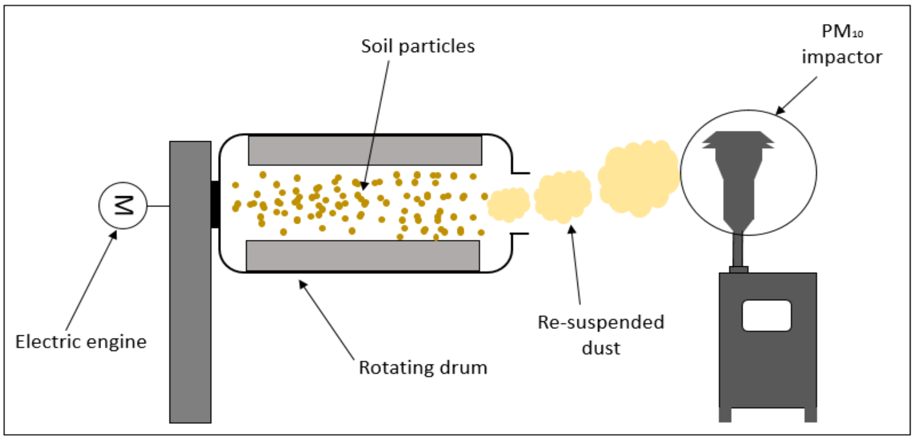


Figure 3. Scheme of the soil resuspension and PM_{10} sampling system.

A sample of 1 kg of soil was re-suspended for each trial (T1 and T2) and the re-suspension activity lasted 1 h for each one.

Before sampling, quartz fibre filters (Ahlstrom Munksjo, Micro-quartz fibre paper MK306, Ø102 mm) were dried at 205 °C for 5 h and conditioned for 48 h at 20 °C and 50% relative humidity. Blank filters were weighed three times every 24 h and kept in PETRI holders. After sampling, filters were brought back to the laboratory and weighted after 24 and 48 h of conditioning at the same temperature and humidity conditions. Filters were analysed for their pseudo-total elemental content as soils to ensure the comparability of the measures. Microwave acid digestion using 10 ml of aqua regia was performed using half filter in PTFE bombs (Ethos D, Milestone). Resulting solutions were filtered on cellulose filters (Whatman Grade 5) and diluted with ultrapure water to a final volume of 50 ml. Elemental contents were determined in all samples using ICP-MS (NexION 350D, Perkin Elmer).

It was assumed that heavy metals content in PM_{10} emitted under field conditions derives entirely from soil and that the eventual contribution of the tractor combustion engine is negligible (Telloli et al., 2014). Therefore, it was possible to relate the chemical analyses on the re-suspended PM to the field measured PM_{10} concentrations. The elemental concentration of TE in PM_{10} (C_{dust}, μg g^{-1}) was then converted to elemental concentration in the air at 4 m distance from the tractor (C_{air}, μg m^{-3}), by referring it to the overall PM_{10} concentration measured in the field (C_{PM10}, g m^{-3}) according to the following formula:

2.6. Statistical analysis

A statistical analysis was conducted using the R software (R Core Team, 2019) to highlight differences among EFs and ERs observed for rotary harrowing with different operational parameters. For T1, the effect of tractor speed on EFs and ERs was tested (significance level chosen was $\alpha < 0.05$) implementing a mixed model (lme procedure from nlme R package; Pinheiro et al., 2018) to account for the nested experimental design. The model was set having tractor speed (S) as a fixed factor and the plot as random factor. The distribution of within-groups errors and random effects were graphically assessed to verify the model assumptions (Pinheiro et al., 2006). The mean EF values were calculated (using emmeans R package; Lenth, 2019) for each tractor speed level and post-hoc test comparison were performed according to the Bonferroni post-hoc method (using the multcomp R package; Hothorn et al., 2008).

For T2, the data were analysed through a mixed model (lme procedure from nlme R package; Pinheiro et al., 2018) accounting for the nested effects included in the split plot layout of the experiment. The model included, as fixed effects, the three operation parameters (bar orientation, distance, and height) and their interaction. The random effects were distributed on the three levels of the split plot, which included the following nested effects: height in distance, distance in orientation and orientation in parcel.

3. Results

3.1. Environmental conditions during the trials: soil characteristics and atmospheric conditions

In T1, wind speed and direction varied consistently during the tractor passages. The average wind speeds were 0.81±0.07 and 0.91±0.07 m s^{-1} at 2 and 4 m above ground, respectively. Atmospheric stability condition was estimated to fall within the B PGclass, meaning that the atmosphere was unstable during the essay. In T2, wind speed was slightly higher as compared to T1 (1.46±0.12 m s^{-1} at 2 m and 1.7±0.15 m s^{-1} at 4 m). Atmospheric stability condition fell in the PGclass C (slightly unstable atmosphere) for most passages, exception made for 6 of them, for which the PGclass was B. The atmospheric stability condition of each passage was used for modelling the EF. Windrose graphs illustrating the frequencies of main wind directions and speeds during T1 and T2 are shown in Figure 4 and 5 (the graphs were obtained applying the openair R package by Carslaw and Ropkins, 2012).

The low wind speed conditions observed are consistent with the annual average wind speed reported for the Piedmont region by the regional ambient protection agency (ARPA Piemonte; Fratianni et al., 2007).

Table 1 illustrates the main physico-chemical characteristics of the analysed soils. Both soils were sub-acid and their total carbon content was similar and in line with their agricultural use, as well as the other determined chemical characteristics. The moisture content of the soils during the trial was 8.64 ± 0.03 % and 9.02 ± 0.02 %, on mass, in T1 and T2, respectively. Although the finer texture of T2 soil as compared to T1 could lead to a higher emission potential, it is speculative to draw conclusion on the base of texture information only, since it is known that also soil aggregates stability can have a great impact on the final emissions (Madden et al., 2010).

The overall environmental conditions observed during both T1 and T2, with coarse soil texture, relatively high soil moisture content and low wind speed conditions, may lead, according to previous studies, to relatively low emissions (Avecilla et al., 2017; Cassel et al., 2003; Madden et al., 2010).

Table 1. Physico-chemical characteristics of the analyzed soils.

Soil characteristics	T1	T2
Coarse sand (%)	23	9
Fine sand (%)	33	31
Coarse silt (%)	12	14
Fine silt (%)	26	28
Clay (%)	6	18
pH (H_2O)	6.1	6.2
TC (%)	1.34	1.10
TN (%)	0.18	0.18
Soil density (g cm^{-3})	1.5	1.4

3.2. EFs for rotary harrowing and effect of operational parameters on the emissions and plume concentrations

The results of the statistical analyses for T1 and T2 tilling events are summarized in Table 2. In T1, the average EF for rotary harrowing with packer roller was 8.9 ± 2.0 mg m^{-2}, considering data gathered at all three speeds. The tractor speed was shown to alter significantly the EFs, with the lower speed (S1) causing higher emissions compared to S2 and S3 (Table 2). On the contrary, tractor speed had no significant effect on the ERs. In T2, the average EF for rotary harrowing with packer roller was of 9.5 ± 2.5 mg m^{-2} (averaging all the trials). No significant effect on the emissions was highlighted for bar height, bar orientation and bar distance nor their interaction. From the obtained results, it appears that only bar distance could possibly affect the emission, since the average EFs are generally higher in D1 as compared to D2 (Table 2), although this effect is not statistically relevant. Some differences, although not significant ($P>0.05$), can be observed for different settings at distance D1, while practically no variation is shown among EFs at distance D2.

Table 2. Calculated EFs (mean and standard error, SE) for T1 and T2 at each adopted tractor speed and levelling bar position.

Trial	Operative parameters			Mean EF ($mg\ m^{-2}$)	SE	Pvalue
T1	Forward speed					
	S1			13.4a	2.1	
	S2			3.6b	1.6	0.002
	S3			4.8b	2.0	
T2	Distance	Height	Orientation			
	D1	H	S	33.7	9.0	
		L	S	12.4	9.0	
		H	I	5.0	7.3	
		L	l	14.9	7.3	0.060
	D2	H	S	5.0	3.3	
		L	S	6.1	3.3	
		H	I	5.5	4.4	
		L	l	3.8	4.4	

Peak concentrations measured during tractor passes, at 4 m distance, were 641±40 $\mu g\ m^{-3}$ in T1 and 3461±329 $\mu g\ m^{-3}$ in T2, averaging all the passages. The average downwind concentration increases near the source (at 1 m height) are plotted in Figure 4 and 5, as estimated for T1 and T2. Estimated PM10 concentration increments averaged between 12 (at the field edge) and 0.1 $\mu g\ m^{-3}$ (at more than 300 m from the source). The plume in T2 appears to be less horizontally spread as compared to T1 (due to the different stability conditions). Downwind concentration in T2 also appears to be slightly higher. This was probably due both to the reduced plume dispersion and to the higher wind speed registered that day.

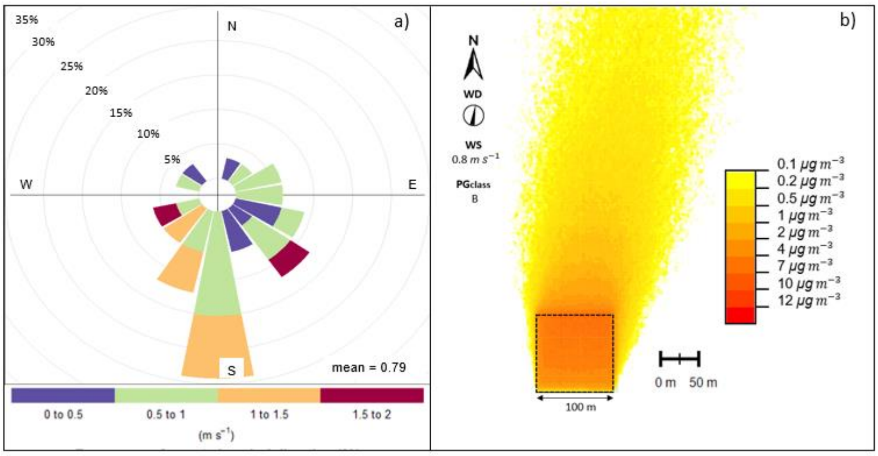


Figure 4. a) Windrose illustrating the frequencies of main wind directions and speeds during T1; b) Estimated downwind concentration increases near source (area of 1 ha) during T1.

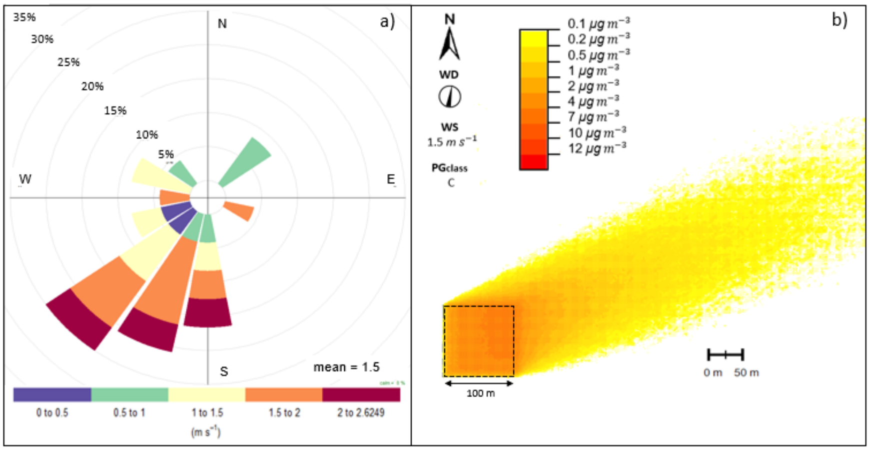


Figure 5. a) Windrose illustrating the frequencies of main wind directions and speeds during T1; b) Estimated downwind concentration increases near source (area of 1 ha) during T1.

3.3. Elemental characterization of soils and soil-emitted PM_{10}

The particle size distribution of the elements in soils has been demonstrated to be a key parameter when exploring the possible risks associated to soil contamination (Ajmone Marsan et al., 2008; Kong et al., 2012; Padoan et al., 2017). Aqua regia extractable concentrations of elements in bulk soils are reported in Table 3. The TE contents in the resuspended PM_{10} fraction is expressed in Table 3 as enrichment ratio, being the ratio between the content of each element in the resuspended PM_{10} and in the bulk soil it originated from.

Table 3. Concentrations (± standard error) of each element determined in the bulk soils and enrichment ratio in soil-derived PM_{10}.

		T1		T2	
		Bulk soil 1	Enrichment ratio in PM_{10} fraction	Bulk soil 2	Enrichment ratio in PM_{10} fraction
Mg	%	0.95 ± 0.02	1.5	1.08 ± 0.04	1.7
Al		3.73 ± 0.02	1.0	3.05 ± 0.21	1.5
K		0.99 ± 0.04	1.0	0.67 ± 0.09	1.5
Ca		0.80 ± 0.07	3.1	0.47 ± 0.03	2.7
Fe		1.24 ± 0.01	2.0	4.36 ± 0.11	0.5
Li	(µg g-1)	50 ± 4	0.8	42 ± 2	1.3
Sc		13 ± 1	1.5	8.8 ± 1.3	1.6
V		86 ± 18	1.8	66 ± 5	1.6
Cr		189 ± 25	6.3	91 ± 24	5.0
Mn		1758± 110	1.5	1225 ± 19	1.5
Co		22 ± 1	2.2	20 ± 2	1.6
Ni		135 ± 11	4.4	84 ± 20	3.1
Cu		62 ± 5	7.3	66 ± 5	4.1
Zn		104 ± 8	7.8	58 ± 5	9.3
As		14 ± 1	0.9	13 ± 1	1.7
Sr		75 ± 3	2.8	34 ± 10	2.4
Mo		4.9 ± 3.7	21	< 0.05	
Cd		0.36 ± 0.05	39	0.13 ± 0.03	94.3
Sn		2.8 ± 0.2	13	2.6 ± 0.2	4.6
Sb		0.58 ± 0.25	20	0.58 ± 0.02	5.2
Ba		246 ± 6	5.5	86 ± 10	7.3

Pb	37 ± 0.4	2.5	27 ± 1	1.7

Both agricultural soils appeared as not contaminated (according to DLgs 152-2006), in accordance with their long-term agricultural use. In soils, most of the elements appeared enriched in the finer fraction. Only the major elements and, to some extent, the elements typical of the parent material (such as Li, Sc, Co) had a similar concentration in both size fractions.

The enrichment in the finer fraction was particularly evident for Cu, Zn, Mo, Cd, Sn and Ba, where the PM_{10} soil had concentrations one order of magnitude higher than the bulk soil.

From the soil-related PM_{10} fraction concentrations, we calculated the resulting concentration in air according to the total concentration of atmospheric PM at 4m of distance from the source (Table 4). From the results appear that the plume is enriched in TE, with point concentrations of As, Cd and Ni higher than the legislation limits for PM_{10} atmospheric pollution, respectively 6, 5 and 20 ng m^{-3} (MATTM, 2010). Although they refer to the annual average concentration, punctual concentrations in the plume during T2 were up to 50 times the limit.

Table 4. Air elemental concentrations at 4 m distance from the tractor.

		T1	T2
Mg	µg m^{-3}	12	62
Al		29	157
K		6.4	34
Ca		8.1	44
Fe		14	76
Mn		1.2	6.2
Li	ng m^{-3}	34	183
Sc		9	50
V		67	363
Cr		294	1585
Co		21	111
Ni		168	906
Cu		176	949
Zn		345	1865

As	14	75
Sr	52	283
Mo	64	347
Cd	8	43
Sn	8	41
Sb	2	10
Ba	401	2168
Pb	29	154

4. Discussion

The PM_{10} emission factors calculated for rotary harrowing (8.9±2.0 in T1 and 9.5±2.5 mg m^{-2} in T2; averaged over all tractor passages) were found to be substantially lower as compared to the one reported by Öttl and Funk (2007) for fixed-tooth harrow in Germany on a sandy soil (83.3% of total sand), which was of 82 mg m^{-2}. The lower emissions observed are probably due to the overall soil and environmental conditions and to the different implement used. The soil, in both T1 and T2, had a high moisture content (8.64% in T1 and 9.02% in T2, on mass), being in the range of the threshold levels of soil moisture, of 2 and 10 % on mass, over which, according to Funk et al. (2008), very low PM emissions occur in sandy and silty soils respectively. The lower sand content in the two Italian soils could have favoured an improved soil structure and aggregation, which it is known to mitigate dust emissions (Madden et al., 2009). The shielding structure which is present in rotary harrows and absent in fixed-tooth ones could have important emission containment effect. Moreover, the wind speed registered during the trial was lower than the 1.9 m s-1 reported by Öttl and Funk (2007). Since the atmospheric conditions registered during the trials are quite common in the Northwest of Italy (Fratianni et al., 2007) and no previous assessments have been done for rotary harrows, the gathered EFs could be considered as a first reference for this type of soil tillage.

A difference between EFs for low (S1), standard (S2) and high tractor speed (S3) was observed during first trial. The emissions observed with S1 were in fact higher as compared to the other treatments, which did not differ significantly among each other. This could be due to the longer period in which the harrower insists on the same volume of soil when operating at the lower speed. This explanation is further confirmed by the fact that no significant difference was observed among the ERs generated at different speeds, meaning that the harrower emits the same amount of PM_{10} per second of work in each thesis. This indirect effect of tractor forward speeds probably could apply only to the rotary harrower, which actively disturbs the soil, but not for traditional soil tilling techniques, which have a passive action on the soil. Usaborisut and Praserkan (2019), and

Kushwaha and Linke (1996) have shown that an increase in the tractor speed did not affect PM_{10} releases during harrowing, although a reduction of soil fragmentation should be obtained by raising the working speed. An increase in forward speed, in fact, determines a stretching of the cycloid described by the harrow rotors tines with a consequent increment of clods diameter (Raparelli et al., 2019).

In T2, altering bar height and orientation had no significant effects on PM_{10} emissions. The obtained results also showed a slight emission reduction while increasing the horizontal distance between the levelling bar and the harrower. However, this effect was not statistically relevant, and the bar distance could possibly affect the efficiency of the levelling bar itself. From field observations it appeared that, when the bar was positioned at distance D2, the soil failed to accumulate in correspondence of the harrower teeth. Therefore, to properly test this mitigation opportunity, further trials should be carried out to better investigate its effect on emissions but also on soil aggregates. It is important, when considering possible PM mitigation options, to maintain the efficacy of the agricultural operation unaltered.

Peak concentration measured during trials near the tractor passes were 641±40 $\mu g\ m^{-3}$ in T1 and 3461±329 $\mu g\ m^{-3}$ in T2. The higher concentration during T2 as compared to T1 was probably attributable to the higher wind speed, causing a more stable and focused plume, and to wind direction, diagonal to the tractor movement, which permitted the operator to put the sensor more in line with the plume centreline. The observed concentration levels were consistent with those reported in previous studies (Moore et al., 2015; Clausnitzer and Singer, 1997) during land preparation activities. The main concerns related to those concentrations are related to farmers' professional health risks. In fact, exposure to high levels of PM_{10} in farming environment can lead to severe health effects and possibly to fatal consequences (Molocznik, 2002; Kirkhorn and Garry, 2000; Schenker, 2000). Although modern tractor cabins are provided with technologies, such as air filters, to protect the operators from these risks, still a lot of assessments are to be done to ensure a sufficient personal protection and to provide a safe work environment for farmers.

Soil-related PM appeared to contain high concentrations of TE, especially those elements deriving predominantly from anthropic sources. Elements such as Cu, Zn, Ni, Cr, Cd, Sn and Ba had, in this fraction, concentrations higher than the legislation limits for soils, as observed in previous studies on different soils (Padoan et al., 2017). This, in turn, affected atmospheric concentrations of metals in the plume. These were calculated, for some of the regulated elements in Italy (Ni, As and Cd), up to 50 times the limit for the annual average threshold levels established by the legislation (MATTM, 2010). Although these were transient conditions, long term exposition to such high concentrations could affect worker's health.

Modelled plume concentrations showed that PM_{10} levels near the emission source can be substantially affected from harrowing operations (Figure 4). In fact, PM_{10}

concentration increases due to one hour of field harrowing, calculated at 100 m downwind of the source, were estimated to be among 2 and 7 µg m^{-3} in both T1 and T2. Even if those concentration increases may seem not too high at a first glance, it is important to take into account that land preparation activities (as well as other cropping activities) are performed over extended cropped regions (areas) and normally for several days or weeks. This concentration of agricultural emissions in space and time is one of the main aspects that lead to sudden air pollution increases in rural areas and nearby cities over specific year periods (Chen et al., 2017; Pavilonis et al., 2013). Moreover, PM coming for agricultural operations can affect air concentrations and cause relevant health effects even at medium and long-range distances (Hill et al., 2019).

5. Conclusions

The PM_{10} EFs for rotary harrowing with levelling bar and for rotary harrowing combined with packer roller were determined in low wind speed conditions. Since the atmospheric conditions in which the trials have been made are quite common in Northwest of Italy (Fratianni et al., 2007) and no previous assessment have been done for rotary harrowing in North Italy, the gathered EFs could be used as a first reference EFs for this type of soil tillage under moist soil conditions. A further assessment should be performed to investigate the PM flux caused by the same implement with drier soil conditions.

It was observed that lowering the tractor forward speed at 0.6 m s^{-1} has a negative effect on PM emissions, causing them to increase significantly.

Major and trace elements in soil-generated PM_{10} were analysed, founding a higher content of TE in the PM_{10} fraction than in the original soil sample, meaning that agricultural activities can play a role in the transient increase of metals content in the atmospheric PM_{10}, even in regions with low soil pollution.

Concentrations of PM_{10} at a distance of 4 m from the tractor passage where found to be up to 69 times higher than the daily limit fixed by WHO (2006), raising some concern for farmers health. Estimated concentration raises near-source were also substantial (plus 2 to 7 µg m^{-3} at 100 m of distance from the emission source). Moreover, elemental (Ni, As and Cd) concentration levels near the tractor path were also high, being several times higher than regulatory threshold levels.

This first study highlighted the need of studies on the assessment of the emissions from agricultural activities and to further investigate the effects of mechanic implements and operative parameters on emission fluxes. Moreover, the dispersion of agricultural PM should be assessed also including long-range transport, and focusing on the investigation of the potential health impact of the contaminants present in soil particulates.

Acknowledgements

Funding: This work has been realized within the projects "Valutazione delle emissioni di materiale particolato dalle operazioni colturali e di trasformazione aziendale del mais" (Evaluation of PM emission from cropping operation and first transformation of Maize), funded by Cassa di Risparmio di Torino (CRT foundation) [grant numbers 2018.2273]; and PRIN 2015 "Ottimizzazione di macchine operatrici attraverso l'analisi del profilo di missione per un'agricoltura più efficiente" (Optimisation of operating machine through mission profile analysis for a more efficient agriculture) , founded by Italian Ministry of University and Research (Prot. 2015KTY5NW).

References

Ajmone-Marsan, F., Biasioli, M., Kralj, T., Grcman, H., Davidson, C.M., Hursthouse, A.S., Madrid, L., Rodrigues, S., 2008. Metals in particle-size fractions of the soils of five European cities. Environ. Pollut. 152:73–81. http://dx.doi.org/10.1016/j.envpol.2007.05.020

Avecilla, F., Panebianco, J.E., Buschiazzo, D.E., 2017. Meteorological conditions during dust (PM 10) emission from a tilled loam soil: Identifying variables and thresholds. Agricultural and Forest Meteorology 244–245, 21–32. https://doi.org/10.1016/j.agrformet.2017.05.016

Brun, L. A., Maillet, J., Hinsinger, P., & Pepin, M., 2001. Evaluation of copper availability to plants in copper-contaminated vineyard soils. Environmental Pollution, 111(2), 293-302.

Carslaw, D. C. and K. Ropkins, 2012. openair --- an R package for air quality data analysis. Environmental Modelling & Software. Volume 27-28, 52-61.

Cassel, T., K. Trzepla-Nabaglo, and R. Flocchini. 2003. PM10 Emission Factors for Harvest and Tillage of Row Crops. 12th International Emission Inventory Conference-B Emission Inventories-Applying New Technologies, [San Diego, CA, April 29YMay 1, 2003].

Cattani, G., Di Menno di Bucchianico, A. Fioravanti, G., Gaeta, A., Gandolfo, G., Lena, F., Leone, G., 2019. Analisi dei trend dei principali inquinanti atmosferici in Italia (2008 – 2017). ISPRA - Istituto Superiore per la Protezione e la Ricerca Ambientale, Rapporti 302/2018. ISBN 978-88-448-0938-6

Chen, W., Tong, D. Q., Dan, M., Zhang, S., Zhang, X., & Pan, Y., 2017. Typical atmospheric haze during crop harvest season in northeastern China: a case in the Changchun region. Journal of Environmental Sciences, 54, 101-113.

Clausnitzer, H., Singer, M.J., 1997. Intensive land preparation emits respirable dust. California Agriculture 51, 27–30. https://doi.org/10.3733/ca.v051n02p27

Colombo, C., Miano, T. (Eds.), 2015. Metodi di Analisi chimica del suolo, thirth ed Società Italiana della Scienza del Suolo, Pubblicità & Stampa, Modugno (BA).

MATTM (Ministero dell'Ambiente e della Tutela del Territorio e del Mare), 2010. Decreto Legislativo 155/2010. Attuazione della direttiva 2008/50/CE relativa alla qualità dell'aria ambiente e per un'aria più pulita in Europa, Gazzetta Ufficiale della Repubblica Italiana n. 126 Suppl. Ordinario n. 217

MATTM (Ministero dell'Ambiente e della Tutela del Territorio e del Mare), 2006. Decreto Legislativo 152/2006. Norme in materia ambientale, Gazzetta Ufficiale della Repubblica Italiana n. 88 Supplemento n. 96/L

EEA, 2019. European Union emission inventory report 1990–2017 under the UNECE Convention on Long-range Transboundary Air Pollution (LRTAP), EEA Report No 08/2019, European Environment Agency.

Faulkner, W.B., 2013. Harvesting equipment to reduce particulate matter emissions from almond harvest. Journal of the Air & Waste Management Association 63, 70–79. https://doi.org/10.1080/10962247.2012.738625

Faulkner, W.B., Goodrich, L.B., Botlaguduru, V.S.V., Capareda, S.C., Parnell, C.B., 2009. Particulate Matter Emission Factors for Almond Harvest as a Function of Harvester Speed. Journal of the Air & Waste Management Association 59, 943–949. https://doi.org/10.3155/1047-3289.59.8.943

Foken, T., & Napo, C. J., 2008. Micrometeorology (Vol. 2). Berlin: Springer.

Fratianni, S., Cagnazzi, B., Cremonini, R., Bosco, F., Gai, V., 2007. Il vento in Piemonte. Torino : Arpa Piemonte ; Torino; Università di Torino. Dipartimento di scienze della terra.

Funk, R., Reuter, H.I., Hoffmann, C., Engel, W., Öttl, D., 2008. Effect of moisture on fine dust emission from tillage operations on agricultural soils. Earth Surface Processes and Landforms 33, 1851–1863. https://doi.org/10.1002/esp.1737

Guo, T., Lou, C., Zhai, W., Tang, X., Hashmi, M. Z., Murtaza, R., ... & Xu, J., 2018. Increased occurrence of heavy metals, antibiotics and resistance genes in surface soil after long-term application of manure. Science of the Total Environment, 635, 995-1003.

Hanna, S., and Chang, J., 1992. Boundary-layer parameterization for applied dispersion modeling over urban areas. Boundary Layer Meteorol.. 58. 229-259. 10.1007/BF02033826.

Hill, J., Goodkind, A., Tessum, C., Thakrar, S., Tilman, D., Polasky, S., ... & Marshall, J., 2019. Air-quality-related health damages of maize. Nature Sustainability, 2(5), 397-403.

Holmén, B., Miller, D., Hiscox, A., Yang, W., Wang, J., Sammis, T., Bottoms, R., 2008. Near-source particulate emissions and plume dynamics from agricultural field operations. Journal of Atmospheric Chemistry 59, 117–134. https://doi.org/10.1007/s10874-007-9086-6

Hothorn, T., Bretz, F., and Westfall, P., 2008. Simultaneous Inference in General Parametric Models. Biometrical Journal 50(3), 346--363.

Jahne, M.A., Rogers, S.W., Holsen, T.M., Grimberg, S.J., Ramler, I.P., 2015. Emission and Dispersion of Bioaerosols from Dairy Manure Application Sites: Human Health Risk Assessment. Environmental Science & Technology 49, 9842–9849. https://doi.org/10.1021/acs.est.5b01981

Kasumba, J., Holmén, B.A., Hiscox, A., Wang, J., Miller, D., 2011. Agricultural PM10 emissions from cotton field disking in Las Cruces, NM. Atmospheric Environment 45, 1668–1674. https://doi.org/10.1016/j.atmosenv.2011.01.004

Kendall, M., Brown, L., & Trought, K., 2004. Molecular adsorption at particle surfaces: a PM toxicity mediation mechanism. Inhalation Toxicology, 16(sup1), 99-105.

Kirkhorn, S. R., & Garry, V. F., 2000. Agricultural lung diseases. Environmental health perspectives, 108(suppl 4), 705-712.

Kong, S., Lu, B., Ji, Y., Zhao, X., Bai, Z., Xu, Y., Liud, Y., Jiang, H., 2012. Risk assessment of heavy metals in road and soil dusts within PM2.5, PM10 and PM100 fractions in Dongying city, Shandong Province, China. J. Environ. Monit. 14:791. http://dx.doi.org/10.1039/C1EM10555H

Knauer, J., El-Madany, T., Zaehle, S., Migliavacca M., 2018. “Bigleaf - An R package for the calculation of physical and physiological ecosystem properties from eddy covariance data.” PLoS ONE_, *13*(8), e0201114. doi: 10.1371/journal.pone.0201114. http://doi.org/10.1371/journal.pone.0201114

Kushwaha, R. L., & Linke, C., 1996. Draft-speed relationship of simple tillage tools at high operating speeds. Soil and tillage research, 39(1-2), 61-73.

Lenth, R., 2019. emmeans: Estimated Marginal Means, aka Least-Squares Means. R package version 1.3.3. https://CRAN.R-project.org/package=emmeans

Li, C., Zhou, K., Qin, W., Tian, C., Qi, M., Yan, X., & Han, W., 2019. A review on heavy metals contamination in soil: effects, sources, and remediation techniques. Soil and Sediment Contamination: An International Journal, 28(4), 380-394.

Madden, N.M., Southard, R.J., Mitchell, J.P., 2010. Soil water and particle size distribution influence laboratory-generated PM10. Atmospheric Environment 44, 745–752. https://doi.org/10.1016/j.atmosenv.2009.11.044

Madden, N. M., Southard, R. J., & Mitchell, J. P., 2009. Soil water content and soil disaggregation by disking affects Pm 10 emissions. Journal of environmental quality, 38(1), 36-43.

Maffia, J., Dinuccio, E., Amon, B., Balsari, P., 2020. PM emissions from open field crop management: Emission factors, assessment methods and mitigation measures – A review. Atmos. Environ. 226, 117381. https://doi.org/10.1016/j.atmosenv.2020.117381

Molocznik, A., 2002. Qualitative and quantitative analysis of agricultural dust in working environment. Annals of agricultural and environmental medicine, 9(1), 71-78.

Moore, K. D., Wojcik, M. D., Martin, R. S., Marchant, C. C., Jones, D. S., Bradford, W. J., ... & Hatfield, J. L., 2015. Particulate-matter emission estimates from agricultural spring-tillage operations using LIDAR and inverse modeling. Journal of Applied Remote Sensing, 9(1), 096066.

OECD, 2010. Report n° 2/2 541. OECD Standard Code 2 for the official testing of agricultural and forestry tractor performance. Paris, France: Organization for Economic Co-operation and Development.

Öttl, D., & Funk, R., 2007. PM emission factors for farming activities by means of dispersion modeling. In International Conference “Particulate Matter in and from Agriculture”.

Öttl, D., A. Goulart, G. Degrazia, D. Anfossi, 2005. A new hypothesis on meandering atmospheric flows in low wind speed conditions. Atmos. Environ., 39, 1739 - 1748.

Öttl, D., R. Almbauer, and P. Sturm, 2002. On the simulation of pollutant dispersion in low wind speed conditions. Proceedings from the EUROTRAC-2 Symposium 2002 Garmisch-Partenkirchen, P.M. Midgley, M. Reuther (Eds.), Margraf Verlag Weikersheim.

Pavilonis, B. T., Anthony, T. R., T O'Shaughnessy, P., Humann, M. J., Merchant, J. A., Moore, G., ... & Sanderson, W. T., 2013. Indoor and outdoor particulate matter and endotoxin concentrations in an intensely agricultural county. Journal of exposure science & environmental epidemiology, 23(3), 299-305.

Padoan, E., Malandrino, M., Giacomino, A., Grosa, M., Lollobrigida, F., Martini, S., Abollino, O., 2016. Spatial distribution and potential sources of trace elements in PM10 monitored in urban and rural sites of Piedmont Region. Chemosphere 145, 495-507. https://dx.doi.org/10.1016/j.chemosphere.2015.11.094

Padoan, E., Rome, C., Ajmone Marsan, F., 2017. Bioaccessibility and size distribution of metals in road dust and roadside soils along a peri-urban transect. Sci. Total Environ. 601-602, 89-98. https://doi.org/10.1016/j.scitotenv.2017.05.180

Pinheiro J, Bates D, DebRoy S, Sarkar D, R Core Team, 2018. _nlme: Linear and Nonlinear Mixed Effects Models_. R package version 3.1-137, <URL: https://CRAN.R-project.org/package=nlme>.

Pinheiro, J., & Bates, D., 2006. Mixed-effects models in S and S-PLUS. Springer Science & Business Media.

R Core Team, 2019. R: A language and environment for statistical computing. R Foundation for Statistical Computing, Vienna, Austria. URL https://www.R-project.org/.

Raparelli T., Eula G., Ivanov A., Pepe G., Ricauda Aimonino D., 2019. Preliminary analysis of interaction among gears, tines and soil in a rotary harrow. International Journal of Mechanics and Control. 20(1):81-91.

Schenker M., 2000. Exposures and health effects from inorganic agricultural dusts. Environ Health Perspect; 108 (Suppl 4): 661.

Sharratt, B., Auvermann, B., 2014. Dust pollution from agriculture. Encyclopedia of Agriculture & Food Systems; Elsevier: New York, NY, USA, 487-504.

Smith, R. J., 1995. A Gaussian model for estimating odour emissions from area sources. Mathematical and computer modelling, 21(9), 23-29.

Stull, R. B., 2012. An introduction to boundary layer meteorology (Vol. 13). Springer Science & Business Media.

Usaborisut, P., Praserkan, K., 2019. Specific energy requirements and soil pulverization of a combined tillage implement. Heliyon, 5, 1-10.

Telloli, C., Malaguti, A., Mircea, M., Tassinari, R., Vaccaro, C., & Berico, M., 2014. Properties of agricultural aerosol released during wheat harvest threshing, plowing and sowing. Journal of Environmental Sciences, 26(9), 1903-1912.

Tonne, C., Halonen, J. I., Beevers, S. D., Dajnak, D., Gulliver, J., Kelly, F. J., et al., 2016. Long-term traffic air and noise pollution in relation to mortality and hospital readmission among myocardial infarction survivors. International Journal of Hygiene and Environmental Health, 219, 72-78.

Wang, J., Pan, Y., Tian, S., Chen, X., Wang, L., & Wang, Y., 2016. Size distributions and health risks of particulate trace elements in rural areas in northeastern China. Atmospheric Research, 168, 191-204.

WHO (World Health Organization), 2006. Air Quality Guidelines. Particulate matter, ozone, nitrogen dioxide and sulphur dioxide. Global Update 2005. Copenhagen, WHO Regional Office for Europe Regional Publications, (2006). http://www.who.int/phe/health_topics/outdoorair/outdoorair_aqg/en/.

Wu, F., Kong, S., Yan, Q., Wang, W., Liu, H., Wu, J., ... & Liu, D., 2020. Sub-type source profiles of fine particles for fugitive dust and accumulative health risks of heavy metals: a case study in a fast-developing city of China. Environmental Science and Pollution Research, 1-20.

Zhang, J., Wu, L., Zhang, Y., Li, F., Fang, X., & Mao, H., 2019. Elemental composition and risk assessment of heavy metals in the PM10 fractions of road dust and roadside soil. Particuology, 44, 146-152.

3.3. ARTICLE III: *"Soil PM_{10} emission potential under specific mechanical stress and particles characteristics"*

The article presented in Paragraph 3.2 provided some very interesting insight on the chemical composition, in term of toxic elements content, of soil emitted PM. Moreover, the two trials performed in Article II, highlighted the importance of environmental conditions and especially of soil humidity and soil texture, on the final emission. Therefore, it was decided to build a resuspension chamber that allows to test the emission potential of different soils and the chemical characteristics of the soil emitted PM. This, in fact, would allow, first, to study the effect of soil texture and moisture and, secondly, to investigate the chemical composition of different soils. Ultimately, the chamber allows to transpose emission factors measured in field into emission curves, which account for soil humidity conditions.

Science of The Total Environment (2021), Volume 779, 146468, ISSN 0048-9697

<u>Authors:</u> Elio Padoan, Jacopo Maffia, Paolo Balsari, Franco Ajmone-Marsan, Elio Dinuccio

Science of the Total Environment 779 (2021) 146468

Contents lists available at ScienceDirect

Science of the Total Environment

journal homepage: www.elsevier.com/locate/scitotenv

Soil PM_{10} emission potential under specific mechanical stress and particles characteristics

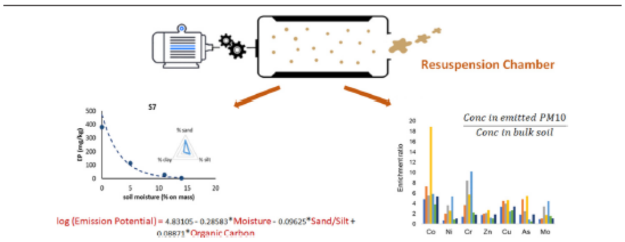
Elio Padoan *, Jacopo Maffia, Paolo Balsari, Franco Ajmone-Marsan, Elio Dinuccio

Dipartimento di Scienze Agrarie, Forestali e Alimentari, Università degli Studi di Torino, Largo Paolo Braccini 2, 10095 Grugliasco, Italy

HIGHLIGHTS

- A soil resuspension chamber has been tested for soil PM_{10} emission potential.
- The effect of soil moisture and characteristics on PM_{10} emissions was modeled.
- PM_{10} decreased exponentially with increasing moisture.
- A field measured emission factor was scaled using the emission potential curves.
- Potentially Toxic Elements concentrations in soil derived PM_{10} were assessed.

GRAPHICAL ABSTRACT



Abstract

Soil can be resuspended in the atmosphere due to wind or mechanical disturbances, such as agricultural activities (sowing, tilling, etc.), producing fine particulate matter (PM). Agriculture is estimated to be the third PM_{10}-emitting sector in Europe, emitting more than the transportation sector. However, very few emission figures are available for the different cropping operations. Moreover, soil Emission Potential (EP) is extremely variable, since is influenced by factors such as humidity, texture, chemical composition, and wind speed. Due to their similarity to tilling emission mechanisms, Soil Resuspension Chambers (SRC) are the most suitable method to estimate the impacts of these factors on soil susceptibility to emit PM_{10} during cropping operations (Emission Potential, EP). The main objective of this work is to assess the EP of different agricultural soils used for maize cropping in North-Western Italy, studying the influence of soil moisture and physico-chemical characteristics. Therefore, a SRC was developed, based on previous studies, with the goal of being relatively small, easy to operate and low-cost. Using the gathered data, a log-linear multiple regression model was developed to allow soil EP estimation from few physico-chemical parameters (moisture, sand/silt ratio and organic carbon content). The model allows to tailor field Emission Factors (EF) of specific cropping operations to different soil and moisture conditions and was applied to an EF for rotary harrowing, defined in a previous study. The concentration of Potentially Toxic Elements (PTE) in soil-emitted PM_{10} was determined, founding an enrichment up to 16 times higher than in the original soil, evidencing a possible cause of concern for operator's safety during agricultural activities.

1. Introduction

Soil is a natural source of fine Particulate Matter (PM), both in urban and in rural environments (Padoan and Amato, 2018; Soleimanian et al., 2019). Soil particles can be suspended in the atmosphere mainly due to wind erosion and to mechanical disturbances, such as agricultural activities (Maffia et al., 2020a; Sharratt and Auvermann, 2014).

Along with the long-term adverse health effects of atmospheric PM_{10} pollution (Tonne et al., 2016), several studies highlighted the importance of crustal components of PM and of soil-derived PM_{10} (Wu et al., 2020; Galindo et al., 2018; Padoan et al., 2016; Kendall et al., 2004). These components are of crucial importance in terms of total emissions and chemical composition and are possibly enriched of inorganic and organic pollutants (Padoan et al., 2017; Brunekreef and Holgate, 2002).

In Europe, agriculture is estimated to be the third PM_{10}-emitting sector, emitting more than the transportation sector according to the European Environment Agency (EEA, 2020). Farm-level agricultural operations, such as land preparation activities (sowing, tillage, etc.) and outdoor animal rearing (herd movement and animal activity), are one of the most relevant contributors to anthropic PM emissions (EEA, 2020). However, very few emission figures are available for the different cropping operations (Maffia et al., 2020b; Öttl et al., 2007; Holmén et al., 2001).

PM emissions from cropping activities are extremely variable, since they are influenced by many factors, such as soil humidity, texture and chemical composition (e.g. the mineral and organic matter content), and wind speed (Avecilla et al., 2017; Funk et al., 2008). These factors, together with the mechanical implements used for cropping operations, determine the field emissions. Addressing these factors one by one, and determining their specific effect on the emissions is, therefore, of crucial importance to standardize field emission data and to compare them successfully.

Several laboratory methodologies have been proposed to investigate the impacts of these factors on soil Emission Potential (EP), the soil capacity to emit PM_{10} per unit weight, over a certain period. Among these methodologies, the most common are soil resuspension chambers (SRC) and wind tunnels (WT) (Mendez et al., 2013; Pietrodangelo et al., 2013; Madden et al., 2010; Moreno et al., 2009; Gill et al., 2006). SRC rely on mechanical disturbance or abrasion to achieve soil resuspension, with the possibility to collect resuspended particles using a depression or forced-air ducts. Conversely, WT rely only on wind speed effect. Due to the similar resuspension mechanism applied, SRC are more suitable than WT to estimate soil susceptibility to emit PM_{10} during cropping operations, while WT are more appropriate to estimate wind erosion rates.

The main objective of the work is to assess the EP of different agricultural soils used for maize cropping in North-Western Italy, studying the influence of soil moisture and physico-chemical characteristics on the EP of those soils. Therefore, a SRC was developed, based on previous studies (Maffia et al., 2020b; Madden et al., 2010), with the goal of being relatively small, easy to build and low-cost. Using the gathered data, we developed a model to allow soil EP estimation from some simple physico-chemical parameters, to tailor field emission factors (EF) of specific cropping operations to different soil and moisture conditions. Moreover, we analysed the Potentially Toxic Elements (PTE) concentration of soil-emitted PM_{10} to assess the health and environmental risk of the resuspended particles, potentially eroded and transported to different environmental compartments or affecting farmers.

2. Materials and methods

2.1. Soil Sampling and physico-chemical characterization

Soils were sampled in different locations in Piemonte (North-West of Italy). The areas were chosen based on the regional soil map (Regione Piemonte, 2020), selecting seven soils with different physico-chemical properties in order to represent the range of soil texture in cultivated soils of Piemonte. The selected soils are typically invested with Maize, which is the most cultivated summer crop in northern Italy. Soil classification was defined according to WRB Soil Taxonomy (IUSS, 2015).

The map with the sampling points (Figure SM1) and the table with coordinates, soil classification and meteorological parameters (Table SM1) are reported in the Supplementary Material (SM).

At each location, 15 subsamples were taken by applying a non-systematic X sampling scheme (Colombo and Miano, 2015). The topsoil subsamples were collected to a depth of 25 cm, which was considered the most used depth in tilling practices and quartered in the field to obtain 7 soil samples.

The samples were air-dried and sieved to 2 mm before physico-chemical analyses. We determined soil texture, pH, total carbon and nitrogen content and carbonates. All analyses were performed according to official Italian methods for soils (Colombo and Miano, 2015). The fraction of particles <10 µm was estimated by repeated sedimentation and decanting, as in Ajmone-Marsan et al. (2008). Field capacity (FC) was then determined for each soil according to the official method proposed by MiPAF (1997).

2.2. Soil resuspension chamber

A soil resuspension chamber (SRC) was developed starting from the rotating drum in Maffia et al. (2020a), using the best experiences from Gill et al. (2006) and Madden et al. (2009). The SRC system is represented in Figure 1. Soil samples were re-suspended in a rotating drum (1) with a 25 L capacity and a rotation frequency of 26 revolutions per minute, powered by an electric engine (2) with 0,75 kW of power and an electric potential of 220 V. During the trials, the drum was closed by a flange. Four flexible PVC tubes (0.4 m long with 8 mm diameter), provided with a series of small holes (diameter 0.3 mm), were nested on the flange and allow clean air to enter the drum. During soil re-suspension, the air was sucked from the drum (1) through an aspiration pipe (4), which allowed the emitted dust to reach a deposition chamber (5). The air stream was forced by a vane pump (5; VTE3, Rietschle), drawing the air from the deposition chamber and inducing an air flow of 30 L min^{-1}, calibrated through a flux meter, through the system. The re-suspended particulate matter was sampled through a sampling port (6) using both an optical PM monitor (Grimm 11-D, Grimm Aerosol Technik), to assess particle quantity, or a filter-based low-volume impactor (MSSI Multistage Impactor, TCR Tecora®), to define particles elemental composition.

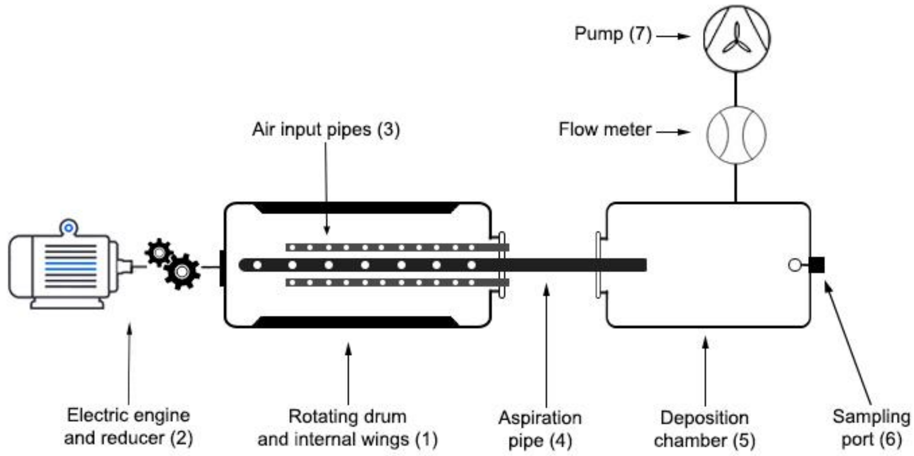


Figure 1. Scheme of the soil resuspension chamber. Soil is manually placed in the rotating drum (1) before the experiment, while PM instrumentation is connected to the sampling port (6).

2.3. Experimental protocol and Emission Potential estimation

Resuspension trials of each sample were accomplished by placing a soil aliquot inside the SRC rotating drum and re-suspending it for 15 min. Different tests were conducted to define the most suitable soil quantity, to generate reproducible data without saturating the PM monitor. The final experiments were conducted using 5g of each soil and were performed in triplicate to ensure the consistency of the method.

The EP was defined at four different moisture contents (calculated as 0, 15, 30 and 40%, by weight, of the soils FC) for each soil, for a total of 84 trials. The equation used to define soil EP (mg kg^{-1}) was the following:

Where C represents the particle concentration (µg m^{-3}) measured by the Grimm PM monitor, P the system airflow (m^{3} min^{-1}), calculated as the sum of the pump flow and the flow of the Grimm internal pump (1.2 L min^{-1}), S the mass of the soil sample used (kg), and t the considered timespan (min).

2.4. Filter-based Particulate Matter sampling and elemental analysis

Soil-emitted PM_{10} was sampled on quartz fibre filters (Ahlstrom Munksjo, Microquartz fibre paper MK360, Ø47 mm). Before use, filters were dried at 205 °C for 5 hours and conditioned for 48 hours at 20 °C and 50 % relative humidity; then weighed three times every 24 h and kept in Petri dishes. Used filters were conditioned for 48 h and weighed using the same procedure.

Between consecutive samples, the SRC was thoroughly washed with deionized water and run for 15 min without soil to avoid cross-contamination.

Major and trace element pseudo-total contents were determined in the original soils and in PM_{10}. One-gram soil samples were digested in *aqua regia* (HNO_3:HCl, 1:3) using microwave extraction (Ethos D, Milestone). Similarly, half of each PM_{10} filter was microwave digested and blank filters were analysed to ensure a correction for their possible elemental release. Solutions were then filtered on cellulose filters (Whatman n° 41) and diluted with ultrapure water before analysis. Elemental concentrations were assessed in all samples using ICP-MS (NexION 350D, PerkinElmer). All the analyses were performed in duplicate and using certified reference materials (CRM 141R and 142R, Community Bureau of Reference, Geel, Belgium) to ensure accuracy and correct recoveries.

The enrichment ratios (ER), i.e. the ratios between elemental concentrations in soil-originated PM_{10} compared to bulk soil, were calculated as follows:

Where C_{PM} is the concentration (mg kg^{-1}) in resuspended PM_{10} and C_{soil} is the concentration in the original soil (mg kg^{-1}).

2.5. Statistical analyses

The effect of the physico-chemical characteristics on the EP of the investigated soils was analysed using multiple log linear regression. Predictors were chosen on the base of their level of correlation with the EP logarithm. The correlation matrix also allowed to check for collinearity. To account for the soil particle size distribution, we tried to use all the three parameters (sand, silt and clay) together, only two of them and using the different ratios. Clay, probably because of its scarce variation in the soil set, did not have a high correlation coefficient with EP and, when added to the model, the prediction (fitting) did not improve. We decided to use the sand-silt ratio as a proxy for the complete particle size distribution because was the one preforming better in the prediction model. This choice was made since, as highlighted by Madden et al. (2010), the ratio between two textural components can be a good descriptor of soil characteristics. Moreover, it allowed to achieve a more parsimonious model. Sand and silt performed better than clay as predictors, probably since these two components are the ones that vary the most in selected soils. The linearity and homoscedasticity assumptions were tested graphically and by means of a Shapiro-Wilk test. The analyses were performed using R statistical software (R core team, 2019).

3. Results

3.1. *Soil physico-chemical characteristics*

The physico-chemical characteristics of the analysed soils are reported in Table 1.

The studied soils presented a relatively wide textural variability with sand contents ranging from 14 to 82 %, silt contents ranging from 9 to 40 % and clay contents ranging from 9 to 33 %. Soil texture, and especially fine fractions content, is known to be a key factor in determining PM_{10} emissions (Madden et al., 2010; Funk et al., 2008), thus the content in <10 µm particles was analysed, ranging from 9.5 to 51 % in the observed soils.

Carbonate concentrations were variable but low in all the soils. Organic carbon (OC) contents were in line with typical Italian agricultural soils (Jones et al., 2020), varying in the range 0.8 – 2.2%.

Table 1. Soil physico-chemical characterization, texture was calculated according to Soil Science Division Staff (2017).

Soil	Sand (%)	Silt (%)	Clay (%)	Textural class	Particles < 10 µm (%)	Field Capacity (% V/V)	pH	OC (g kg^{-1})	Inorganic C (g kg^{-1})	N (g kg^{-1})	C/N ratio
S1	51	40	9	Loam	18.2	37.9	8.2	8.8	2.7	1.4	9
S2	30	56	14	Silt Loam	25.3	32.3	7.5	8.3	1.2	1.3	8
S3	14	53	33	Silty Clay Loam	51.4	33.0	6.9	11.6	1.0	1.8	7
S4	82	9	9	Loamy Sand	9.5	23.6	6.9	9.5	8.5	1.1	16
S5	30	54	16	Silt Loam	37.9	45.7	6.2	22.0	1.9	3.2	8
S6	40	46	14	Loam	31.6	24.9	7.7	10.0	1.0	1.8	6
S7	59	31	10	Sandy Loam	19.8	35.6	6.0	11.8	1.7	1.8	8

3.2. *Emission Potential*

Air-dried soils were considered as with zero percent moisture. Water was then added to each soil to achieve the desired percentage levels of FC (0, 15, 30 and 40%). Figure 2 shows the EP of the soils at the different soil moisture content. In Fig. 2 the mass percentage was used to normalize moisture values in the different soils. An exponential decrease of the soil EP with the increase of moisture found for all soils.

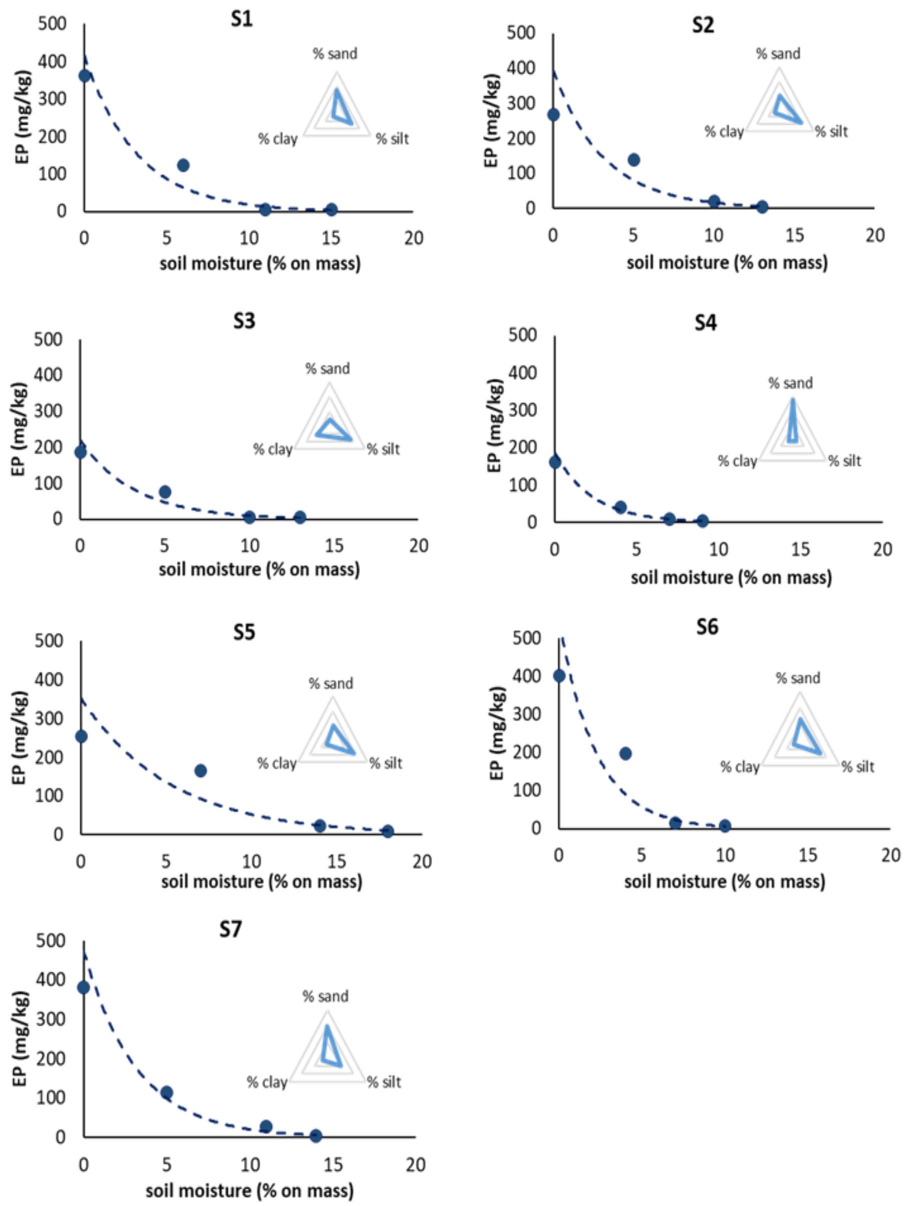


Figure 2. Emission Potential of selected soils as measured using the PM monitor.

Between the analysed chemical parameters, carbonate and total nitrogen contents were not linearly correlated to the EP of the soils. The effect of soil moisture content, texture, and OC content on the EP of the investigated soils was analysed by means of regression models.

Regarding texture, giving that the three components are interrelated, we calculated the model results using all the three parameters together and/or with each single fraction, finding no correlations with EP. Then, we used different ratios between two of them, finding this as best option, as in Madden et al. (2010). Among the possible ratios, the sand to silt quotient was the one better performing in the model, giving consistent results for all soils.

A multiple log linear regression best fitted the exponential response seen for the effect of moisture. All three tested variables had a highly significant ($P<0.001$) effect on the EP and the effect of each of those variables is summarized in the following formula:

Where H is the soil moisture content (% on mass), Ss is the Sand/silt ratio in the soil and OC is the organic carbon content (g kg^{-1}).

The model fitted the observed EP data well at both high and low moisture contents, with an adjusted-R^2 of 0.838. Figure 3 shows a comparison between observed and predicted log transformed EP data, according to the multiple regression model.

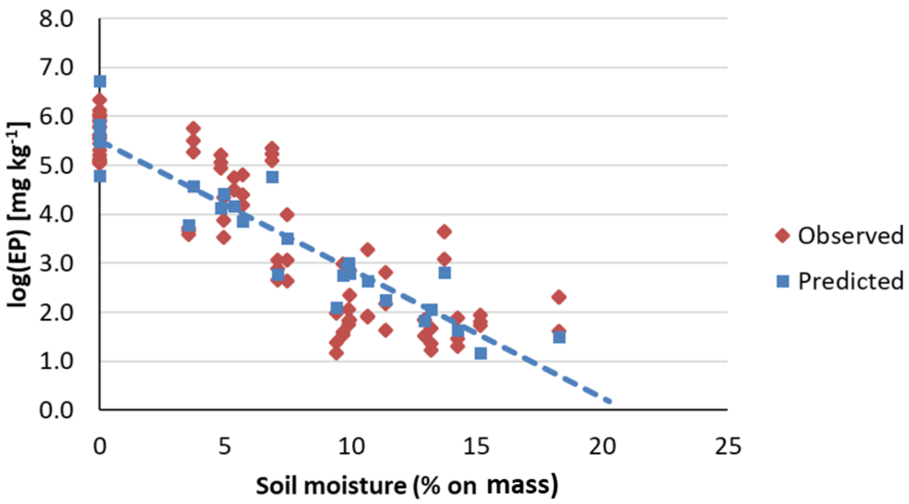


Figure 3. Observed and predicted data, as obtained using the log-linear prediction model

3.3. *Elemental contents in soil and soil-originated PM_{10}*

The concentrations of major and trace elements in the analyzed bulk soils and in their resuspended fraction are summarized in Tables 2 and 3.

Selected soils appeared as natural, uncontaminated areas, with elemental and PTE concentrations in line with the regional baseline values (ARPA Piemonte, 2014) and lower than regional legislative limits for agricultural soils (Regione Piemonte, 2000) and national limits for green areas (MATTM, 2006).

Table 2. Elemental concentrations of major and trace elements in soils S1 to S7.

	S1	S2	S3	S4	S5	S6	S7
				$g\ kg^{-1}$			
Mg	14.2 ± 1.0	7.8 ± 0.1	10.1 ± 0.4	9.8 ± 0.7	9.4 ± 0.4	6.2 ± 0.3	7.5 ± 1.0
Al	22.8 ± 2.2	28.1 ± 1.2	36.6 ± 0.4	14.0 ± 1.7	25.9 ± 3.2	34.7 ± 3.5	23.7 ± 4.1
K	4.7 ± 0.3	7.5 ± 0.7	13.7 ± 0.7	5.1 ± 1.1	14.3 ± 3.6	7.2 ± 2.6	4.3 ± 2.0
Mn	0.9 ± 0.1	0.9 ± 0.01	1.1 ± 0.1	0.8 ± 0.03	1.4 ± 0.01	1.3 ± 0.01	1.3 ± 0.2
Fe	16.2 ± 5.4	14.1 ± 4.8	18.6 ± 2.3	12.1 ± 1.1	14.8 ± 2.2	18.2 ± 1.7	16.5 ± 2.5
				$mg\ kg^{-1}$			
Li	38 ± 1	39 ± 0.1	52 ± 1.1	33 ± 1	55 ± 1	46 ± 2	37 ± 2
Co	18 ± 0.5	17 ± 0.2	22 ± 0.4	10 ± 0.4	19 ± 0.3	22 ± 2	17 ± 0.7
V	51 ± 4	64 ± 5	84 ± 2	31 ± 2	52 ± 3	65 ± 4	57 ± 4
Ni	108 ± 3.1	84 ± 2	108 ± 2	85 ± 3	63 ± 1	85 ± 10	94 ± 8
Cr	122 ± 6	104 ± 3	154 ± 3	88 ± 6	64 ± 2	85 ± 9	100 ± 4
Zn	78 ± 3	79 ± 5	107 ± 3	78 ± 5	195 ± 4	136 ± 28	85 ± 17
Cu	36 ± 2	28 ± 0.6	34 ± 0.6	22 ± 1	69 ± 1	61 ± 3	35 ± 4
As	9 ± 4.5	6 ± 3	9 ± 3	4 ± 1.4	19 ± 5	19 ± 3	10 ± 3
Sr	62 ± 22	41 ± 2	71 ± 2	98 ± 3	45 ± 5	32 ± 10	26 ± 3
Mo	11 ± 0.2	12 ± 0.2	12 ± 0.1	12 ± 0.3	12 ± 0.1	12 ± 0.1	13 ± 1
Cd	7 ± 0.8	7 ± 0.8	7 ± 0.8	7 ± 0.8	7 ± 0.8	7 ± 0.8	7 ± 0.8

Sn	11 ± 0.5	11 ± 0.4	11 ± 0.2	12 ± 0.3	11 ± 0.1	11 ± 0.4	11 ± 0.4
Sb	9 ± 1.0	9 ± 1.0	9 ± 0.9	9 ± 1.0	10 ± 1.0	10 ± 1.0	9 ± 0.9
Ba	70 ± 3	109 ± 2	120 ± 3	59 ± 5	139 ± 10	127 ± 12	101 ± 17
Pb	21 ± 0.2	20 ± 0.4	25 ± 0.6	25 ± 1	31 ± 0.7	31 ± 0.5	26 ± 3

Resuspended PM_{10} fraction of soils present concentrations higher than bulk soils for most of the elements, both crustal and PTE, in accordance with previous studies demonstrating a higher PTE concentration in fine soil fractions (Maffia et al., 2020b; Padoan et al., 2018). Conversely to previous studies, also major elements, such as Mg, Sl, Fe and K, present higher values in soil-derived PM_{10} of some soils.

Soil and soil-derived PM concentrations appear correlated both most of the soils, using Pearson values, apart for soils S3 and S5, soils with the highest concentrations of Cr, Zn and Mg, in particular. At the same time, these soils were the ones with the higher concentration of particles < 10 µm.

Table 3. Elemental concentrations of major and trace elements in soil-derived PM_{10}.

	S1	S2	S3	S4	S5	S6	S7
				g kg^{-1} PM_{10}			
Mg	24 ±12	42 ± 29	32 ± 19	51 ± 34	141 ± 27	22 ± 11	25 ± 13
Al	75 ±31	73 ± 30	53 ± 24	85 ± 35	35 ± 21	41 ± 24	51 ± 12
K	19 ±4	29 ± 8	12.4 ± 1.4	32 ± 6	9.8 ± 1.5	18 ± 6	22 ± 3
Mn	1.9 ± 0.7	2.1 ± 0.6	1.1 ± 0.4	2.2 ± 0.5	1.6 ± 0.4	0.7 ± 0.4	2.0 ± 0.1
Fe	71 ± 20	77 ± 19	54 ± 0.4	80 ± 11	60 ± 24	89 ± 55	62 ± 3
				mg kg^{-1}			
Li	84 ± 15	74 ± 22	59 ± 30	89 ± 14	47 ± 12	54 ± 9	50 ± 18
Co	89 ± 22	124 ± 34	123 ± 49	199 ± 46	111 ± 41	85 ± 16	93 ± 26

V	123 ± 15	129 ± 20	152 ± 42	172 ± 9	121 ± 50	84 ± 8	94 ± 7
Ni	81 ± 29	169 ± 37	395 ± 24	219 ± 46	341 ± 16	74 ± 16	102 ± 21
Cr	174 ± 17	383 ± 154	1298 ± 148	504 ± 79	652 ± 216	192 ± 7	182 ± 21
Zn	135 ± 53	160 ± 70	229 ± 140	213 ± 98	243 ± 156	151 ± 99	160 ± 89
Cu	120 ± 22	126 ± 10	136 ± 33	104 ± 5	166 ± 10	163 ± 48	121 ± 4
As	17 ± 4	31 ± 9	22 ± 8	24 ±2	16 ± 11	10 ± 0.2	18 ± 3
Sr	57 ± 7	78 ± 15	70 ± 11	84 ± 16	70 ±28	77 ± 17	57 ± 4
Mo	11 ± 3	12 ± 3	39 ± 16	21 ± 7	54 ± 19	20 ± 3	14 ± 3
Cd	4.1 ± 2.1	5.2 ± 2.5	18 ± 8	9.6 ± 3.9	26 ± 11	7.4 ± 3.1	6.2 ± 2.5
Sn	31 ± 27	36 ± 42	45 ± 46	19 ± 17	61 ± 30	16 ± 11	18 ± 3
Sb	6.2 ± 2.5	7.6 ± 2.9	22 ± 11	13 ± 6	31 ± 16	10 ± 4	8.5 ± 3.5
Ba	443 ± 134	557 ± 70	591 ± 135	710 ± 36	586 ± 112	463 ± 34	395 ± 11
Pb	44 ± 17	49 ± 14	46 ± 0.4	62 ± 8	81 ± 2	32 ± 8	50 ± 2

The ERs, thus the enrichment in soil-emitted PM_{10} compared to the bulk soils, varied largely between the samples. Values for selected elements are reported in Figure 4. Increases of elemental content, as compared to the original soil, up to 19, 10, 5, 5, 4, 4, and 3 times were observed for PTE such as Co, Cr, Ni, Cu, Mo, Cd and Pb, respectively. The enrichment in elements was more pronounced for some soils, as S4, the sandier one, and S5, the soil containing more OC.

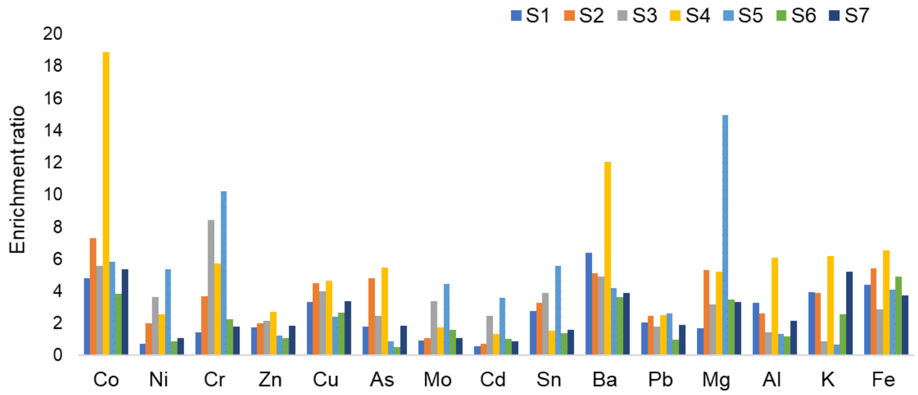


Figure 4. Enrichment ratios in resuspended PM_{10}

4. Discussion

The soils presented a wide range of sand and silt quantities, well representing the variety of the agricultural soils used for cereal cultivation in the Po plain. The observation of the EP curves (Figure 2) revealed an exponential relation among the EP and soil moisture content. It was also observed that the slope of the curve, the maximum emission value (at dry soil conditions), and the threshold moisture content at which no further emission is produced, varied according to soil type. The implemented log-linear regression model allowed to better understand and describe the influence of moisture, texture, and soil organic carbon content on the emissions. Soil moisture was shown to be the main emission driver, being negatively correlated with the EP. The granulometry also significantly affected the EP, with the sand to silt ratio being the most useful for model calculations, probably because in our set of soils these two parameters had a higher variability than the clay fraction, thus better representing the soil set. Indeed, single parameters, such as the total PM_{10} content in the soil were not good predictors of soil EPs, having low correlation coefficients.

Comparing these results with previous studies we can hypothesize that the choice among Clay/Silt ratio and Sand/Silt ratio for representing soil texture in regression models has to be made according to the textural characteristics of the analysed soil samples.

Higher Sand/Silt ratios implied lower emissions, as most of the PM_{10} particles belong to the silt fraction of the soils. This finding is in slight contrast with that of Madden et al. (2010), who observed a better agreement of the emissions with the Silt/Clay ratio although also in that case, a higher silt fraction implied higher emission.

The importance of ratios is evident also in the result of the soil S3, which had the highest fraction of <10μm particles (51.4%) and high clay but a relatively balanced silt/clay ratio, being the second lowest between our soils. This low ratio resulted in low emissions.

The findings of this study confirmed that utilizing two soil fractions to predict the emission is generally more effective and reliable than just using silt as a single predictor, as suggested by Carvacho et al. (2001) and also as suggested for PM_{10} emissions due to traffic in the case of unpaved roads (EPA, 1998). The soil organic carbon content also has a significant effect on the EP, with high OC corresponding to high emissions. The combined effects observed for soil moisture, texture and OC are in accordance with previous findings by Funk et al. (2008), although the results they presented were obtained from a range of soils with more extreme characteristics.

As for the effect detected for soil OC, the observed emission enhancement is probably due to different factors; the first one is possibly linked to the density of organic particles, lower than mineral particles especially in the case of dry soils, a second factor could have been connected to the fact that organic particles in soils are often in the $<PM_{10}$ range and, therefore, when there is a higher OC content, more fine particles can be potentially emitted. This finding agrees with those of Funk et al. (2008), who found a similar relationship with soil humus content. Nonetheless, a higher OC content could also favor soil structure, which can reduce the emissions (Madden et al., 2009; Tatarko et al., 2020).

In conclusion, our calculations based on soils used in cereal cultivation because it is the most common practice in floodplain fields in Europe, but the emission potential estimation is applicable to every soil with similar characteristics. The EPs are intended as maximum emission values for agronomical practices such as ploughing or harrowing, and they are applicable to every crop type and soil to study the emission factors dependence with soil moisture.

To do so, an equation is proposed, to adapt the obtained EP curves to emissions from agricultural operations, allowing to estimate emission factors (EF; mg m^{-2}) for different soils at different moisture levels:

Where EF^* and EP^* are, respectively, the EF measured in field conditions on a specific soil and with a specific moisture content and the EP related for that soil and moisture, and EP_M is the EP for all other moisture levels needed to define an EF curve. This procedure has been applied on the EF (8.9 mg m^{-2}) experimentally found for rotary harrowing operations from Maffia et al. (2020b) and the graphical output is shown in Figure 5. Soil characteristics are reported in the original paper. The EF*/EP* ratio could be proposed as a factor identifying the effect of the mechanical tilling implements used for agricultural operations. Further studies should be performed to calculate and compare EF*/EP* ratios for different agricultural operations.

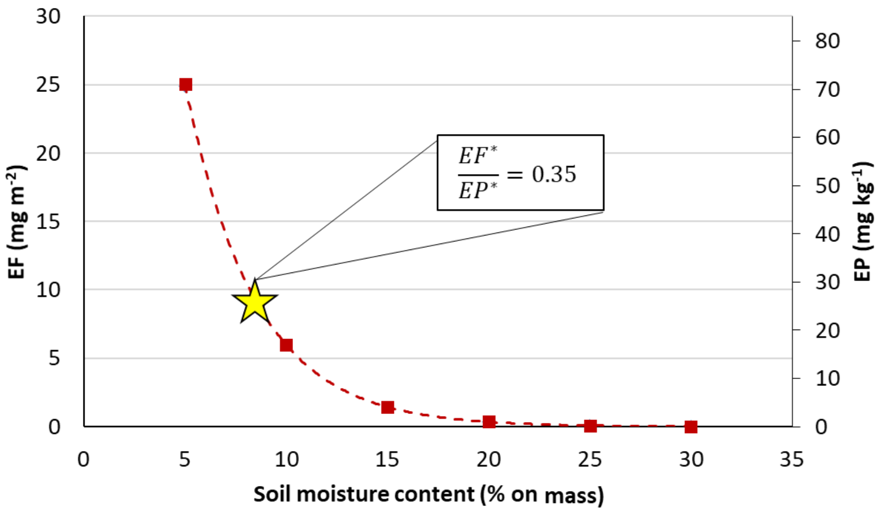


Figure 5. EF curve estimated for rotary harrowing operations (calculated from Maffia et al., 2020b)

The concentrations of trace elements in soils and soil-originated PM (Table 2 and 3) resulted very different. Generally, an increase of the elemental contents in PM_{10} as compared to the original soils was observed. The elements exhibiting the highest enrichment are the ones regarded as crustal-related, according to previous studies in the same area (Padoan et al., 2017; Biasioli et al., 2012). Chromium, Ba, Co, Mg, Ni and Fe were the elements mostly accumulated in the emitted particulate. Although not all of them are considered toxic, all of them were found at very high concentrations in all samples and, for PTE such as Cr, these values could be a cause of concern for operator's safety during agricultural activities, as highlighted during a previous trial (Maffia et al., 2020).

It has been observed that the soils in which the ER (Figure 4) raised to the highest levels (S4 and S5) had particular characteristics. Soil 4 was the sandiest one and S5 had a very high fraction of particles <10 µm. This behavior is in accordance with previous studies and could be due to the fact that these elements are mostly bound to the clay fraction of soils, which has a higher prevalence of adsorbing phase, such as iron oxides and organic material with high specific surface (Padoan et al., 2020; 2017; Ajmone-Marsan et al., 2008). Moreover, S5 was the one with the highest OC content, which had an emission enhancement effect.

5. Conclusions

An easy to build and low-cost soil resuspension chamber has been tested to assess PM_{10} EP from soil and study the chemical characteristics of the emitted PM_{10}. The Emission Potential (EP) of 7 different soils, representing the variety of soil types for the cereal cropping area in the North-West of Italy, has been estimated at different moisture contents, obtaining soil-specific EP curves. A log-linear regression model, based on soil moisture, Sand/silt ratio and organic carbon content, was developed to describe the effect that those variables had on the emissions. The model showed a good fit to the experimental data and it will be possible to implement it, in order to obtain specific EF curves for typical cropping operations (e.g. tillage, harrowing, sowing etc.) on North-West Italian soils but also on different soils with similar characteristics, allowing to estimate emission factors (EF; mg m^{-2}) for different soils at different moisture levels with limited effort. This will allow to overcome the difficulty of perming field trials in several moisture conditions to retrieve reliable EFs.

The elemental content of both major and trace elements in soil-originated PM_{10} resulted higher than in the original soil itself. It has been observed that the soils in which the ERs were the highest were the ones with the higher clay and PM_{10}. The increase ratios reached one order of magnitude for some elements such as Cr, Co and Ba, reaching values of concern with regard to the operator's safety during agricultural activities.

Acknowledgements

This work has been partly funded from the project "Valutazione delle emissioni di materiale particolato dalle operazioni colturali e di trasformazione aziendale del mais" (Evaluation of PM emission from cropping operation and first transformation of Maize), by Fondazione Cassa di Risparmio di Torino, grant number 2018.2273.

References

Ajmone-Marsan, F., Biasioli, M., Kralj, T., Grčman, H., Davidson, C.M., Hursthouse, A.S., Madrid, L., Rodrigues, S., 2008. Metals in particlesize fractions of the soils of five European cities. Environmental Pollution 152, 73–81. https://doi.org/10.1016/j.envpol.2007.05.020

ARPA Piemonte, 2014. Analisi ambientale sulla contaminazione diffusa (suolo e acque sotterranee) del territorio regionale per la definizione di valori di fondo per diverse categorie di inquinanti (in Italian). https://www.arpa.piemonte.it/approfondimenti/temi-ambientali/suolo/relazione-suolo (accessed 07 December 2020).

Avecilla, F., Panebianco, J.E., Buschiazzo, D.E., 2017. Meteorological conditions during dust (PM 10) emission from a tilled loam soil: Identifying variables and thresholds. Agricultural and Forest Meteorology 244–245, 21–32. https://doi.org/10.1016/j.agrformet.2017.05.016

Biasioli, M., Fabietti, G., Barberis, R., Ajmone-Marsan, F., 2012. An appraisal of soil diffuse contamination in an industrial district in northern Italy. Chemosphere 88, 1241-1249. https://doi.org/10.1016/j.chemosphere.2012.03.081

Brunekreef, B., Holgate, S.T., 2002. Air pollution and health. Lancet 360, 1233-1242. http://dx.doi.org/10.1016/S0140-6736(02)11274-8

Carvacho, O.F., Ashbaugh, L.L., Brown, M.S., & Flocchini, R.G., 2001. Relationship between san joaquin valley soil texture and pm10 emission potential using the UC Davis dust resuspension test chamber. Transactions of the ASAE, 44(6), 1603.

Colombo, C., Miano, T. (eds) (2015) Metodi di Analisi chimica del suolo, 3rd edn. Società Italiana della Scienza del Suolo. Pubblicità & Stampa, Modugno (BA). (in Italian)

EEA, 2020. European Union Emission Inventory Report 1990-2018 under the UNECE Convention on Long-Range Transboundary Air Pollution (LRTAP), EEA Report No 05/2020. European Environment Agency. https://www.eea.europa.eu/publications/european-union-emission-inventory-report-1990-2018

Funk, R., Reuter, H.I., Hoffmann, C., Engel, W., Öttl, D., 2008. Effect of moisture on fine dust emission from tillage operations on agricultural soils. Earth Surface Processes and Landforms 33, 1851–1863. https://doi.org/10.1002/esp.1737

Galindo, N., Yubero, E., Nicolás, J.F., Varea, M., Crespo, J., 2018. Characterization of metals in PM1 and PM10 and health risk evaluation at an urban site in the western Mediterranean. Chemosphere, 201, 243-250. https://doi.org/10.1016/j.chemosphere.2018.02.162

Gill, T.E., Zobeck, T.M. Stout, J.E., 2006. Technologies for laboratory generation of dust from geological materials. Journal of hazardous materials, 132(1), 1-13.

Holmén, B.A., James, T.A., Ashbaugh, L.L., Flocchini, R.G., 2001. Lidar-assisted measurement of PM10 emissions from agricultural tilling in California’s San Joaquin Valley – Part II: emission factors. Atmospheric Environment 35, 3265–3277. https://doi.org/10.1016/S1352-2310(00)00519-7

IUSS Working Group WRB, 2015. World Reference Base for Soil Resources 2014, update 2015, International soil classification system for naming soils and creating legends for soil maps. World Soil Resources Reports No. 106. FAO, Rome

Jones, A, Fernandez-Ugalde, O., Scarpa, S., 2020. LUCAS 2015 Topsoil Survey. Presentation of dataset and results, EUR 30332 EN, Publications Office of the European Union: Luxembourg. 2020, ISBN 978-92-76-21080-1, doi:10.2760/616084

Kendall, M., Brown, L., Trought, K., 2004. Molecular adsorption at particle surfaces: a PM toxicity mediation mechanism. Inhalation Toxicology 16(1), 99-105. https://doi.org/10.1080/08958370490443187

Madden, N. M., Southard, R. J., Mitchell, J. P., 2009. Soil water content and soil disaggregation by disking affects PM 10 emissions. Journal of environmental quality, 38(1), 36-43.

Madden, N.M., Southard, R.J., Mitchell, J.P., 2010. Soil water and particle size distribution influence laboratory-generated PM10. Atmospheric Environment 44, 745–752. https://doi.org/10.1016/j.atmosenv.2009.11.044

Maffia, J., Dinuccio, E., Amon, B., Balsari, P., 2020a. PM emissions from open field crop management: emission factors, assessment methods and

mitigation measures – a review. Atmospheric Environment 226, 117381. https://doi.org/10.1016/j.atmosenv.2020.117381
Maffia, J., Balsari, P., Padoan, E., Ajmone-Marsan, F., Aimonino, D. R., Dinuccio, E., 2020b. Evaluation of particulate matter (PM10) emissions and its chemical characteristics during rotary harrowing operations at different forward speeds and levelling bar heights. Environmental Pollution 265, 115041. https://doi.org/10.1016/j.envpol.2020.115041
MATTM, Italian Republic, 2006. Decree of the Ministry of the Environment "Decreto Legislativo 152/2006, norme in materia ambientale", Gazzetta Ufficiale della Repubblica Italiana 88, Supplemento 96/L (in Italian)
Mendez, M.J, Panebianco, J.E., Buschiazzo, D.E., 2013. A new dust generator for laboratory dust emission studies. Aeolian Research 8, 59-64. https://doi.org/10.1016/j.aeolia.2012.10.007
MiPAF, Ministero per le Politiche Agricole e Forestali, 1997. Metodi di Analisi fisica del suolo. Società Italiana della Scienza del Suolo. Franco Angelo, Milano (in Italian)
Moreno, T., Amato, F., Querol, X., Alastuey, A., Elvira, J., Gibbons, W., 2009. Bedrock controls on the mineralogy and chemistry of PM10 extracted from Australian desert sediments. Environmental Geology 57, 411. https://doi.org/10.1007/s00254-008-1312-2
Öttl, D., Funk, R., 2007. PM emission factors for farming activities by means of dispersion modeling. Landbauforsch Völkenrode SH 308, 173-177.
Padoan, E., Malandrino, M., Giacomino, A., Grosa, M., Lollobrigida, F., Martini, S., Abollino, O., 2016. Spatial distribution and potential sources of trace elements in PM10 monitored in urban and rural sites of Piedmont Region. Chemosphere 145, 495-507. https://doi.org/10.1016/j.chemosphere.2015.11.094
Padoan, E., Rome, C., Ajmone Marsan, F., 2017. Bioaccessibility and size distribution of metals in road dust and roadside soils along a peri-urban transect. Sci. Total Environ. 601-602, 89-98. https://doi.org/10.1016/j.scitotenv.2017.05.180
Padoan E., Amato F., 2018. Vehicle Non-Exhaust Emissions: Impact on Air Quality, In: Non-Exhaust Emissions, An Urban Air Quality Problem for Public Health; Impact and Mitigation Measures (Eds. Amato F), pp 21-65. https://doi.org/10.1016/B978-0-12-811770-5.00002-9
Padoan, E., Romè, C., Mehta, N., Dino, G.A., De Luca, D.A., Ajmone-Marsan, F., 2020. Bioaccessibility of metals in soils surrounding two dismissed mining sites in Northern Italy. International Journal of Environmental Science and Technology https://doi.org/10.1007/s13762-020-02938-z
Pietrodangelo, A., Salzano, R., Rantica, E., Perrino, C. (2013). Characterisation of the local topsoil contribution to airborne particulate matter in the area of Rome (Italy). Source profiles. Atmospheric Environment 69, 1-14. https://doi.org/10.1016/j.atmosenv.2012.11.059
R Core Team, 2019. R: A language and environment for statistical computing. R Foundation for Statistical Computing, Vienna, Austria. URL.

Regione Piemonte, 2000. L.R. n. 42 del 7 aprile 2000 - Bonifica e ripristino ambientale dei siti inquinati, Bollettino Ufficiale della Regione Piemonte (in Italian).

Regione Piemonte, 2020. Geoportale Piemonte. http://www.geoportale.piemonte.it/geocatalogorp/?sezione=mappa (accessed 21 December 2020)

Sharratt, B., Auvermann, B., 2014. Dust pollution from agriculture. In: Van Alfen, N.K., editor. Encyclopedia of Agriculture and Food Systems. Volume 2. Cambridge, MA, Elsevier Academic Press. p. 487-504.

Soil Science Division Staff (2017) Soil survey manual. In: Ditzler C, Scheffe K, Monger HC (eds) USDA handbook 18. Government Printing Office, Washington, DC

Soleimanian E., Taghvaee, S., Mousavi A., Sowlat M.H., Hassanvand M.S., Yunesian M., Naddafi K., Sioutas C., 2019. Sources and Temporal Variations of Coarse Particulate Matter (PM) in Central Tehran, Iran. Atmosphere 2019, 10, 291. https://doi.org/10.3390/atmos10050291

Tatarko, J., Mucharski, M., Li, Ho., Li, Hu., 2020. PM2.5 and PM10 emissions by abrasion of agricultural soils, Soil and Tillage Research 200, 104601. https://doi.org/10.1016/j.still.2020.104601

Tonne, C., Halonen, J.I., Beevers, S.D., Dajnak, D., Gulliver, J., Kelly, F.J., et al., 2016. Long-term traffic air and noise pollution in relation to mortality and hospital readmission among myocardial infarction survivors. International Journal of Hygiene and Environmental Health 219, 72-78 https://doi.org/10.1016/j.ijheh.2015.09.003

U. S. Environmental Protection Agency, 1998. Emission Factor Documentation for AP-42, Unpaved Roads, Final Report. Online resource: https://www.epa.gov/sites/production/files/2020-10/documents/ap-42_13.2.2_background_report_unpaved_roads.pdf (accessed 10-01-2021)

Wu, F., Kong, S., Yan, Q., Wang, W., Liu, H., Wu, J., 2020. Sub-type source profiles of fine particles for fugitive dust and accumulative health risks of heavy metals: a case study in a fast-developing city of China. Environ. Sci. Pollut. Control Ser. 1-20. DOI: 10.1007/s11356-020-08136-1

3.4. ARTICLE IV: *"Assessing particulate matter (PM_{10}) emissions from outdoor runs in laying hen houses by integrating wind tunnel and lab-scale measurements"*

This article was the outcome of an abroad semester spent in Wageningen, working on PM emission assessment from outdoor runs in laying hen houses. The emissions deriving from poultry barns are well-known, but recently free range rearing systems with large outdoor runs are becoming increasingly popular throughout Europe. Therefore, this work aimed at making a first step towards gaining an understanding of the PM emission decrease achieved with free range rearing systems as opposed to conventional ones. The difficulty lied in the absence of a recognized methodology for assessing emissions from outdoor runs and linking it with hen activity. The scope of this work was to develop and test a new methodology developed for this purpose.

Biosystems Engineering, Volume 210, 2021, Pages 1-12, ISSN 1537-5110
Authors: Jacopo Maffia, André J.A. Aarnink, Johan P.M. Ploegaert, Elio Dinuccio, Paolo Balsari, Hilko H. Ellen

BIOSYSTEMS ENGINEERING 210 (2021) 1–12

ELSEVIER

Available online at www.sciencedirect.com

ScienceDirect

journal homepage: www.elsevier.com/locate/issn/15375110

Biosystems ENGINEERING

Research Paper

Assessing particulate matter (PM_{10}) emissions from outdoor runs in laying hen houses by integrating wind tunnel and lab-scale measurements

Jacopo Maffia [a,b,*], *André J.A. Aarnink* [b], *Johan P.M. Ploegaert* [b], *Elio Dinuccio* [a], *Paolo Balsari* [a], *Hilko H. Ellen* [b]

[a] Dipartimento di Scienze Agrarie, Forestali e Alimentari, Università di Torino, Largo Paolo Braccini 2, 10095, Grugliasco, Italy

[b] Wageningen University and Research, Livestock Research, P.O. Box 338, 6700 AH, Wageningen, the Netherlands

Abstract

Laying hen houses are a known source of fine particulate matter (PM_{10}), but no information is available on the contribution of outdoor runs to the overall emissions. This study aims to investigate some of the main factors driving PM emissions from outdoor runs. A wind tunnel device was built to assess the effect of hen density (HD, hens m^{-2}) on PM emissions from outdoor runs. Moreover, a laboratory trial, using a soil resuspension chamber, was conducted to describe the influence of soil moisture on the emissions. The gathered information was then used to estimate PM_{10} emissions over a 1-year period. PM emissions increased exponentially with increasing HD and decreased exponentially with increasing soil water content. The average PM_{10} emissions from hen activities at the study farm, estimated using meteorological data from year 2019, were of 8.9 mg hen^{-1} d^{-1}. This emission is much lower than those reported by previous studies for indoor hens rearing.

Nomenclature

Symbol	**Description**	**Unit**
A	Area enclosed by the tunnel	m^2
C	Particle concentration in the soil resuspension chamber	µg m^{-3}
cf	Correction factor for pressure deficit during ammonia flow testing	-
C_{in}	Pollutant concentration in air incoming to the tunnel	mg m^{-3}
$C_{N\text{-}NH4}$	Ammonium nitrogen content retrieved captured by impingers	mg L^{-1}
C_{out}	Pollutant concentration in tunnel output air	mg m^{-3}
E_d	Daily particulate matter emissions	mg m^{-2} d^{-1}
EP	Soil particulate matter emission potential	mg kg^{-1}
EP_d	Daily emission potential based on soil moisture conditions	mg kg^{-1}
EP_{WT}	Emission potential based wind tunnel trials soil moisture	mg kg^{-1}
ER	Emission rate	mg m^{-2} hr^{-1}
ER_{HD}	Emission rate calculated on the base of expected daily hen density	mg m^{-2} hr^{-1}

ET	Evapotranspiration	-
ET0	Daily potential evapotranspiration	mm
ETc	Daily actual evapotranspiration	mm
$ExpWS_{(0.2\ m)}$	Expected average yearly wind speed at 0.2 m from ground level	$m\ s^{-1}$
F1, F2, F3	Ammonia flow levels used to test the wind tunnel capture efficiency	-
FC	Field capacity	mm
H	Number of hours in which the hens are free to visit outdoor runs	-
HD	Hen density	hens m^{-2}
HNO_3	Nitric acid	-
HS	Hargreaves–Samani evapotranspiration estimation method	-
I_{NH3}	Amount of ammonia captured with the impinger method	mg
Kc	Correction coefficient to account for bare soil conditions	-
K_{HS}, K_T	Dimensionless coefficient in Hargreaves–Samani equation	-
ks	Stress coefficient	-
L	Amount of acid solution inside the impinger bottle	L
LW	Leaching water	mm
NH_3	Ammonia	-
NH_{3Mmass}	Molar mass of ammonia	g mol^{-1}
N_{hens}	Number of hens present inside the tunnel	-
N_{Mmass}	Molar mass of nitrogen	g mol^{-2}
PM	Particulate matter	-
PM_{10}	Particles with aerodynamic diameter of less than 10 µm	-
$PM_{2.5}$	Particles with aerodynamic diameter of less than 2.5 µm	-
PM_4	Particles with aerodynamic diameter of less than 4 µm	

Q	Airflow of soil resuspension chamber system	m^3 min^{-1}
R_a	Extraterrestrial radiation (as equivalent evaporated water depth)	mm d^{-1}
Rain	Daily rainfall	mm
S1, S2, S3	Sampling positions evaluated during the wind tunnel validation test	-
SRC	Soil resuspension chamber	-
T	Time of the experiment	s
t	Soil resuspension experiment time-span	min
T_a	Average daily temperature	°C
T_{max}	Maximum daily temperature	°C
T_{min}	Minimum daily temperature	°C
WC	Estimated daily average water content of the first 15 cm of soil	mm
WC_i	Soil water content at the start of each day	mm
$WS_{(10\ m)}$	Average yearly wind speed at 10 m from ground level	m s^{-2}
WS_{tunnel}	Wind speed inside the wind tunnel	m s^{-1}
WT	Wind tunnel	-
WT_{flow}	Flow of air passing through the tunnel	m^3 hr^{-1}
WT_{NH3}	Amount of ammonia captured by the wind tunnel system	mg
z_0	Roughness length of the outdoor run	-

1. Introduction

High environmental concentrations of particulate matter (PM) are regarded as a cause of concern for human health (Pope, 2007). Livestock activities are long known to play an important role in PM concentration raises both in indoor and outdoor environments (Cambra-López, Aarnink, Zhao, Calvet, & Torres, 2010; EEA, 2016). In fact, both the coarser (PM_{10}; particles with an aerodynamic diameter <10 µm) and finer ($PM_{2.5}$; particles with an aerodynamic diameter <2.5 µm) fractions of PM are held responsible for negative health effects in farmers and local residents surrounding livestock houses. Furthermore, high dust concentrations affect indoor air quality and health and welfare of animals (Borlée et al., 2017; Cambra-López et al., 2010). Several studies have addressed the issue of PM emissions from poultry houses, quantifying the emission fluxes (Hayes et al., 2006; Roumeliotis and Van Heyst, 2008; Yao et al., 2018) and proposing mitigation measures (Cambra-López et al., 2009; R. W. Melse et al., 2012; Winkel et al., 2016). Most of these studies focused on emissions coming from poultry houses, while very little information is available on the contribution of the outdoor runs on the overall emissions. Nonetheless, in Europe, free range rearing systems, which give poultry access to large outdoor runs, are becoming more common due to their positive effects on poultry and hens welfare and wellbeing (Coton et al., 2019; Moyle et al., 2014). In particular, according to EU regulation requirements (Commission Delegated Regulation (EU) 2017/2168), free range laying hens rearing is characterized by continuous daytime access to outdoor runs, with 4 m^2 hen^{-1} of open space. Due to the increasing development of these production systems, it is necessary to investigate the magnitude of emissions deriving from outdoor areas. Assessing emissions from area sources in open space environments presents some difficulties, especially in case the sources are not homogeneous (Dumortier et al., 2019). The main methodologies that have been used to address this kind of sources in similar applications, such as cattle feedlots, are micrometeorological techniques and wind tunnel methods (Misselbrook et al., 2005). Micrometeorological techniques such as the integrated flux method (Denmead, 1983) and dispersion models (Bonifacio et al., 2012; Flesch et al., 2004) have proven to be very effective in back calculating emission fluxes from open field emission sources. These systems, however, despite their large range of application, have the common disadvantage of being unsuited to estimate emissions from sources, such as the outdoor runs, which are in proximity of multiple other sources of the same pollutant (e.g. barn, manure storage facilities etc.), due to cross interference. Wind tunnels are enclosure systems which have been widely used to assess PM and gaseous emissions from soil or other ground level area sources (Dinuccio et al., 2012; Gao et al., 2020; Kabelitz et al., 2020) and allow to monitor the emissions, gathering data under standardized wind speed conditions. Aarnink, Hol, & Beurskens (2006) used a ventilated chamber technique to assess ammonia (NH_3) emissions from outdoor runs in laying hen houses, but did not address PM emissions. The main constraint regarding the use of a classical wind tunnel method to assess emissions from outdoor runs is linked with the hens behavior. In fact, hens often engage in dust bathing behavior, which was recognized as a form of personal hygiene and also as a social behavior which has beneficial effects on animal welfare (Abrahamsson et al., 1996; van Liere et al., 1990; Vestergaard et al., 1997). When hens dustbathe in outdoor runs soil, they can cause soil (re)suspension in the air leading to PM emissions. Therefore, in order for a wind tunnel to effectively assess outdoor runs PM emissions, it should allow to assess the emission deriving from dustbathing and other hen activities.

The main aim of this work is to develop a multi-step methodology to assess outdoor runs emissions of PM and identify the role of hens behavior and soil moisture as main drivers of the emission. A wind tunnel prototype was designed to allow the hens to enter it willingly and dustbathe inside of it, in order to assess the effect of hen density (HD, hens m^{-2}) on the emissions. Moreover, the emission potential of the outdoor run soil was assessed, using a Soil Resuspension Chamber (SRC) method to assess the effect of soil humidity on PM release. The gathered information, combined with daily meteorological data and evapotranspiration (ET) modelling, was utilized to assess PM emissions over a 1-year period.

The gathered results will allow to acquire a better understanding of poultry generated PM emissions by addressing some of the main factors driving PM formation from free range areas in poultry houses. Moreover, it will provide a new perspective on hens behavior, addressing its influence on PM emissions.

2. Materials and methods

2.1. Wind tunnel design

Wind tunnels used for PM and gaseous emission assessments have a wide variety of shapes, but they usually share some common elements. They are built in sturdy material, such as plastic or stainless steel, they have a main chamber, which has the purpose of enclosing the studied area source, and they are provided with input and output pipes. The wind speed inside the tunnel (WS_{tunnel}, m s^{-1}) is generated using a ventilator and normally set to a value that matches the average outdoor wind speed (Dinuccio et al., 2012). The pollutant concentrations (mg m^{-3}) are normally monitored through sampling ports placed on the inlet and outlet pipe. The emission rate (ER, mg m^{-2} hr^{-1}) is then calculated as in equation (1).

(1)

Where C_{out} (mg m^{-3}) is the outlet concentration, C_{in} is the pollutant concentration in the incoming air (mg m^{-3}), WT_{flow} is the total airflow passing through the tunnel (m^3 hr^{-1}), and A is the area enclosed inside the wind tunnel (m^2).

The wind tunnel design proposed for assessing emissions from outdoor runs in poultry follows the same concept as described above, but it was modified to allow the assessment of emissions caused by dustbathing hens. To do so the inlet pipe was removed and the front of the tunnel was left open in order to allow the hens to walk in. The main chamber of the tunnel was built using a solid metal framework and wrapping a transparent plastic foil around it. This solution was adopted to allow sunlight to enter the tunnel, since the hen's behavior is affected by light. The funnel structure connecting the main chamber to the pipe was constituted by an iron wire framework covered by the same plastic foil covering the tunnel. Moreover, a metal grid was placed in between the main chamber and the funnel structure to prevent the hens from entering the funnel structure or the pipe. A ventilator with a 35 cm diameter was used (VOSTERMANS, Multifan IP 55 KLF). The overall design of the wind tunnel is illustrated in Figure 1.

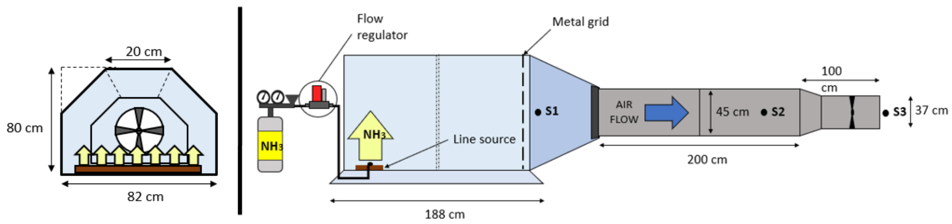


Figure 1. Wind tunnel design (lateral and frontal view) and experimental layout for the wind tunnel validation test; S1, S2 and S3 are the concentration measuring positions tested during the experiment.

The final design choices were forced by the necessity of allowing hens to dustbathe inside the wind tunnel. Similar designs were previously adopted by Balsari et al. (2006), for assessing ammonia emissions after manure spreading and by Roney et al. (2006) for fugitive dust emissions from soil. While similar in the overall design, the wind tunnel adopted by those two authors relied on different solutions for measuring the outlet concentration. To validate the wind tunnel design for emission assessment and to define a suitable concentration sampling strategy, a laboratory test was carried out using a tracer gas to test the tunnel capture efficiency. The wind tunnel flow and internal wind speed were also characterized under laboratory conditions.

2.2. Wind tunnel flow, internal wind speed and expected environmental wind speed

The flow of the tunnel was assessed by measuring, using a hotwire anemometer (Testo, 435), the wind speed (m s^{-1}) at the inlet of the ventilator pipe in 5 different positions and multiplying it by the section area of the pipe (116.2 cm^2).

The tunnel wind speed was set in order to match the external wind speed in the poultry farm area. The average external wind speed at 0.2 m meters from ground level was estimated using equation (2), using the mean wind speed data retrieved from KNMI Deelen weather station (KNMI, 2020).

(2)

Where $ExpWS_{(0.2\ m)}$ is the external mean wind speed (m s^{-1}) at 0.2 m height from ground level, $WS_{(10\ m)}$ is the mean wind speed (average of hourly wind speed data for year 2020; 4.1 m s^{-1}) at 10 m from ground level (measured at Deelen station), and z_0 is the roughness length (set to 0.01). The equation used is explained in detail by Stull (2012).

The wind speed inside the tunnel was assessed by using the same hotwire anemometer, attached on a tripod (at 0.2m from the ground) and placed in 12 different positions inside the tunnel. The fan rotational speed was regulated using an external regulator (Stienen, SPM-6).

2.3. *Assessment of Wind Tunnel capture efficiency*

The capture efficiency of the WT was tested through a tracer gas experiment, using pure ammonia as tracer (the setup is shown in Figure 1). Ammonia was released from a cylinder and emitted inside the tunnel from a 30 cm long line source, constituted by a dead-end Teflon tube (4 mm ø), which had holes (performed with a 3 mm ø drill) every 10 cm. The line source was placed perpendicularly to the WT flow at 20 cm from the WT entrance. The NH_3 flow was regulated using a mass flow controller (Bronkhorst, EL-FLOW®), which was set at three flow levels F1, F2 and F3. The mass flow regulator was calibrated for the regulation of atmospheric airflow, therefore the amount of NH_3 emitted with the three flow settings (F1, F2 and F3) utilized had to be assessed in a further laboratory experiment. A scheme of the experimental layout is shown in Figure 2. The assessment consisted in fluxing the ammonia into an acid bottle, capped with an impinger, which contained 0.5 molar HNO_3 acid. A flow meter was connected to the outlet of the impinger to check whether all ammonia was captured by the acid solution. A safety outlet tubing was placed at 2 m height to prevent exposure for the operator. The experiment was repeated twice for each flow level and the fluxing time was 4 minutes per sample. The collected acid samples were then analysed for the NH_4-N content ($C_{N\text{-}NH4}$, mg L^{-1}). During the experiment the formation of a negative pressure inside the acid bottle was observed, especially at low pressure from the ammonia tank. This caused a pressure deficit, affecting the flow passing through the system. This issue was due to the height difference among the system outlet (2 m height) and the impinger (at ground level). To solve this imbalance, a correction factor (cf) was calculated by measuring, using a flow meter, the incoming and the outcoming flow to the impinger. This later assessment was performed using water in place of the acid and pressured air instead of ammonia, for safety reasons.

The amount of ammonia captured with the impinger method (I_{NH3}, mg) at the three flow levels was then assessed according to equation (3).

(3)

Where *L* is the amount of acid solution in the impinger bottle (L), NH_{3Mmass} and N_{Mmass} are the molar masses of NH_3 and N (g/mol) respectively and *cf* was found to be 1.3 (± 0.21), 1.09 (± 0.18) and 1.04 (± 0.17) for F1, F2 and F3 respectively.

During the capture efficiency test, the ammonia concentration at the outlet and inlet of the tunnel (mg m^{-3} was measured using electrochemical sensors (Polytron® 8100 EC, Dräger). The outlet concentration was measured in three different sampling points (S1, S2 and S3, as shown in Figure 1). The concentration measurements lasted 15 minutes for each of the NH_3 flows and sampling point combinations, for a total of 135 minutes. The observed concentrations were then averaged over three minutes time intervals and used to calculate the total amount of ammonia captured by the WT system (WT_{NH3}, mg), according to equation (4).

(4)

Where C_{out} (mg m^{-3}) is the outlet concentration measured in S1, S2 and S3, C_{in} is the background ammonia concentration (mg m^{-3}), WT_{flow} is the wind tunnel flow (m^{-3} s^{-1}) and T is the time (s) of the experiment. It was assumed that the PM particles are transported by the air flow in a similar way as NH_3, as previously done by other authors (Maffia et al., 2020; Pattey and Qiu, 2012), and that the capture efficiency remains the same.

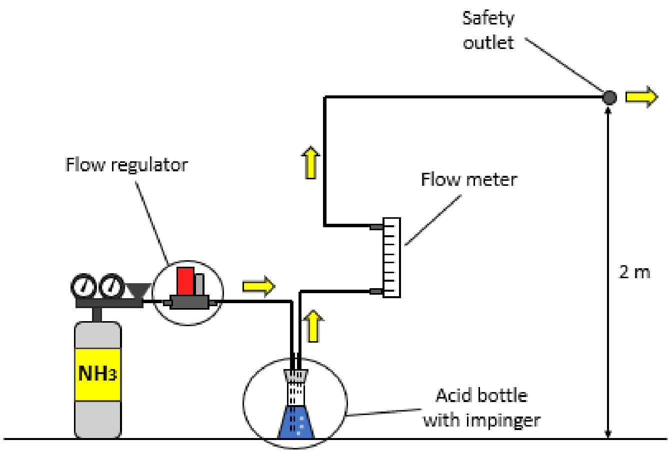


Figure 1. Ammonia flow assessment with impingers.

2.4. *Field measurement protocol for wind tunnel trials*

Field measurements were performed in a free range laying hen house sited in the Netherlands (52°05'58.6"N 5°34'38.2"E), in an area characterized by sandy soils. The farm is provided with a large outdoor area and the hens are allowed out from 10 am till sunset. The wind tunnel equipment was placed at 6 m from the barn, inside of the area where, according to Niekerk et al. (2016), most of the hens stand when outside. The measurements where performed, on sunny days, twice a week for 1 month and a short period was needed for the hens to adapt to the tunnel and start entering inside. Each measurement event lasted 3-4 hours and the hens where left free to enter the tunnel at will. Concentration measurements were performed using optical particle counters (DustTrak II, TSI) for PM_{10} measuring both at the inlet and the outlet (position S3) of the tunnel. The measuring frequency was of one measurement every 10 seconds. The two instruments were compared before the experiment, by measuring for 6 h in the same spot, and gave consistent results.

The first measurement was made with a 0.95 m^3 s^{-1} WT_{flow}, which generates a wind speed inside the tunnel more similar to the actual wind conditions in the region. Then, since it was observed that the hens preferred to enter the tunnel under slightly lower wind speed conditions, WT_{flow} was set at 0.73 m^3 s^{-1}. Being that this work aims mainly to assess PM emissions deriving from hens activity and that those emissions are predominantly caused by mechanical resuspension of soil, it was assumed that having a slightly lower wind speed as compared to the natural one is acceptable. The ERs were calculated with the same method used for the wind tunnel efficiency assessment, described in section 2.3, expressing the emissions as mg m^{-2} hr^{-1}.

A video camera (HERO 7 Silver, GoPro) was placed inside the tunnel to observe hens activity and count the number of hens inside the tunnel. This was necessary to relate the obtained ERs to the hen density (HD, hens $m^{-2}hr^{-1}$), which was calculated using equation (5).

(5)

Where N_{hens} is the number of hens present inside the tunnel and A is the enclosed area (m^2).

When the hen density was over 3.2 hens m^{-2} (5 hens inside the tunnel at the same time), the density was considered simply as >3.2 hens m^{-2}, since, due to fouling of the tunnel, it was impossible to distinguish the exact number of hens.

The ERs were then averaged over the HD, in order to obtain a dataset with an average ER for each HD category (0.6, 1.3, 1.9, 2.6, 3.2, >3.2 hens m^{-2}) for each measurement event. Each HD category correspond to an exact number of hens inside the tunnel (1, 2, 3, 4, 5 and >5 hens).

The soil moisture content on each measuring day was assessed by collecting a soil sample inside the tunnel, before and after the measurement, and assessing soil humidity with a gravimetric method by drying in a hoven at 105°C for 24 h.

2.5. *Soil resuspension chamber experiment to determine soil moisture effect*

A soil resuspension chamber (SRC), which has been fully described in a previous paper (Padoan et al., 2021), was used to resuspend the outdoor run soil. The chamber was composed of a rotating drum, with a 25 L capacity, and a rotation frequency of 26 revolutions per minute, powered by an electric engine with 0.75 kW of power and an electric potential of 220 V. During the trials, the drum was closed by a flange, on which were nested four flexible PVC tubes (0.4 m long with 8 mm diameter), provided with a series of small holes (diameter 0.3 mm), allowing clean air inside the rotating drum. The air was sucked from the drum through an aspiration pipe, which pulled the emitted dust towards a deposition chamber. A vane pump (PICCOLINO series VTE3, Thomas) was used to draw the air from the deposition chamber and induced an air flow of 30 L min^{-1} through the system. The re-suspended particulate matter was sampled, through a sampling port, using both an optical PM monitor (Grimm 11-D, Grimm Aerosol Technik), to assess particle quantity. A scheme of the system is provided in Figure 3.

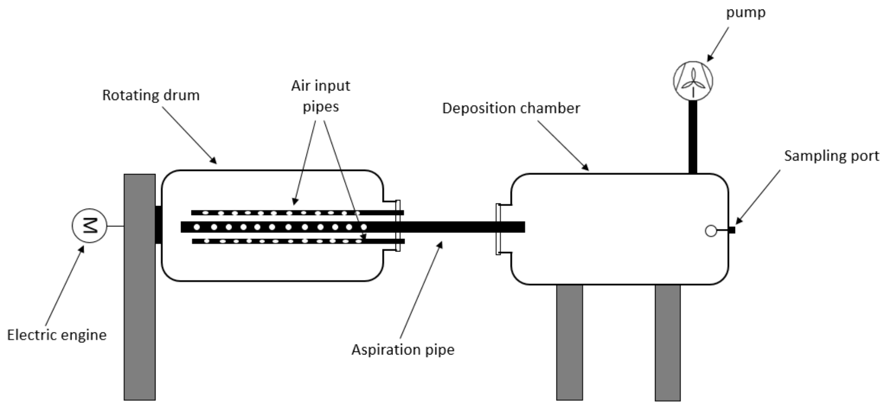


Figure 3. Scheme of Soil Resuspension Chamber (SRC) system.

Soil samples (three replicas per each soil humidity level) were resuspended by placing a soil aliquot inside the SRC rotating drum for 15 min. The experiments were conducted using soil samples of 5 g. The emission potential (EP, mg kg^{-1}) was defined at four different moisture contents (calculated as 0, 15, 30 and 40%, by weight, of the soil field capacity). Soil EP (mg kg^{-1}) was calculated according to equation (6).

(6)

Where C is the particle concentration (µg m^{-3}) measured with the Grimm PM monitor, Q is the SRC airflow (m^3 min^{-1}), calculated as the sum of the pump and the flow of the Grimm internal pump (1.2 L min^{-1}), S is the soil sample mass (kg), and t the considered time-span (min).

The soil samples used were sampled from the outdoor run, following the scheme described in chapter 2.6.

A detailed description of the sampling systems and intervals is provided in Padoan et al. (2021) Soil emission potentials were calculated in terms of PM_{10}, PM_4 and $PM_{2.5}$.

2.6. Soil humidity estimation and PM_{10} emission estimation over one year period

Soil humidity was assessed on the base of weather data, applying a water balance approach. The soil water balance was calculated by applying the Hargreaves–Samani equation (HS, Hargreaves & Samani, 1985) to calculate the potential evapotranspiration (ET0). The HS method, equation (6), was chosen since it is, among the simplified ET estimation methods, the one that finds better agreement with the Penman-Monteith recommended method from FAO 56 (Allen et al., 2005).

(6)

Where K_{HS} and K_T are dimensionless coefficients, T_a is the average daily temperature (°C), T_{max} is the maximum daily temperature (°C), T_{min} is the minimum daily temperature and R_a is the extra-terrestrial radiation, expressed in terms of equivalent evaporated water depth (mm d^{-1}).

T_a, T_{max}, T_{min} and R_a where derived from nearby KNMI weather stations located in Deelen (2019 dastaset).

The actual evapotranspiration ETc was then derived by multiplying ET0 by the coefficient Kc (which was set to 1.1 for bare soil conditions). The soil water content (WC, mm) was then calculated as in equation (7), considering a soil depth of 15 cm.

(7)

Where Rain is the daily rainfall (mm), k_s is the stress coefficient (derived as in Allen et al., 2005), LW is the leaching water (mm) and WC_i is the soil water content at the start of the day (WC the first day of the series was set to FC, since it was after a heavy rain event). LW was calculated as the difference among WC_i, net of the ET flux, and soil Field capacity.

The 15 cm depth of soil considered was selected observing the average depth of ridges caused by hens activity in the outdoor run area. Soil physical characteristics and field capacity were experimentally assessed. Fifteen subsamples of soil were taken by applying a X sampling scheme (Colombo & Miano, 2015). The topsoil subsamples were collected to a depth of 15 cm, which was considered the depth interested by hens dustbathing activities. Field capacity was determined for each soil according to the official method proposed by MiPAF (1997) and soil texture was defined according to the Soil Science Division Staff (2017) guidelines.

Finally, the daily emissions (Ed, mg m^{-2} d^{-1}) were calculated by integrating soil emission potential (as affected by humidity) and outdoor run emission level, according to equation (8).

(8)

Where, EP_d (mg kg^{-1}) is the emission potential related to the soil moisture conditions of the day, ER_{HD} is the emission rate (mg m^{-2} hr^{-1}) calculated on the base of the HD expected on the specific day, EP_{WT} (mg kg^{-1}) is the emission potential related to the moisture conditions occurred during the wind tunnel trials and H is the number of hours in which hens are allowed outside.

The HD expected on each specific day was estimated on basis of literature information. The few studies available on this topic reported very different data regarding the number of hens (% on total flock consistence), ranging from around 10 to 40% (Gebhardt-Henrich et al., 2014; Hegelund et al., 2005; Hirt and Zeltner, 2000). This large variability is due to several aspects that influence hens behavior and their usage of outdoor spaces. The main influencing parameters are the flock size (Gebhardt-Henrich et al., 2014), the environmental conditions (Pettersson et al., 2016) and the presence of sheltering structures in the outdoor run (Zeltner and Hirt, 2008, 2003). Moreover, most of free ranging hens (60-95%) tend to graze in the first 20 m from the outdoor run, causing complete destruction of the canopy in that area (Fürmetz et al., 2005). The farm in which this study was performed had a large flock size (24,000 hens) and an outdoor area of 9.6 ha. On basis of this information, it was considered that only 20% of laying hens are found outside at one moment and 80% of those are found in the over grazed area at short distance from the house. This area, presented in Figure 4, was measure to be equal to 6,263 m^2. Therefore, the emission from the overgrazed area of the outdoor run was assessed considering an average HD of 0.6 hens m^{-2}. The number of hours in which the hens were let outside (7 h in winter and 11 h in summer) was also considered when assessing the daily emission.

Figure 4. Photo of the barn and of the outdoor run area where the experiments were performed. The area contoured in yellow is the overgrazed area (6,263 m2), where most hens gather when outside, which differs from the areas around it for the absence of grass cover.

2.7. Statistical analysis

Statistical analyses were performed to test the fluxes of NH_3 observed during the wind tunnel efficiency estimation trial, with the 3 concentration sampling position (S1, S2, S3), as compared to the actual amount of ammonia released from the ammonia vessel determined with the impinger method (I_{NH3}). A two-way ANOVA procedure, performed using the R statistical software (R core team, 2019), followed by a Bonferroni post-hoc test, was used. Observed differences were considered significant for $P<0.05$. A linear regression was applied to investigate the relation between the natural logarithm of PM_{10} ER and HD and that between EP and soil water content.

3. Results

3.1. Wind tunnel flow and wind speed charts

The first flow rate tested was of 0.95 ± 0.01 m^{-3} s^{-1}, leading to a wind speed of 1.8 ± 0.03 m s^{-1}, which matches the expected wind speed of the area ($ExpWS_{(0.2\ m)}$ = 1.8 m s^{-1}). Since the hens were reluctant to enter the tunnel at this high wind speed, a lower flow rate of 0.73 ± 0.01 m^{-3} s^{-1} was used, leading to an average wind speed inside the tunnel of 1.5 ± 0.11 m s^{-1}. The average wind speed inside the tunnel was measured at 12 positions, at 0.20 m height, and resulted in higher values in the central row and slightly lower values in the side rows (Figure 5). At the tunnel inlet the wind speed was less evenly distributed than in the central and back portion of the tunnel.

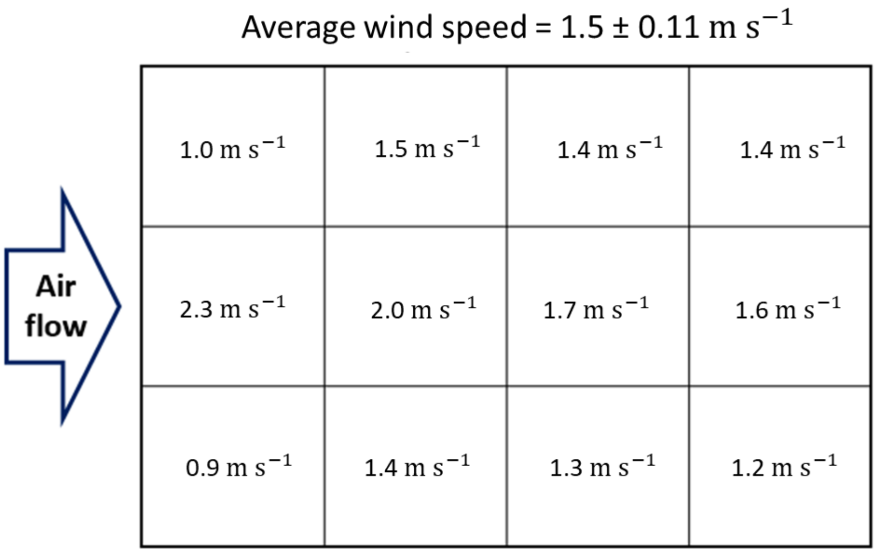


Figure 5. Average wind speed (m s^{-1}) inside the tunnel as measured at 12 positions (at the center of each square area highlighted with black lines in the graph) at 0.2 m height inside the wind tunnel chamber.

3.2. Assessment of WT capture efficiency

The ammonia concentration observed during the wind tunnel validation test, as measured in S1, S2 and S3, with F1, F2 and F3 NH_3 flows are summarized in Figure 6. The observed concentration varied slightly among the three sampling points. It was also highlighted that the standard deviation of the results obtained from measurements in S3 is lower than those of S1 and S2, allowing for a steadier signal.

Table 1 shows the results of the ANOVA comparing the amount of ammonia emitted from the cylinder (I_{NH3}), assessed with the impinger method, and the amount detected with the wind tunnel, WT_{NH3}, in the three sampling positions. The WT_{NH3} observed in S2 and S3 does not differ significantly from I_{NH3} with all the flux levels tested. The S1 assessment is instead significantly lower than expected at maximum NH_3 flow level.

3.3. *Results of wind tunnel assessments*

The average PM_{10} ER calculated as a result of the field trials was equal to 100.2 ± 26.4 mg m^{-2} hr^{-1}.

The linear regression analysis showed that HD had a significant ($P<0.05$) effect on the logarithm of PM_{10} emissions, showing a linear correlation (Figure 7). This means that the increase of HD causes an exponential increase of the ERs, defined by equation (9).

(9)

Where the intercept value (2.14) accounts for the effect of wind erosion and the slope value (0.94) accounts for the effect of HD. The linear model shows a good fit (R^2 = 0.76). In general, PM_{10} emissions ranged from 10.5 ± 2.1 mg m^{-2} hr^{-1} (with HD = 0 hens m^{-2}) to 170.7 ± 47.1 mg m^{-2} hr^{-1} (with HD = 3.2 hens m^{-2}).

Soil humidity was found to be equal to 0.84 ± 0.14 % (on mass) and remained almost constant throughout the experiment, due to the presence of the tunnel, which prevented the precipitations to reach the enclosed soil.

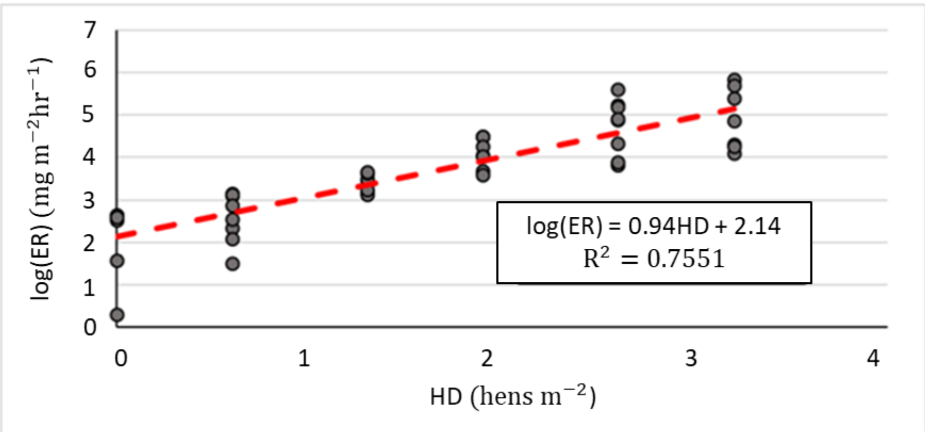


Figure 7. Linear regression showing the relation between the logarithmic function of PM10 ER (mg m^{-2} hr^{-1}) and HD. The equation and R2 are shown in the graph.

3.4. *Effect of soil moisture on PM emission potential*

The emission potentials curves for outdoor run soil, as well as the soil textural components, are presented in Figure 8. It can be observed that the EP decreases exponentially with the increase of soil water content. The regression curves were able to describe the EP trend with good fit and the overall results are similar to those presented by previous authors who adopted similar methods to study the effect of soil moisture on soils' EP (Carvacho et al., 2004; Funk et al., 2008; Madden et al., 2010, 2009). It was also observed that of the soil emitted as PM_{10} 56% and 17% is in the PM_4 and $PM_{2.5}$ ranges respectively. The soil texture in the study farm was Sandy (92% sand, 5% silt and 2% clay).

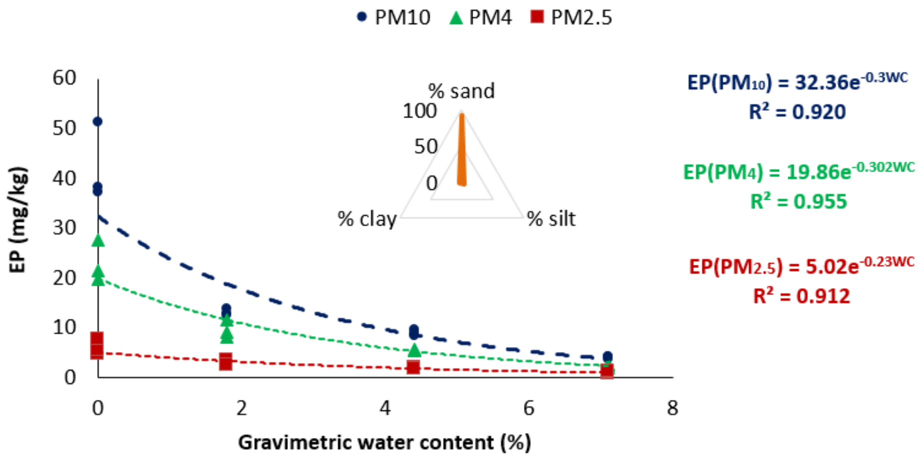


Figure 8. Soil EP curves as influenced by moisture content (% on mass)

3.5. *Estimated PM emissions from overgrazed area of outdoor runs*

The information gathered on the effect of HD and soil moisture on PM_{10} emissions, coupled with meteorological data, allowed to provide a first estimation of daily PM_{10} emissions from the overgrazed areas of outdoor runs. The estimated E_d were averaged on a monthly basis and are presented, together with monthly rainfall (mm) and ET fluxes (mm), in Figure 9. The average gravimetric soil water content was maximum in January (14%) and rapidly decreased in April, reaching its minimum value in July (7%), then it rose again from September. PM emissions were highly seasonal, with higher emissions occurring in the central months of the year. The total PM_{10} emissions over 2019, as estimated with the simplified procedure described in paragraph 2.6, were of 12.5 g m^{-2} yr^{-1} (this estimation is referred only to the overgrazed area of the outdoor run, 6,263 m^2).

Figure 9. Estimated PM_{10} emission flux, rainfall and evapotranspiration (ET) fluxes, on a monthly basis.

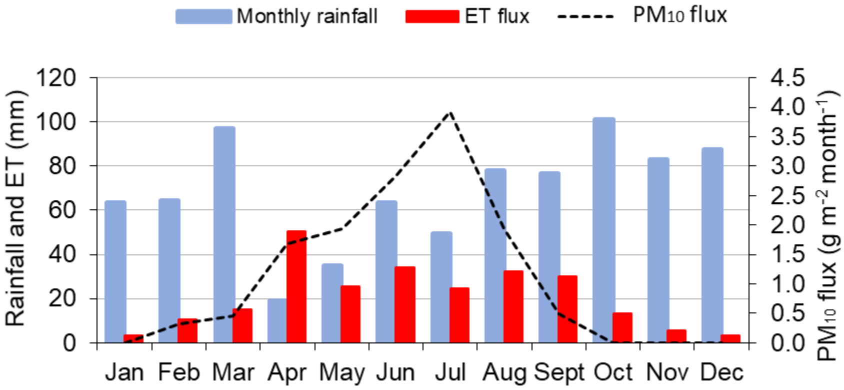


Figure 9. Estimated PM_{10} emission flux, rainfall and evapotranspiration (ET) fluxes, on a monthly basis.

4. Discussion

4.1. Wind tunnel validation: internal wind speed and capture efficiency

The results showed a slightly uneven distribution of the wind speed inside the tunnel. This is due to the friction effect of the tunnel walls and to the turbulence created by the funnel structure leading to the outlet pipe. The variations observed are consistent with those observed by Balsari et al. (2006, 2007), who adopted a similar wind tunnel design. The average wind speed inside the tunnel, of approx. 1.5 m s^{-1}, is only slightly lower than the expected WS at that height (1.8 m s^{-1}), calculated on basis of the 10 m average annual wind speed of the location where the measurements were done (approx. 4.1 m s^{-1}; KNMI, 2020). It was preferred to set a slightly lower wind speed since it was observed that the hens were more comfortable with this lower flow rate than with higher ones. Moreover, the hens normally gather around obstacles and trees, which act as repairs against the wind. In fact, the surface roughness effect, as well as the presence of natural obstacles, drastically reduce the wind speed at ground level (Stull, 2012).

Observing the results of the wind tunnel validation test (Table 1) it appears that both S2 and S3 sampling solutions are suitable for measurement and show a good agreement with the impinger method assessment. The WT_{NH3} observed in S2 and S3, in fact, did not differ significantly from I_{NH3} with all the flux levels tested. At S1, however, NH_3 concentrations were significantly lower than expected from I_{NH3} at maximum NH_3 flow level.

Table 1. Mean values and the 95% confidence intervals (CL) of ammonia emissions detected with the Impinger (INH3) and wind tunnel (S1, S2, S3) methodologies, at three different NH3 flow regulation levels (F1, F2 and F3). N = number of observations.

Sampling method	NH_3 regulation	N	NH_3 flux (mg)[a]		Lower CL	Upper CL
S3	F3	30	1672	a	1499	1844
I_{NH3}			1559	a	1386	1731
S2			1492	ab	1319	1664
S1			1271	b	1099	1444
S3	F2	30	1106	a	933	1279
I_{NH3}			993	a	820	1165
S2			926	ab	753	1098
S1			706	b	533	878
S3	F1	30	645	a	472	817
I_{NH3}			532	a	359	704
S2			465	ab	292	637
S1			244	b	72	417

Nonetheless, the S3 sampling point appears to perform more consistently and provide data with lower standard variation (as highlighted in Figure 6). Moreover, the S2 sampling solution is not suitable for PM measurements, since the DustTrak instrument is not designed for isokinetic sampling and, therefore, is not suited for measurement inside a pipe with a strong airflow. It was noticed that the average values derived from the measurements in S3 were slightly higher than the expected ones (I_{NH3}, as shown in Table 1), but the difference was not statistically significant. In conclusion, the S3 sampling point performed better than S1 and S2 and was identified as the best option to determine the emissions.

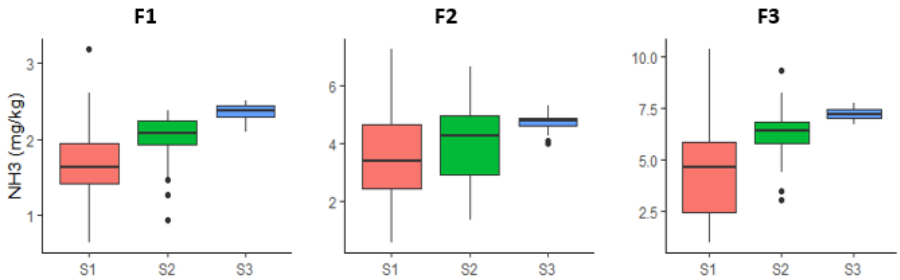


Figure 6. Boxplot graphs representing the distribution of the measured ammonia concentrations (mg kg-1) in sampling positions S1, S2 and S3 and in combination with the three ammonia flow levels tested (F1, F2 and F3).

4.2. *Influence of hen density and soil moisture on particulate matter emissions*

The first field assessments allowed to estimate PM_{10} emissions from hens outdoor activities, which were found to be equal to 100.2 ± 26.4 mg m^{-2} hr^{-1}. It has been also shown that dust emissions were affected by the density of hens in the outdoor runs. In fact, when HD increased PM_{10} emissions increased exponentially. The obtained ELs must be referred to the particular soil humidity conditions monitored during the experiment, which were extremely dry. Since, as highlighted by Funk et al. (2008), dry soil conditions lead to high PM emissions, the ERs calculated in these first field assessments should be considered as emission potentials, indicating the maximum amount of PM_{10} that can be derived from the outdoor runs in critical environmental conditions.

4.3. *Influence of soil moisture on particulate matter emission potential*

The exponential decrease of soil emission potential with increasing soil water content, observed during SRC experiment is in agreement with previous findings (Carvacho et al., 2004; Madden et al., 2010, 2009; Padoan et al., 2021). Moreover, previous researches showed that soil texture is a crucial factor in influencing EP and hydrological properties of soil. According to these findings, the very high sand % of the soil analyzed in this study, could have led to a lower maximum EP level in dry soil condition. Nonetheless, a more compact soil usually has more capacity to retain water and a higher field capacity, being less prone to the dryer conditions that are necessary for PM_{10} to be emitted.

4.4. *Estimation of PM emissions over a 1-year period*

The estimated PM_{10} emission fluxes were highly seasonal, with most of PM losses occurring during the central months of the year. This is attributable to the higher temperatures and lower precipitation, which promote dry soil condition and favor PM formation. The estimated emissions for overgrazed outdoor run areas were of 12.5 g m^{-2} yr^{-1}. These emissions, if divided for the total number of hens reared in the farm, are equal to 8.9 mg hen^{-1} d^{-1}. Shepherd et al. (2015) reported, in their assessment of PM_{10} emissions from indoor hen houses (aviary type rearing), emissions up to 100.3 mg hen^{-1} d^{-1}. Therefore, PM_{10} emitted from outdoor spaces appears to be lower than that deriving from the indoor areas of the farm. Nonetheless, since the hens are using only a small portion of the outdoor area, their activity causes significant degradation of soil, with formation of furrows where hens gather to dustbathe. The degradation on soil in these areas, and its bare conditions may also increase PM emissions due to wind erosion. Moreover, the concentration of many hens on little space can lead to other environmental issues linked with the concentration of nutrients on small areas (Menzi et al., 1998). Therefore, measures to favor the usage of a bigger portion of outdoor runs by hens should be implemented.

More studies should be performed to provide precise assessments of the usage of outdoor spaces by hens and identify the main factors influencing it, since current information is insufficient. The parametrization of average HD through the year is, in fact, the main drawback of the estimation technique used for assessing emissions. Moreover, since PM emissions from soil are also strongly affected by wind speed conditions (Avecilla et al., 2017), improvements should be made also in the parametrization of this factor, through further wind tunnel experiments.

5. Conclusions

A wind tunnel method to assess the effect of hen density on PM emission from outdoor runs in free range laying hens houses was successfully developed. The methodology allowed to measure PM emissions levels from hens activity and to study the influence of hens behavior on the emissions. HD influences PM_{10} emissions, causing them to increase exponentially when a higher number of animals are present per surface area unit ($ER = e^{(0.94\,HD+2.14)}$). The emission fluxes deriving from the outdoor runs under dry soil conditions, ranged from 10.5 ± 2.1 mg m^{-2} hr^{-1} (with HD = 0.0 hens m^{-2}) to 170.7 ± 47.1 mg m^{-2} hr^{-1} (with HD = 3.2 hens m^{-2}).

A laboratory experiment allowed to assess the effect of soil moisture on the emissions, deriving emission potential (EP, mg kg^{-1}) curves, showing an exponential decrease of EP with increasing soil moisture. This information allowed to scale the emission levels assessed with the wind tunnel, according to soil water content, estimated with a soil water balance procedure and averaged on a daily basis. An estimation of PM_{10} emission occurring from the overgrazed areas of outdoor runs was provided and resulted equal to 12.5 g m^{-2} yr^{-1}. These emissions, if divided for the total number of hens reared in the farm, are equal to 8.9 mg hen^{-1} d^{-1}, while EF for indoor hens farms in literature are up to 100.3 mg hen^{-1} d^{-1}. Therefore, PM_{10} emitted from outdoor spaces is less of a concern than in-house emissions. Nonetheless, by using only a small portion of the outdoor area, hens activity can cause significant degradation of soil, with formation of furrows where hens gather to dustbathe. Therefore, new solutions should be implemented to face this issue and to favor the spreading of hens on larger surfaces.

Acknowledgements

Funding: This study has been funded by the Ministry of Infrastructure and Water Management of the Netherlands.

References

Aarnink, A. J. A., Hol, A. M. G., & Beurskens, A. G. C. (2006). Ammonia emission and nutrient load in outdoor runs of laying hens. Netherlands Journal of Agricultural Science, 54(2), 223–234.

Abrahamsson, P., Tauson, R., & Appleby, M. C. (1996). Behaviour, health and integument of four hybrids of laying hens in modified and conventional cages. British Poultry Science, 37(3), 521–540. https://doi.org/10.1080/00071669608417882

Allen, R. G., Pereira, L. S., Smith, M., Raes, D., & Wright, J. L. (2005). FAO-56 Dual Crop Coefficient Method for Estimating Evaporation from Soil and Application Extensions. Journal of Irrigation and Drainage Engineering, 131(1), 2–13. https://doi.org/10.1061/(ASCE)0733-9437(2005)131:1(2)

Avecilla, F., Panebianco, J. E., & Buschiazzo, D. E. (2017). Meteorological conditions during dust (PM 10) emission from a tilled loam soil: Identifying variables and thresholds. Agricultural and Forest Meteorology, 244–245, 21–32. https://doi.org/10.1016/j.agrformet.2017.05.016

Bonifacio, H. F., Maghirang, R. G., Auvermann, B. W., Razote, E. B., Murphy, J. P., & Harner, J. P. (2012). Particulate matter emission rates from beef cattle feedlots in Kansas—Reverse dispersion modeling. Journal of the Air & Waste Management Association, 62(3), 350–361. https://doi.org/10.1080/10473289.2011.651557

Borlée, F., Yzermans, C. J., Aalders, B., Rooijackers, J., Krop, E., Maassen, C. B. M., … Smit, L. A. M. (2017). Air Pollution from Livestock Farms Is Associated with Airway Obstruction in Neighboring Residents. American Journal of Respiratory and Critical Care Medicine, 196(9), 1152–1161. https://doi.org/10.1164/rccm.201701-0021OC

Cambra-López, M., Winkel, A., Harn, J. van, Ogink, N. W. M., & Aarnink, A. J. A. (2009). Ionization for reducing particulate matter emissions from poultry houses. Transactions of the ASABE / American Society of Agricultural and Biological Engineers, 52(5), 1757–1771.

Cambra-López, María, Aarnink, A. J. A., Zhao, Y., Calvet, S., & Torres, A. G. (2010). Airborne particulate matter from livestock production systems: A review of an air pollution problem. Environmental Pollution (Barking, Essex: 1987), 158(1), 1–17. https://doi.org/10.1016/j.envpol.2009.07.011

Carvacho, O. F., Ashbaugh, L. L., Brown, M. S., & Flocchini, R. G. (2004). Measurement of PM2.5 emission potential from soil using the UC Davis resuspension test chamber. Geomorphology, 59(1–4), 75–80. https://doi.org/10.1016/j.geomorph.2003.09.007

Commission Delegated Regulation (EU) 2017/2168 of 20 September 2017 amending Regulation (EC) No 589/2008 as regards marketing standards for free range eggs where hens' access to open air runs is restricted. OJ L 306, 22.11.2017, p. 6–8. http://data.europa.eu/eli/reg_del/2017/2168/oj

Coton, J., Guinebretière, M., Guesdon, V., Chiron, G., Mindus, C., Laravoire, A., … Michel, V. (2019). Feather pecking in laying hens housed in free-range or furnished-cage systems on French farms. British Poultry Science, 60(6), 617–627. https://doi.org/10.1080/00071668.2019.1639137

Denmead, O. T. (1983). Micrometeorological methods for measuring gaseous losses of nitrogen in the field. In J. R. Freney & J. R. Simpson (Eds.), Gaseous Loss of Nitrogen from Plant-Soil Systems (pp. 133–157). Dordrecht: Springer Netherlands. https://doi.org/10.1007/978-94-017-1662-8_5

Dinuccio, E., Gioelli, F., Balsari, P., & Dorno, N. (2012). Ammonia losses from the storage and application of raw and chemo-mechanically separated slurry. Agriculture, Ecosystems & Environment, 153, 16–23. https://doi.org/10.1016/j.agee.2012.02.015

Dumortier, P., Aubinet, M., Lebeau, F., Naiken, A., & Heinesch, B. (2019). Point source emission estimation using eddy covariance: Validation using an artificial source experiment. Agricultural and Forest Meteorology, 266–267, 148–156. https://doi.org/10.1016/j.agrformet.2018.12.012

European Environment Agency. (2016). EMEP/EEA air pollutant emission inventory guidebook 2016: Technical guidance to prepare national emission inventories. Retrieved from http://bookshop.europa.eu/uri?target=EUB:NOTICE:THAL16020:EN

Flesch, T. K., Wilson, J. D., Harper, L. A., Crenna, B. P., & Sharpe, R. R. (2004). Deducing Ground-to-Air Emissions from Observed Trace Gas Concentrations: A Field Trial. Journal of Applied Meteorology, 43(3), 487–502. https://doi.org/10.1175/1520-0450(2004)043<0487:DGEFOT>2.0.CO;2

Funk, R., Reuter, H. I., Hoffmann, C., Engel, W., & Öttl, D. (2008). Effect of moisture on fine dust emission from tillage operations on agricultural soils. Earth Surface Processes and Landforms, 33(12), 1851–1863. https://doi.org/10.1002/esp.1737

Fürmetz, A., Keppler, C., Knierim, U., Deerberg, F., & Heß, J. (2005). Laying hens in a mobile housing system-Use and condition of the free-range area. Ende Der Nische, Beiträge Zur 8. Wissenschaftstagung Ökologischer Landbau, 313–314.

Gao, S., Wang, Y., Shan, M., Teng, Y., Hong, N., Sun, Y., … Zhang, H. (2020). Wind-tunnel and modelled PM10 emissions and dust concentrations from agriculture soils in Tianjin, northern China. Aeolian Research, 42, 100562. https://doi.org/10.1016/j.aeolia.2019.100562

Gebhardt-Henrich, S. G., Toscano, M. J., & Fröhlich, E. K. F. (2014). Use of outdoor ranges by laying hens in different sized flocks. Applied Animal Behaviour Science, 155, 74–81. https://doi.org/10.1016/j.applanim.2014.03.010

Hayes, E. T., Curran, T. P., & Dodd, V. A. (2006). Odour and ammonia emissions from intensive poultry units in Ireland. Bioresource Technology, 97(7), 933–939. https://doi.org/10.1016/j.biortech.2005.04.024

Hegelund, L., Sørensen, J. T., Kjaer, J. B., & Kristensen, I. S. (2005). Use of the range area in organic egg production systems: Effect of climatic factors, flock size, age and artificial cover. British Poultry Science, 46(1), 1–8. https://doi.org/10.1080/00071660400023813

Hirt, H., & Zeltner, E. (2000). Laying hen husbandry: Group size and use of henruns. In: Alffldi, T., Lockeretz, W., Niggli, U. (Eds.), Proceedings 13th International IFOAM Scientific Conference, 363.

Kabelitz, T., Ammon, C., Funk, R., Münch, S., Biniasch, O., Nübel, U., … Amon, T. (2020). Functional relationship of particulate matter (PM) emissions, animal species, and moisture content during manure application.

Environment International, 143, 105577. https://doi.org/10.1016/j.envint.2020.105577
Madden, N. M., Southard, R. J., & Mitchell, J. P. (2009). Soil Water Content and Soil Disaggregation by Disking Affects PM10 Emissions. Journal of Environmental Quality, 38(1), 36–43. https://doi.org/10.2134/jeq2008.0209
Madden, N. M., Southard, R. J., & Mitchell, J. P. (2010). Soil water and particle size distribution influence laboratory-generated PM10. Atmospheric Environment, 44(6), 745–752. https://doi.org/10.1016/j.atmosenv.2009.11.044
Maffia, J., Dinuccio, E., Amon, B., & Balsari, P. (2020). PM emissions from open field crop management: Emission factors, assessment methods and mitigation measures – A review. Atmospheric Environment, 226, 117381. https://doi.org/10.1016/j.atmosenv.2020.117381
Menzi, H., Katz, P. E., Fahrni, M., Neftel, A., & Frick, R. (1998). A simple empirical model based on regression analysis to estimate ammonia emissions after manure application. Atmospheric Environment, 32(3), 301–307. https://doi.org/10.1016/S1352-2310(97)00239-2
Misselbrook, T. H., Nicholson, F. A., Chambers, B. J., & Johnson, R. A. (2005). Measuring ammonia emissions from land applied manure: An intercomparison of commonly used samplers and techniques. Environmental Pollution, 135(3), 389–397. https://doi.org/10.1016/j.envpol.2004.11.012
Moyle, J. R., Arsi, K., Woo-Ming, A., Arambel, H., Fanatico, A., Blore, P. J., … Donoghue, A. M. (2014). Growth performance of fast-growing broilers reared under different types of production systems with outdoor access: Implications for organic and alternative production systems. Journal of Applied Poultry Research, 23(2), 212–220. https://doi.org/10.3382/japr.2013-00882
Niekerk, T. G. C. M. van, Leenstra, F. R., Reuvekamp, B. F. J., Buisonjé, F. E. de, Aarnink, A. J. A., Ellen, H. H., & Koerkamp, P. W. G. G. (2016). Inventarisatie van de effecten van uitloop pluimveehouderij op bodem-, water- en Luchtkwaliteit. https://doi.org/10.18174/385390
Padoan, E., Maffia, J., Balsari, P., Ajmone-Marsan, F., & Dinuccio, E. (2021). Soil PM10 emission potential under specific mechanical stress and particles characteristics. Science of The Total Environment, 779, 146468. https://doi.org/10.1016/j.scitotenv.2021.146468
Pattey, E., & Qiu, G. (2012). Trends in primary particulate matter emissions from Canadian agriculture. Journal of the Air & Waste Management Association, 62(7), 737–747. https://doi.org/10.1080/10962247.2012.672058
Pettersson, I. C., Freire, R., & Nicol, C. J. (2016). Factors affecting ranging behaviour in commercial free-range hens. World's Poultry Science Journal, 72(1), 137–150. https://doi.org/10.1017/S0043933915002664
Pope, C. A. (2007). Mortality Effects of Longer Term Exposures to Fine Particulate Air Pollution: Review of Recent Epidemiological Evidence.

Inhalation Toxicology, 19(sup1), 33–38. https://doi.org/10.1080/08958370701492961

R. W. Melse, P. Hofschreuder, & N. W. M. Ogink. (2012). Removal of Particulate Matter (PM10) by Air Scrubbers at Livestock Facilities: Results of an On-Farm Monitoring Program. Transactions of the ASABE, 55(2), 689–698. https://doi.org/10.13031/2013.41378

Roumeliotis, T. S., & Van Heyst, B. J. (2008). Summary of Ammonia and Particulate Matter Emission Factors for Poultry Operations. Journal of Applied Poultry Research, 17(2), 305–314. https://doi.org/10.3382/japr.2007-00073

Shepherd, T. A., Zhao, Y., Li, H., Stinn, J. P., Hayes, M. D., & Xin, H. (2015). Environmental assessment of three egg production systems—Part II. Ammonia, greenhouse gas, and particulate matter emissions. Poultry science, 94(3), 534-543.

van Liere, D. W., Kooijman, J., & Wiepkema, P. R. (1990). Dustbathing behaviour of laying hens as related to quality of dustbathing material. Applied Animal Behaviour Science, 26(1), 127–141. https://doi.org/10.1016/0168-1591(90)90093-S

Vestergaard, K. S., Skadhauge, E., & Lawson, L. G. (1997). The Stress of Not Being Able to Perform Dustbathing in Laying Hens. Physiology & Behavior, 62(2), 413–419. https://doi.org/10.1016/S0031-9384(97)00041-3

Winkel, A., van Riel, J. W., van Emous, R. A., Aarnink, A. J. A., Groot Koerkamp, P. W. G., & Ogink, N. W. M. (2016). Abatement of particulate matter emission from experimental aviary housings for laying hens by spraying rapeseed oil. Poultry Science, 95(12), 2836–2848. https://doi.org/10.3382/ps/pew261

Yao, Q., Yang, Z., Li, H., Buser, M. D., Wanjura, J. D., Downey, P. M., … Hapeman, C. J. (2018). Assessment of particulate matter and ammonia emission concentrations and respective plume profiles from a commercial poultry house. Environmental Pollution (Barking, Essex: 1987), 238, 10–16. https://doi.org/10.1016/j.envpol.2018.02.039

Zeltner, E., & Hirt, H. (2003). Effect of artificial structuring on the use of laying hen runs in a free-range system. British Poultry Science, 44(4), 533–537. https://doi.org/10.1080/00071660310001616264

Zeltner, Esther, & Hirt, H. (2008). Factors involved in the improvement of the use of hen runs. Applied Animal Behaviour Science, 114(3), 395–408. https://doi.org/10.1016/j.applanim.2008.04.007

3.5. ARTICLE V: *"Particulate Matter Emissions from Soil Preparation Activities as Influenced by Minimum and Strip Tillage Practices"*

The review of the literature performed with Article I (Paragraph 3.1) highlighted the lack of a complete overview of PM emission from land preparation activities, tilling to sowing. Moreover, all available articles were performed in Central Europe, North America or China, while the environmental conditions or Northern Italy are very different, especially in terms of wind speed (Fratianni et al., 2007). Moreover, although minimum tillage had been proposed as a mitigation measure for reducing land preparation emissions, the available information was limited, since there was no study that provide emission flux estimations for each single implement from the same trial, and no information was available on strip tillage. This conference paper presents a first trial, performed adopting the same measurement system used in Article II (Paragraph 3.2), aiming to provide emission factors for land preparation in Northern Italy and to assess the potential of strip tillage and minimum tillage as mitigation measures.

Proceedings of the AGENG 2021 Conference (Submitted)
Authors: Jacopo Maffia, Massimo Blandino, Luca Capo, Elio Padoan, Luca Rollé, Paolo Balsari, Elio Dinuccio

Abstract

Land preparation activities are one of the main contributors to particulate matter (PM) emissions from agriculture. Nonetheless, particulate matter emissions from tillage operations are poorly studied, especially in southern Europe, where few assessments have been made. Moreover, it is important to describe the influence of tilling implements and soil preparation practices on the emissions of fine PM (PM_{10}) from fields. A research project, titled "Evaluation of particulate matter emissions from cropping and farm transformation activities in Maize production systems", has been funded by CRT foundation (grant numbers: 2018.2273) to tackle the issue of PM emissions from Maize cropping systems, including land preparation. This study, in particular, presents the results of field trials with assessment of three land preparation scenarios for maize: traditional tillage with ploughing at 30 cm followed by rotary harrow (TT), minimum tillage with disk harrowing (MT) and strip tillage, with soil tilled in strips of 25 cm wide at a working depth of 15 cm (ST). Emissions of PM10 resulted being of 149, 30 and 114 mg m^{-2} respectively for TT, MT and ST. These results give a first insight into reduced soil disturbance practices as mitigation measures for tillage induced direct PM_{10} emissions and highlight MT as the less emitting tillage practice.

1. Introduction

Particulate matter (PM) emissions are a growing cause of concern due to their impact on human health and environment. The agricultural sector is responsible of the 17% of the total anthropogenic emission of sub 10 µm PM particles (PM_{10}; EEA, 2016). The main sources of fine PM in agriculture are livestock rearing facilities and field operations, such as tillage, harvesting, manure spreading (Kabelitz et al., 2020; Maffia et al., 2020b). Agricultural PM has been long seen as a risk for field operators and farmers, but it is now also considered for its long range effect on regional air quality (Chen et al., 2017). Many studies have addressed PM emissions from livestock houses (Cambra-Lopez et al., 2010; Winkel et al., 2016), while fewer information is available on open field activities. Moreover, most studies assessing emissions from tillage or harvesting just focus on few of the operations commonly performed by farmers, while others are neglected (Maffia et al., 2020b). Since the amount of PM_{10} emitted, as well as the particles characteristics, varies greatly according to the kind of operation, the environmental conditions (soil humidity and wind speed) and the mechanical implement used (Avecilla et al., 2017; Cassel et al., 2003), it is important to define emission factors (EF) for all different environments and specific activities. After having assessed valid and up to date EF, it is necessary to consider the availability of mitigation measures to reduce the emissions and improve farmer health and general air quality. Minimum and strip tillage are tillage practices that allow seedbed preparation with reduced soil disturbance. These practices have been developed to reduce soil erosion by wind and runoff events and are especially diffused in areas where erosion events are frequent and severe, such as North and South America. Strip tilling, in particular, acts only on the rows of soil where sowing will take place, leaving the inter-rows untouched. This approach allows to grant higher soil coverage (by stalks and leftovers) even during the first growing period of crops, increasing soil protection and reducing seedbed preparation costs and time (Laufer et al., 2016). Few studies addressed of this practices on direct PM emissions during tillage (Baker et al., 2005; Coates, 1996), and none have investigated the emission deriving from sowing itself.

The aim of this study is to assess PM_{10} emissions from land preparation activities in Northern Italy, including sowing, providing new EF figures and evaluating the effect of three different land preparation approaches, Conventional (TT), Minimum (MT) and Strip Tillage (ST), on the emissions.

2. Materials and Methods

2.1. Experimental layout

The trial was performed in an experimental farm situated in Carmagnola, North-west of Italy (44° 53' 10" N 7° 40' 59" E). The experimental field (Figure 1) was divided in three main plots that were subjected to the three different land preparation strategies (TT, MT and ST). The same tillage strategy was applied in each main plot in the previous 5 growing seasons, in which the field was cultivated continuously with maize for grain. The maize residues from the previous growing season have been totally maintained on the soil surface before the tillage operation. Each plot was divided in six subplots, each one corresponding to one sowing passage (4.5x40 m). The seedbed preparation passages performed for TT, MT and ST thesis are summarized in Table 1. TT consisted of a traditional ploughing (30 cm depth), followed by two rotary harrowing passages before maize sowing. MT consisted of a single two rows disk harrower passage followed by sowing. ST consisted of a strip tillage passage followed by sowing. In all three scenarios, two fertilizer passages were made with potassium chloride, KCl (60%, Pastorelli SPA) and triple superphosphate, Ca(H2PO4) (46% of P_2O_5; RaFertil Group). Four different tractors were used during the trial, depending on the implement (Table 1). All field operations were performed in one day, in order to reduce environmental variability as much as possible.

Measurements of PM_{10} were carried out at each tractor passage using an optical PM monitor (TSI, DustTrack™ II model 8530), with a sampling frequency of 1 Hz. The PM monitor was placed alongside the tilled area at 5 m distance (Figure 1). The instrument was moved near to the next passage line after each pass. The instrument was always kept downwind (skewed at most by a 30° angle) of the passage line. Background PM_{10} concentration was assessed before and after trials. A weather station was mounted at the corner of the field, far from obstacles, and provided wind measurements by means of two 2D sonic anemometers (GILL, UltraSonic), placed at 2 and 4 m height.

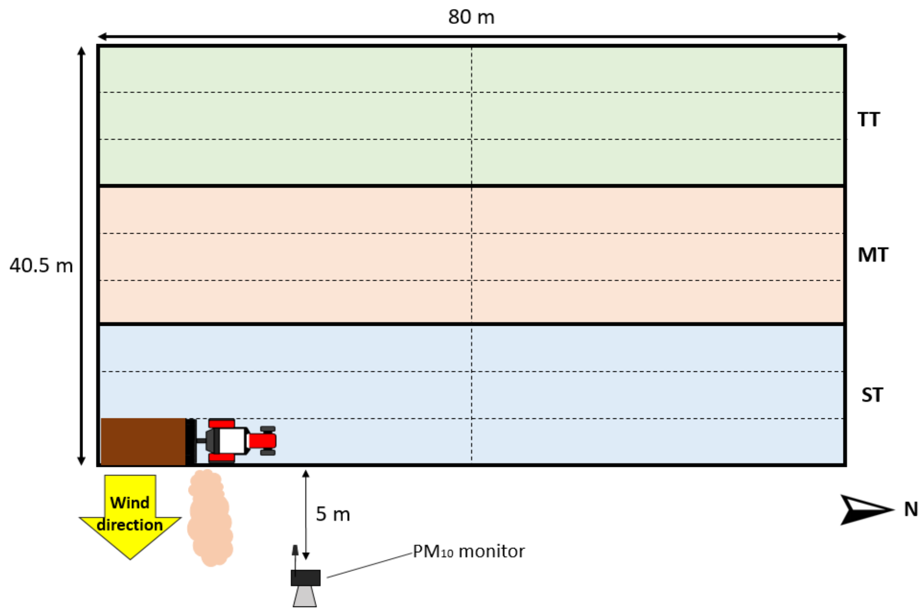


Figure 1. Experimental layout (full lines identify main plots; dashed lines identify sub-plots).

Table 1. Seedbed preparation activities in traditional tillage (TT), minimum tillage (MT) and strip tillage (ST), implements used, working widths and advancement speeds.

	Operation	Implement	Tractor	Working width (m)	Speed (km h^{-1})
TT	Ploughing	Vittone (two ploughshares)	FIAT 90-90 DT	1.1	2.5
	Rotary harrowing (1st pass)	Breviglieri, MEKFARMER 100	FIAT 70-66	2.5	4.5
	Rotary harrowing (2nd pass)	Breviglieri, MEKFARMER 100	FIAT 70-66	2.5	4.5
	KCl spreading	KUHN, AERO 1120	FIAT 55-66	12	2.5
	P_2O_5 spreading	KUHN, AERO 1120	FIAT 55-66	12	2.5
	Sowing	ALPEGO, Fertidrill ASF	CLAAS 550 ARION	4.5	7.5
MT	Disk harrowing	Harrower (two disk rows)	FIAT 90-90 DT	2.5	2.5
	KCl spreading	KUHN, AERO 1120	FIAT 55-66	12	2.5
	P_2O_5 spreading	KUHN, AERO 1120	FIAT 55-66	12	2.5
	Sowing	ALPEGO, Fertidrill ASF	CLAAS 550 ARION	4.5	7.5
ST	Strip tillage	MOM, Strip Hawk Easy	CLAAS 550 ARION	3	7.5
	KCl spreading	KUHN, AERO 1120	FIAT 55-66	12	2.5
	P_2O_5 spreading	KUHN, AERO 1120	FIAT 55-66	12	2.5
	Sowing	ALPEGO, Fertidrill ASF	CLAAS 550 ARION	4.5	7.5

2.2. Elaboration of wind data

Start and end times of each tractor passage were recorded during field measurements. The passage time intervals were used to clip the output file of the anemometer, to obtain the average wind speed and direction at the time of each PM concentration peaks. The atmospheric stability class was estimated for each passage, according to the Pasquill-Gifford class method (Pasquill, 1961).

2.3. Soil physico-chemical analysis

Three soil samples were collected in each plot (TT, MT and ST), adopting an "X" sampling strategy and quartering subsamples in field. Soil samples were collected at 0–15 cm depth both before the start of the trial and before sowing, to assess the effect of the tillage treatment on soil humidity.

The samples were air-dried and sieved to 2 mm before physico-chemical analyses. We determined soil texture, pH, total carbon and nitrogen content and carbonates. The fraction of particles <10 μm was estimated by repeated sedimentation and decanting. Field capacity was also determined. The methods used for the analysis are described in Padoan et al. (2021).

2.4. Emission factor estimation

EF were assessed using a backward lagrangian model (WindTrax). The input parameters to the model were: wind speed, wind direction, atmospheric stability class, air temperature, average PM_{10} concentration (at 5 m from the operation line) and background PM_{10} concentration. The model was set to simulate the dispersion of 1 million particles and the surface roughness was set to the reference value (1 cm), parameterized for "bare soil" conditions. The emission source was modelled as an area source having the same dimension of the plot tilled at each passage (as in Maffia et al., 2020a).

A simulation was performed per each tractor passage. The output of the model is an Emission Rate (ER, mg m^{-2} s^{-1}) referred to the modelled area source. The ER can be later converted in EF (mg m^{-2}) according to the following formula:

$$EF = ER \times tpass \quad (1)$$

where tpass is the elapsed time (s) between the start and the end of each passage.

2.5. Statistical analysis

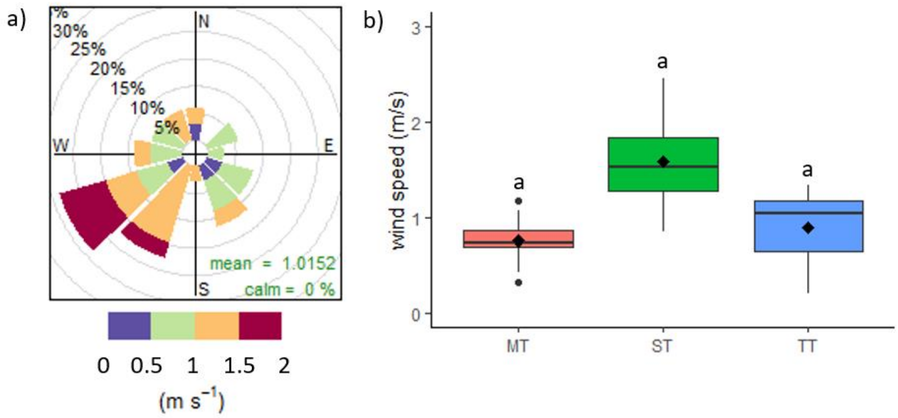
An analysis of variance (ANOVA), followed by a Tukey post hoc test was performed to assess differences in EF among operations and in total emissions among thesis (TT, MT, ST). Wind speed population in the three thesis was also tested. A log transformation was applied to EF data, in order to meet the normality assumption of ANOVA. Normality and homoscedasticity were then confirmed through a Shapiro Wilk test and a Levene test, respectively. All analysis were performed using R (R Core Team, 2019).

3. Results and Discussion

3.1. Wind conditions during field trial

The overall wind conditions observed during the trial are presented in Figure 2. Wind speed averaged at around 1 m s-1 and remained among 0.5 and 2.5 m s^{-1} for the length of the trial. These relatively low wind speeds are representative of the area where the experiment took place. Moreover, the post hoc test performed to assess wind speed differences among treatment confirmed no evident significant difference, although during ST tests there was a slight numerical increase in wind speed. Wind direction was constant (WSW, WS) for most of the trial. Nonetheless, it was necessary to move the DustTrakTM monitor to the opposite side of the passage line during few TT and MT passages, since wind was blowing from ESE.

Figure 2. a) WindRose graph highlighting wind speed and direction frequencies during the trial (obtained with OpenAir R package; Carslaw et al., 2012); b) Boxplot graph with post hoc test results (means with the same letter are not statistically different for P<0.05; means are represented by rhombuses).



3.2. Soil characteristics and humidity

Soil characteristics are presented in Table 2. The soil where the trial took place is a silt loam textured soil, with a low organic carbon content. No relevant difference, in terms of soil characteristic was highlighted among plots. Soil humidity at the beginning of the trial was of 18.8±0.6 % on mass in all plots, while humidity before sowing changed slightly, due to the operations performed, and reached 13.9±0.4, 17.6±0.5 and 14.8±0.4 % in TT, MT and ST, respectively. The difference between TT and ST and the MT plot, which was more wet, is probably due, for TT, to the aeration caused by ploughing, which could have caused the soil to dry up faster, while for ST, the type of implement used could have induce less mixing of the upper soil layer (dryer) with the lower one (more wet).

Table 2. Soil characteristics in the three different land preparation approaches, Conventional (TT), Minimum (MT) and Strip Tillage (ST).

		TT	MT	ST
Sand	%	34.1	34.7	34.0
Silt	%	59.8	58.8	60.0
Clay	%	6.1	6.5	6.0
pH		8.2	8.1	8.2
Total limestone	%	2.8	2.4	2.8
organic C	%	0.9	1.6	0.9
CEC	meq/100g	7.9	8.5	8.0

3.3. Particulate matter emissions as affected by tilling practice

Table 3 shows the results of a post hoc test comparing the PM_{10} EF derived for all operations performed. It was observed that the main tilling operations, ploughing and strip tilling caused the highest emissions, while no significant difference was observed among the other operations. A slight trend of emission increase, although not significant, was observed among the first and second rotary harrowing passage. This result is consistent with the observations of Madden et al. (2009), who highlighted that progressive disaggregation of soil aggregates leads to higher emissions. In general, the observed EF are consistent to those found in literature (summarized in Maffia et al., 2020). An interesting result is the assessment of the EF for fertilizers spreading passages, which have been almost completely neglected in previous literature. PM derived from fertilizer spreading operations could, in fact, have different composition than the one from tillage (composed mainly of soil particles) and should therefore be investigated in further studies for its chemical composition and size fraction range.

Emissions from sowing are reported in Table 4. No significant differences among the three theses were observed. Due to the slightly dryer soil conditions in TT and ST we may expect higher emissions than in MT. However, this effect was not observed. The slightly higher EF value for ST could be due to the passage of tractor wheels on untilled inter rows, which have a particularly dry upper layer (first 2 cm). In general, sowing is, after ploughing, the most emitting operation in terms of PM_{10}. It is therefore important to consider it when assessing seedbed preparation impact, and to propose sowing implements with reduced emission potential. Moreover, previous studies have observed that sowing produces not only resuspension of soil particles, but also of seed and seed coating fragments, with presence of pesticides, which have a potentially higher impact on farmers' and animal (bees) health and environment.

The overall emissions occurred with TT, MT and ST, and the post hoc comparison among them, are presented in Figure 3. A significant difference was highlighted between MT and the other two thesis, with MT emitting 79 and 73 % less PM_{10} than TT and ST, respectively. These results are consistent with a previous study

(Coates, 1996), assessing the effect of minimum tillage on total solid particles emitted, observing a 45% reduction as compared to traditional tillage. Baker et al. (2005), instead, observed a reduction of up to two thirds of respirable dust concentration during land preparation with conservation tillage practices as opposed to conventional ones. In this study, the reduction of PM_{10} emissions observed with ST was slighter and did not induce a significant difference in statistical terms. Moreover, it was highlighted that most of PM_{10} emissions are caused by principal heavy-duty operations, such as ploughing and strip tillage, while secondary passages, such as disk or rotary harrowing, are less important. Therefore, as a general rule, to reduce PM_{10} emissions from seedbed preparation, it would be preferable to avoid principal operation which involve a deeper tilling and profound soil turning and to rely on superficial interventions. In fact, even if, as Coates et al. (1996) suggested, reducing the number of passages is the one of the most effective ways of reducing PM emissions, it is also true that the choice of the implement and the operation type play a vital role in determining dust production. Providing more detailed emission figures is therefore important to inform adequate soil management choices, without forgetting that PM emissions from soils are affected by soil and weather conditions and that the implement choices should be tuned to accommodate for the specific characteristics of the area. Moreover, while addressing PM emissions is should never be forgotten that soil management should first aim to soil preservation and overall agronomic performance and that these should remain the main drivers of management choices made.

Table 3. Post hoc test results highlighting differences among emission factor (EF) of soil tilling operations performed (means followed by same letter are not statistically different for $\alpha<0.05$).

Operation	**EF ($mg\ m^{-2}$)**		**Lower CL***	**Upper CL***	**N****	**P**
Ploughing	76.1	b	23.7	244.2	12	<0.001
Strip tilling	68.0	b	33.3	138.9	5	
Disk harrowing	2.2	a	1.2	4.1	5	
P_2O_5 spreading	2.2	a	0.9	5.3	5	
2nd rotary harrowing	1.3	a	0.6	2.9	5	
1st rotary harrowing	0.7	a	0.3	1.7	5	
KCl spreading	0.5	a	0.2	1.2	5	

*LowerCL and UpperCL are the lower and upper 95% confidence limits.
**N is the number of tractor passages.

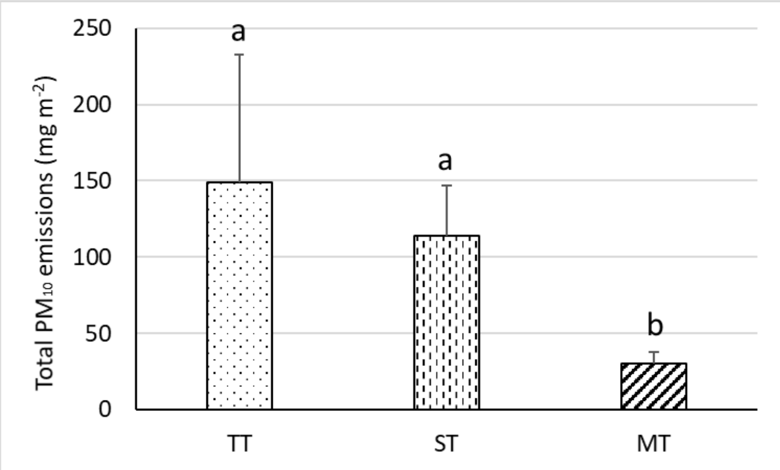
Table 4. Post hoc test results highlighting differences among emission factor (EF) of soil tilling operations performed (means followed by same letter are not statistically different for α<0.05).

	Sowing EF (mg m^{-2})		Lower CL*	Upper CL*	N	P
TT	21.5	a	10.8	42.9		
MT	23.3	a	12.9	42.5	3	0.6
ST	28.2	a	14.1	56.2		

*LowerCL and UpperCL are the lower and upper 95% confidence limits.

**N is the number of tractor passages.

Figure 2. Post hoc test results highlighting differences among total PM_{10} emissions derived from each tillage practice (means with the same letter are not statistically different for α<0.05).



4. Conclusions

This preliminary study allowed to provide new EF for tillage in Northern Italy, for which no EF were available. Moreover, the effect of different soil tillage approaches on PM_{10} emissions was observed, highlighting a substantial emission reduction, of 79% when applying MT as compared to TT. ST, instead, did not provide a significant emission reduction benefit. It was observed that the operations which are the main drivers of PM_{10} emissions, are principal tillage operations, such as ploughing, strip tillage, and sowing. To improve the knowledge of the processes leading to PM emission from agricultural operations, future studies may address also finer size fractions of PM ($PM_{2.5}$ and PM_1) and the influence of soil moisture on the EF, and may characterize the profile of emitted particulate in order to provide more accurate emission figures.

Acknowledgements

This work has been realized within the projects “Valutazione delle emissioni di materiale particolato dalle operazioni colturali e di trasformazione aziendale del mais” (Evaluation of PM emission from cropping operation and first transformation of Maize), funded by Cassa di Risparmio di Torino (CRT foundation) [grant numbers 2018.2273].

References

Avecilla, F., Panebianco, J.E., Buschiazzo, D.E., 2017. Meteorological conditions during dust (PM 10) emission from a tilled loam soil: Identifying variables and thresholds. Agricultural and Forest Meteorology 244–245, 21–32. https://doi.org/10.1016/j.agrformet.2017.05.016

Baker, J.B., Southard, R.J., Mitchell, J.P., 2005. Agricultural Dust Production in Standard and Conservation Tillage Systems in the San Joaquin Valley. Journal of Environment Quality 34, 1260. https://doi.org/10.2134/jeq2003.0348

Cambra-López, M., Aarnink, A.J.A., Zhao, Y., Calvet, S., Torres, A.G., 2010. Airborne particulate matter from livestock production systems: a review of an air pollution problem. Environ Pollut 158, 1–17. https://doi.org/10.1016/j.envpol.2009.07.011

Carslaw, D. C. and K. Ropkins, 2012. openair --- an R package for air quality data analysis. Environmental Modelling & Software. Volume 27-28, 52-61.

Cassel, T., Trzepla-Nabaglo, K., Flocchini, R., 2003. PM10 Emission Factors for Harvest and Tillage of Row Crops. In 12th International Emission Inventory Conference, San Diego, CA.

Chen, W., Tong, D.Q., Dan, M., Zhang, S., Zhang, X., Pan, Y., 2017. Typical atmospheric haze during crop harvest season in northeastern China: A case in the Changchun region. Journal of Environmental Sciences 54, 101–113. https://doi.org/10.1016/j.jes.2016.03.031

Coates, W., 1996. Particulates generated by five cotton tillage systems. Transactions of the American Society of Agricultural Engineers 39, 1593–1598.

EEA, European Environmental Agency, 2016. EMEP/EEA air pollutant emission inventory guidebook 2016: technical guidance to prepare national emission inventories.

Kabelitz, T., Ammon, C., Funk, R., Münch, S., Biniasch, O., Nübel, U., Thiel, N., Rösler, U., Siller, P., Amon, B., Aarnink, A.J.A., Amon, T., 2020. Functional relationship of particulate matter (PM) emissions, animal species, and moisture content during manure application. Environment International 143, 105577. https://doi.org/10.1016/j.envint.2020.105577

Laufer, D., Loibl, B., Märländer, B., Koch, H.-J., 2016. Soil erosion and surface runoff under strip tillage for sugar beet (Beta vulgaris L.) in Central Europe. Soil and Tillage Research 162, 1–7. https://doi.org/10.1016/j.still.2016.04.007

Madden, N.M., Southard, R.J., Mitchell, J.P., 2009. Soil Water Content and Soil Disaggregation by Disking Affects PM10 Emissions. Journal of Environmental Quality 38, 36–43. https://doi.org/10.2134/jeq2008.0209

Maffia, J., Balsari, P., Padoan, E., Ajmone-Marsan, F., Ricauda Aimonino, D., Dinuccio, E., 2020a. Evaluation of particulate matter (PM10) emissions and its chemical characteristics during rotary harrowing operations at different forward speeds and levelling bar heights. Environmental Pollution 265, 115041. https://doi.org/10.1016/j.envpol.2020.115041

Maffia, J., Dinuccio, E., Amon, B., Balsari, P., 2020b. PM emissions from open field crop management: Emission factors, assessment methods and mitigation measures – A review. Atmospheric Environment 226, 117381. https://doi.org/10.1016/j.atmosenv.2020.117381

Padoan, E., Maffia, J., Balsari, P., Ajmone-Marsan, F., Dinuccio, E., 2021. Soil PM10 emission potential under specific mechanical stress and particles characteristics. Science of The Total Environment 779, 146468. https://doi.org/10.1016/j.scitotenv.2021.146468

Pasquill, F., 1961. The estimation of the dispersion of windborne material. Met. Mag., 90, 33.

R Core Team, 2019. R: A language and environment for statistical computing. R Foundation for Statistical Computing, Vienna,Austria. URL https://www.R-project.org/.

Winkel, A., van Riel, J.W., van Emous, R.A., Aarnink, A.J.A., Groot Koerkamp, P.W.G., Ogink, N.W.M., 2016. Abatement of particulate matter emission from experimental aviary housings for laying hens by spraying rapeseed oil. Poultry Science 95, 2836–2848. https://doi.org/10.3382/ps/pew261

4. RESEARCH WORKS ON AMMONIA EMISSIONS

The field of ammonia emissions is a more developed field as compared to PM emissions and it is a field in which the Waste Management research Group in Torino is working from several years, providing insights on emissions deriving from several steps of the manure management chain and developing and testing mitigation measures. The research works presented in this section were performed as part of the broader activities of the Waste Management Group and in line with the objectives of different research Projects.

Articles VII and VIII were written in the framework of the European Life Project Agriclose, which is entitled “Improvement and disclosure of efficient techniques for manure management towards a circular and sustainable agriculture” (AGRICLOSE - LIFE17 ENV/ES/000439). The Project aims at closing the gap between livestock rearing and agriculture, promoting cross-fertilization strategies that can help improve manure use efficiency, reduce nutrient surplus and ammonia losses, increase organic matter in depauperated soils and improve nutrient use efficiency on the regional scale. This is achieved through the implementation of solutions such as mechanical separation of solid and liquid fraction of slurry and composting of the solid fraction. The two articles VII and VIII present an alternative slurry acidification solution, to be implemented before mechanical separation of slurry. The technique, which aims to reduce ammonia and greenhouse gas emission, was addressed in terms of its acidification effect and emission reduction potential (Articles VII and VIII) and then applied in full scale through the implementation of a prototype, tested in a commercial farm (Article VIII).

Article VI, IX and X are standalone articles. Article VI focuses on a strategy to reduce gaseous emissions from manure spreading with the use of a nitrification inhibitor (NLock^{TM}), applied to the soil. Article IX presents an innovative laboratory approach to test a passive ammonia sampler. Article X was written in the framework of a research project, founded by the CRT foundation, entitled “Strategie innovative per la riduzione dell'impatto ambientale e l'incremento delle performance produttive negli allevamenti suinicoli” (Innovative strategies for reducing environmental impact and increasing production performance on pig farms). It focuses on emissions from pig houses and pig slurry storage and aims at evaluating the use of natural zeolites, in addition to pig diets, to reduce emissions of NH_3 and greenhouse gases while positively affecting pih health and performances.

The following articles, although not being all interconnected, allowed to address several different technologies and to expand the knowledge of mitigation measures to be used at different stages of the manure management process (Articles VI, VII, VIII and X) and also the measurement strategies to be used in field experiments (Article IX).

4.1. ARTICLE VI: *"Application of nitrification inhibitor on soil to reduce NH_3 and N_2O emission after slurry spreading"*

This article aims at testing the use of a nitrification inhibitor to reduce gaseous emissions from manure (NLock^{TM}). The interest in testing this methodology lies in the fact that the most prominent and effective techniques for reducing NH_3 emissions from land spreading are injection or immediate slurry incorporation techniques (Santonja et al., 2017). Those techniques, although extremely effective in containing fugitive ammonia, may induce an increase of N_2O emissions. Therefore, coupling of slurry injection and slurry incorporation may help to solve the main downside of slurry incorporation, while also favoring nitrogen availability for plants and reducing nitrate leaching. This conference paper presents the first results of a multiple years trial and gives a first insight on NH_3 and N_2O emission dynamics.

IEEE International Workshop on Metrology for Agriculture and Forestry (MetroAgriFor, 2020), pp. 58-62, doi: 10.1109/MetroAgriFor50201.2020.9277570.

<u>Authors:</u> Jacopo Maffia, Luca Rollé, Simone Pelissetti, Francesco Vocino, Marcin Dzikowski, Matteo Ceruti, Elio Dinuccio

Abstract

Manure spreading is one of the main sources of ammonia (NH_3) emissions in the livestock sector, which is responsible of the 75 % of anthropogenic NH_3 losses. For liquid manure, the most effective distribution technique to abate NH3 emissions is direct injection, which allows for a NH_3 emission abatement up to 90 %. Nonetheless, direct injection has been shown to potentially increase, under certain environmental conditions, nitrous oxide (N_2O) emissions from soil after slurry spreading. The aim of this study is to assess the effect of the commercial nitrification inhibitor N-Lock^{TM} (CORTEVA^{TM} agriscience) on NH_3 and N_2O emissions after spreading of two different slurry types. The product was tested in a field trial on two different soils (loam and sandy-loam) and in combination with two different types of manure (cattle slurry and digestate). The N-Lock^{TM} product appears to have a good potential for N_2O emission reduction from fields after slurry spreading with direct injection techniques. Nonetheless, proper emission abatements (up to 79 %) were obtained only in one of the two soils included in the study and N-Lock^{TM} efficiency differed depending also on slurry type.

1. **Introduction**

Nutrient surplus is an important environmental issue in livestock dense areas across the world (Leip et al., 2015; Sutton et al., 2011). The amount of nutrients contained in livestock manure often exceeds crops uptake capacity and leads to environmental impacts on the atmosphere, through ammonia (NH_3) and green house gases (GHG) emissions, and on water resources, through leaching of nitrates from fields into the watersheds. The livestock sector, in facts, contributes for the 75% and 14.5% to the NH_3 and GHG anthropogenic emissions and is held accountable for water eutrophication (Gerber et al., 2013; Sommer & Hutchings, 2001; Webb et al. 2005). Several solutions have been proposed to reduce NH_3 emissions by improving manure distribution. For liquid manure, the best distribution technique is direct injection, which allows for a NH_3 emission abatement up to 90% (Santonja et al., 2017). Nonetheless, direct injection has been shown to potentially increase, under certain environmental conditions, nitrous oxide (N_2O) emissions from soil after slurry spreading. N_2O is an important greenhouse gas (with a global warming potential of 265 CO_2 equivalents) and it is an end product of the soil nitrification and denitrification processes (Firestone et al., 1980). Nitrification inhibitors, acting on the nitrifying bacteria present in soils, have been proposed as a tool to reduce N_2O emissions (Firestone et al., 1980; Ruser et al., 2015). Nitrification inhibitors effects can also lead to a reduction of nitrate leaching from soils, as highlighted by Di & Cameron (2007). According to Randall et al., 1999, nitrification inhibitors can have a positive effect on grain yield, through an increase of N availability that allows for greater production. The aim of this study is to assess the effect of the commercial nitrification inhibitor N-Lock^{TM} (CORTEVA^{TM} agriscience) on NH_3 and N_2O emissions from Maize cropping system, after spreading of two different slurry types. The product was tested in a field trial on two different soils (loam and sandy-loam) and in combination with two different types of manure (cattle slurry and digestate).

2. Material and methods

2.1. Experimental layout

The trial was conducted in two experimental plots of about 700 m^2 each. The two big plots, S1 and S2, are characterized by two different soil textures, being classified respectively as loam and sandy-loam. The two soils are in the same area (Candiolo, TO) of the province of Turin (Italy). The area is characterized by an intenze Maize production and by the presence of a high number of livestock units per ha. The experimental layout was designed in order to test the product N-LockTM (containing nitrapyrine at 25.97 % on weight), with two different dosages (D1 and D2), on two different soil type and in combination with two different slurry types. The D1 dose (2.5 L ha^{-1}) is the one suggested by the producer of N-LockTM, while the D2 dose (5 L ha^{-1}) is the double of it. The two slurry types used for the experiment were cattle slurry and digestate (derived from anaerobic digestion of cattle slurry and maize silage).

It was chosen not to adopt a classical split plot design, since it was preferred to work in real operational conditions and it is not possible to obtain a good homogeneity of distribution with a manure spreader in plots of small dimensions. In terms of atmospheric emissions the homogeneity of distribution, meaning the amount of slurry per unit of surface, is of crucial importance in order to perform a successful comparison among different thesis. The two dosages of N-LockTM were applied in bands of 30 m of width and a 100 m of length, while one band was left untreated (NT). Successively, the slurries were distributed, using an injection system, perpendicularly to the N-Lock^{TM} treatment, in order to create 6 square plots of 30 x 30 m in both S1 and S2. The distribution rate of the two slurries was set in order to apply 170 kg of N per ha in each plot. After the distribution, instrumentations for NH_3 and GHG monitoring were mounted in each plot. The distribution of the N-Lock^{TM} product and the slurries, as well as the final experimental layout, are shown in Fig. 1.

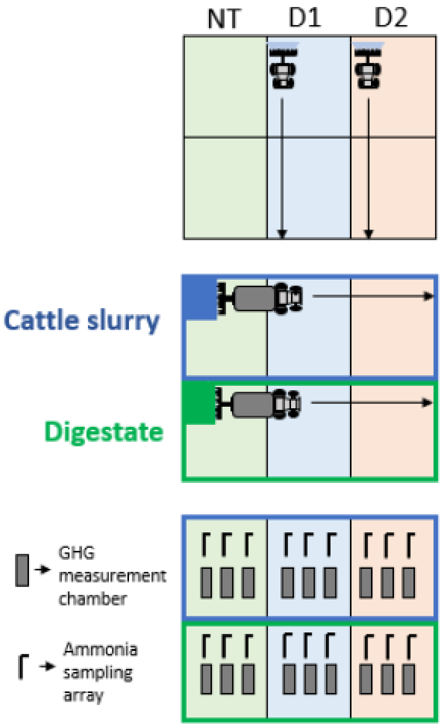


Figure 1. Field preparation and experimental layout scheme.

Both S1 and S2 were managed with a furrow irrigation system, which has been shown, among the most common watering systems, to be the one producing higher N_2O emissions (Ye et al., 2018). This system is the most commonly used one in the study area.

2.2. Emissions measurement

N_2O emissions were measured using a closed static chamber method (Maffia, 2020; Bertora et al., 2018). The measurement protocol was fully described by (Bertora et al., 2018). Maize plants were let growing inside the chamber till they reached 15 cm of height and then they were cut to permit field operations. NH3 emissions were assessed applying a micrometeorological method, by coupling passive NH_3 samplers (alpha-samplers, Tang et al., 2001) and the WindTrax dispersion model (Flesch et al., 2004). The method used is similar to the one described by Carozzi et al. (2012). NH_3 sampling lasted for the first 4 days after manure spreading, since NH_3 emissions occur mostly in the first days after spreading events. N_2O emissions were measured for the duration of Maize cropping season (from slurry spreading and sowing to harvesting).

2.3. Meteorological data and manure and soil characterization

Wind speed and wind direction were measured for the first 4 days of trial, using a 3D (GILL, Windmaster 3D) and a 2D (GILL, UltraSonic) sonic anemometers, placed at the corners of both fields at a height of 2 m. Wind data were elaborated as described in (Maffia et al., 2020). The two slurry types were analyzed in laboratory to determine dry matter content (OM; % on weight), pH, soil organic matter (SO; % on dry matter), total nitrogen (Total N, mg kg^{-1}), ammonium nitrogen (NH_4-N, mg kg-1) and organic nitrogen (Organic N, mg kg^{-1}). S1 and S2 were also characterized to define their texture (sand, silt and clay content; %), their total N content (mg kg^{-1}), their pH and their cation exchange capacity (CEC, meq hg^{-1}). The official AOAC method was apllied for slurry analyses (AOAC, 2006).

2.4. Statistical analysis

The effect of the N-Lock™ treatment on total NH_3 and N_2O emissions was assessed through an ANOVA procedure. The ANOVA was followed by a Tuckey post-hoc test ($P<0.05$). The results of the post-hoc tests are presented in Fig. 3. A separate ANOVA was performed per each soil:slurry combination. Therefore, it is not possible to evaluate directly slurry and soil type effects on the emissions.

3. Results and Discussion

3.1. Manure and soil characteristics

The chemical characteristics of the two slurry types used during the field experiments are shown in Tab. 1. The slurries have similar total N contents, but the cattle slurry has a lower NH_4-N content as compared to digestate. Tab. 2 shows phisical and chemical characteristics of soils S1 and S2. S2 has a lighter texture as compared to S1. Having S2 a higher macroporosity and a lower overall field capacity, it is probably more susceptible to the fload defload events that trigger N_2O emissions. Moreover, S2 also has a higher Ntot content and a lower C:N ratio, as compared to S1, while maintaining a higher soil OM. Therefore, S2 characteristics let presume a generally higher microbial activity. Both S1 and S2 have slightly acidic pH and an average CEC.

Table 1. Slurry chemical characteristics

	Cattle slurry	Digestate
Dry matter (%)	4.66	4.48
pH	7.14	7.6
OM (% on dry matter)	84.53	81.27
Organic N (mg kg^{-1})	1.88	1.43
NH_4-N (mg kg^{-1})	1.49	2.31
Total N (mg kg^{-1})	3.37	3.74

Table 2. soils chemical and physical characteristics

	S1	S2
Sand (%)	37.3	59.5
Silt (%)	44.5	30.6
Clay (%)	18.2	9.9
pH (H_2O)	6.4	6.1
OM (%)	2.41	3.36
Total N (mg kg^{-1})	1.53	2.45
CEC (meq hg^{-1})	16.7	14.5

3.2. Ammonia and Nitrous oxide emissions

NH_3 emissions, shown Fig.2, were quite low in all the observed plots. This can be explained by the fact that the distribution method used (direct injection) has been proved to be very efficient for NH_3 emission abatement (Santonja et al., 2017). The N-Lock™ treatment had no significant effect on the emissions, although a general trend of reduction with the increase of the dose can be observed. This is probably due to the fact that the product exerts its effects on the soil and needs some time to start affecting the bacterial communities in it, while the NH3 emissions happen, for the most part, in the first 6-12 hours after spreading (Santonja et al., 2017).

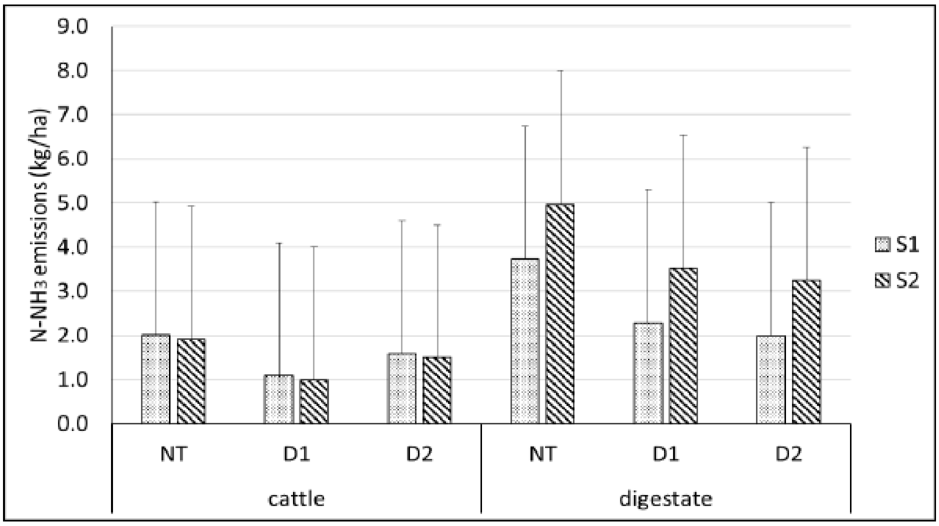


Figure 2. Total N losses through ammonia emissions observed during the trial.

The observed N_2O emissions were very different in the two soils, with digestate being the most emitting one in both S1 and S2 (Fig. 3). Moreover, the N-Lock^{TM} product appears to have affected the emissions very differently in the two experimental plots. In S1, the N-Lock^{TM} treatment had no significant effect on N2O emissions. In S2 instead, significant emission reductions were observed for both cattle slurry and digestate. For cattle slurry, the emissions were abated by 60 %, with the D2 dose, while D1 dose did not produce any significant effect. For digestate, both D1 and D2 doses were effective, with reductions of N_2O emissions of about 30 and 79 % as compare to the control. In general, N_2O emissions observed in S1 were low as compared to those in S2. The overall magnitude of the emissions in the two soils could have affected the significancy of the N-Lock^{TM} treatment. Where very low emissions occurred, the variability of soil conditions on a microscale could have generated a higher variability in fanal emissions than the treatment itself.

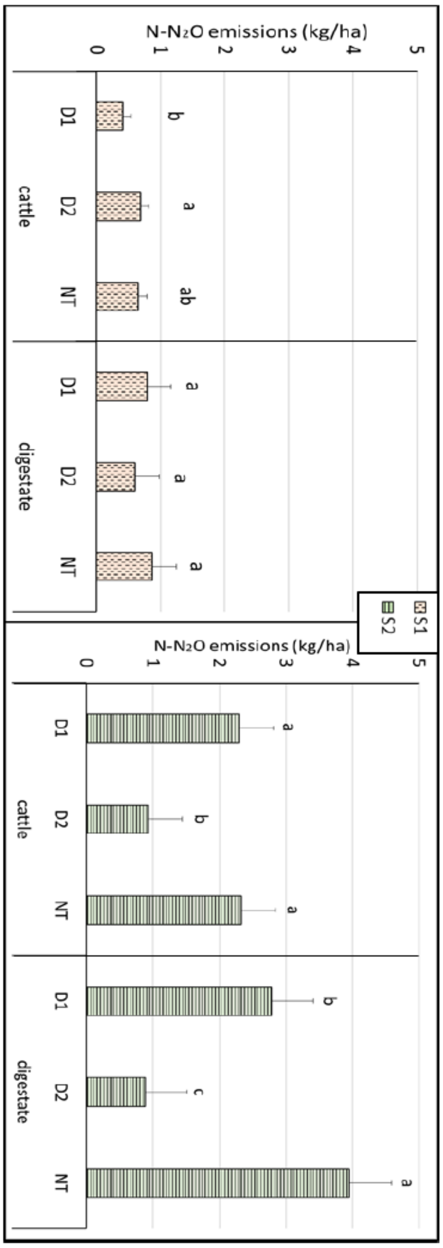


Figure 3. Total N losses through nitrous oxide emissions observed during the trial.

The fact that the N-Lock[TM] product performed so differently on the two plots (S1 and S2) is probably linked to the soil characteristics, since the two plots are in the same area and the precipitations were the same. The soil in S2, where the treatment was shown to be more effective, is a lighter soil with a higher sand content. Possibly, this could have facilitated the spreading of the product into soil pores, allowing for an improved action. Moreover, having S2 a higher macroporosity and being generally more moist could have led to higher nitrification and made the effect of NLock™ more evident. In fact, emissions in S1 were lower than in S2. In any case, further studies should be performed to better evaluate the effect of soil characteristic on the efficiency of this abatement strategy.

4. Conclusions

The N-Lock™ product appears to have a good potential for N_2O emission reduction from fields after slurry spreading with direct injection technique. Nonetheless, the emission abatements obtained with N-Lock™ were different in the two soils in which the product was tested and for different types of slurry. In fact, better results were obtained on a more sandy-loam soil, while on a loam soil the effects of the treatments were not significant and overall emissions were very low. Moreover, the best results were obtained in combination with digestate, where both the D1 and the D2 doses caused significant N_2O emission reductions of 30 and 79 % respectively. The soil S2, on which the N-Lock™ treatment had the better effect, was also the one in which the overall highest emissions occurred. Emissions in S1 were, in fact, below 1 kg ha^{-1} of N-N_2O in all thesis.

Further studies should be conducted to better investigate how soil and slurry type can affect N-Lock™ efficiency for emission reduction. A special attention should be put into testing other N-Lock™ distribution methods that can maybe help to overcome the disparity of results obtained on different soils.

The presented results are preliminary. The trial included also an assessment of CO_2 and CH_4 emissions, as well as an evaluation of the ammonium and nitrate content in soil during the entire cropping season. Moreover, field experiments will continue in wintertime, with an emission assessment of a winter-wheat succession. These further activities and results will be presented in future studies.

References

AOAC International, 2006. Official methods of analysis of the Association of Official Analytical Chemists, 18th ed. Association of Official Analytical Chemists, Gaithersburg, MD.

Bertora, C., Peyron, M., Pelissetti, S., Grignani, C., & Sacco, D., 2018. Assessment of methane and nitrous oxide fluxes from paddy field by means of static closed chambers maintaining plants within headspace. JoVE (Journal of Visualized Experiments), (139), e56754.

Carozzi, M., Ferrara, R. M., Fumagalli, M., Sanna, M., Chiodini, M., Perego, A., ... & Acutis, M., 2012. Field-scale ammonia emissions from surface spreading of dairy slurry in Po Valley. Italian Journal of Agrometeorology, 4, 25-34.

Di, H. J., & Cameron, K. C., 2007. Nitrate leaching losses and pasture yields as affected by different rates of animal urine nitrogen returns and application of a nitrification inhibitor—a lysimeter study. Nutrient Cycling in Agroecosystems, 79(3), 281-290.

Firestone, M. K., Firestone, R. B., & Tiedje, J. M., 1980. Nitrous oxide from soil denitrification: factors controlling its biological production.

Flesch, T.K., Wilson, J.D., Harper, L.A., Crenna, B.P., and R.R. Sharpe. 2004. Deducing ground-air emissions from observed trace gas concentrations: A field trial. J. of Applied Meteorology. 43:487-502. (Documents the foundation of WindTrax)

Gerber, P. J., Steinfeld, H., Henderson, B., Mottet, A., Opio, C., Dijkman, J., ... & Tempio, G. , 2013. Tackling climate change through livestock: a global assessment of emissions and mitigation opportunities. Food and Agriculture Organization of the United Nations (FAO).

Leip, A., Billen, G., Garnier, J., Grizzetti, B., Lassaletta, L., Reis, S., ... & Westhoek, H., 2015. Impacts of European livestock production: nitrogen, sulphur, phosphorus and greenhouse gas emissions, land-use, water eutrophication and biodiversity. Environmental Research Letters, 10(11), 115004.

Maffia, J., Balsari, P., Padoan, E., Ajmone-Marsan, F., Aimonino, D. R., & Dinuccio, E., 2020. Evaluation of particulate matter (PM10) emissions and its chemical characteristics during rotary harrowing operations at different forward speeds and levelling bar heights. Environmental Pollution, 265, 115041.

Parkin, T. B., & Venterea, R. T., 2010. USDA-ARS GRACEnet project protocols, chapter 3. Chamber-based trace gas flux measurements. Sampling protocols. Beltsville, MD p, 1-39.

Randall, G. W., Schmitt, M. A., & Schmidt, J. P. (1999). Corn production as affected by time and rate of manure application and nitrapyrin. Journal of production agriculture, 12(2), 317-323.

Ruser, R., & Schulz, R., 2015. The effect of nitrification inhibitors on the nitrous oxide (N2O) release from agricultural soils—a review. Journal of Plant Nutrition and Soil Science, 178(2), 171-188.

Santonja, G. G., Georgitzikis, K., Scalet, B. M., Montobbio, P., Roudier, S., & Sancho, L. D., 2017. Best available techniques (BAT) reference document for the intensive rearing of poultry or pigs. EUR 28674 EN.

Sommer, S. G., & Hutchings, N. J., 2001. Ammonia emission from field applied manure and its reduction. European journal of agronomy, 15(1), 1-15.

Sutton, M. A., Howard, C. M., Erisman, J. W., Billen, G., Bleeker, A., Grennfelt, P., ... & Grizzetti, B. (Eds.)., 2011. The European nitrogen assessment: sources, effects and policy perspectives. Cambridge University Press.

Tang, Y. S., Cape, J. N., & Sutton, M. A., 2001. Development and types of passive samplers for monitoring atmospheric NO2 and NH3 concentrations. TheScientificWorldJOURNAL, 1.

Webb, J., Menzi, H., Pain, B. F., Misselbrook, T. H., Dämmgen, U., Hendriks, H., & Döhler, H., 2005. Managing ammonia emissions from livestock production in Europe. Environmental pollution, 135(3), 399-406.

Ye, X. H., Han, B., Li, W., Zhang, X. C., Zhang, Y. L., Lin, X. G., & Zou, H. T. (2018). Effects of different irrigation methods on nitrous oxide emissions and ammonia oxidizers microorganisms in greenhouse tomato fields. Agricultural Water Management, 203, 115-123.

4.2. ARTICLE VII: *"Addition of powdery sulfur to pig slurry to reduce NH_3 and GHG emissions after mechanical separation"*

This article addresses the use of powdery sulfur as an additive to reduce ammonia and greenhouse gases emissions from slurry and slurry separated fractions. The main interest of using powdery sulfur as an alternative to strong acids arises from the difficulties of handling strong acids in a farm environment, especially with regards to safety issues. Moreover, the use of strong acids can cause foam formation, which can pose issues in slurry storage and handling.

The article presents the results of a laboratory trial, which aimed at uncovering the acidification dynamics of slurry after sulfur addition and the potential for emission reduction in a controlled environment.

IEEE International Workshop on Metrology for Agriculture and Forestry (MetroAgriFor, 2020), pp. 49-52, doi: 0.1109/MetroAgriFor50201.2020.9277551.

Authors: Jacopo Maffia, Fabrizio Gioelli, Luca Rollé, Gianfranco Airoldi, Paolo Balsari, Elio Dinuccio

Abstract

Agriculture is the cause of almost the 95% of total ammonia (NH_3) emissions in Europe, where livestock manure and fertilizers are the main emitters. In Italy, manure management represents about the 46% of the total NH_3 losses from the agricultural activities. The environmental impacts are greater in areas with high livestock density, where nutrient application rates on fields often exceed the crop uptakes. Mechanical separation of slurry into its solid and liquid components is widely used to ease the transport of nutrients surplus outside livestock dense areas towards livestock-free plantations. However, mechanical separation may increase greenhouse gases (GHG) and NH_3 emission mainly due to high emissions during the solid fraction storage. The main objective of this research has been evaluating the effect of acidification by adding elementary sulfur (S) before slurry mechanical separation. Ammonia and GHG emissions were monitored during storage of raw slurry, solid and liquid fraction.

KEYWORDS - Ammonia, manure, acidification, sulfur, emissions

1. Introduction

Agriculture is the cause of almost the 95% of total ammonia (NH_3) emissions in Europe (EEA, 2015), where livestock manure and fertilizers are the main emitters. In Italy manure management represents about the 46% of the total NH_3 losses from the agricultural activities (ISPRA, 2015). Moreover, manure management contributes to 13% of N_2O emission and to 8% of CH_4 emission, 46% of which from pig breeding (ISPRA, 2014). The environmental impact is greater in areas with high livestock density. In Valle Po are bred the 36%, 64% and 30% of cattle, pigs and poultry nationwide (ISTAT, 2011). Therefore, the nutrient application rates on fields often exceed the crop uptakes. Mechanical separation of slurry into its solid and liquid components is widely used to easily transport the nutrients surplus outside livestock dense areas towards livestock-free crop production areas, where manure spreading can be beneficially increase soil organic matter content (Hjorth et al., 2010 and Møller et al., 2007). However, mechanical separation may increase greenhouse gases (GHG) and NH_3 emission (Amon et al., 2006; Dinuccio et al., 2008; Fangueiro et al., 2008) mainly due to high emissions during the solid fraction storage. The main strategy used in North Europe to reduce NH_3 volatilization consists in slurry acidification (Schils et al., 1999; Eriksen et al., 2008). Ammonia losses from acidified slurry, that reaches a pH of 5.5, can be reduced up to 27 to 98% (Kai et al., 2008; Kaiying et al., 2014, Fangueiro et al., 2015). Moreover, slurry acidification can reduce CH_4 emissions by 17% to 87% (Ottosen et al., 2009; Petersen et al., 2012; Kaiying et al., 2014, Fangueiro et al., 2015). Nevertheless, the use of strong acids, such as concentrated sulfuric acid, poses some concerns. In fact, strong acids are considered hazardous materials, due to the potential health risk, and handling these kind of materials undergoes some regulation restrictions. The main objective of this research has been evaluating the effect of acidification by adding elementary sulfur (S), which does not pose health concerns, before slurry mechanical separation. Ammonia and GHG emissions were monitored during storage of raw slurry, solid and liquid fraction.

2. Materials and methods

The effect of addition of sulfur to different pig slurry fractions on NH3 and GHG emission was assessed in laboratory condition. Raw slurry was collected from a pig-breeding farm, where 2500 sows and 2300 fattening pigs were raised on a slatted floor without litter. The pigs' diet was mainly comprised of corn mash, and, in lower quantities, of barley, soybean, wheat and bran.

2.1. Slurry treatment and separation test

Elementary S was added to fresh raw slurry 24 h before separation test in 2 doses: 0.1% (w/w) and 0.5% (w/w). The rationale behind acidification with elemental sulfur relies on the chemical reaction described as follows:

$$S^0 + ½\, O_2 + 2H_2O \Leftrightarrow CH_2O + 2H^+\, SO_4^{2-} \qquad (1)$$

Raw slurry was mechanical separated using a lab-scale screw press device, described by Popovic et al. (2014). In order to determine the separation efficiency (Et) were weighed the amount of raw slurry (input) and the amounts of the solid and liquid fractions produced at the end of each trial. The mass was determined by a precision balance with 0.1 g sensibility and a carrying capacity of 6 kg (Kern PCB). The separation efficiency was then defined as the ratio (%) between the total mass of nutrients recovered in the solid fraction and the total nutrient input with the raw slurry (as described in Møller et al., 2002).

Table 1. Average characteristics of the raw slurry, soli and liquid fractions before the storage. Values of standard deviation are between brackets.

Treatment	**TS (%)**	**VS (%)**	**pH**	**N_{tot} (g kg^{-1})**	**N-NH_3 (%Ntot)**	**S (mg kg^{-1})**
RS	4.62 (0.05)	3.51 (0.03)	7.18	1.12 (0.10)	17.33	64.86 (46.41)
LF	2.15 (0.03)	1.40 (0.01)	7.29	0.70 (0.01)	9.33	84.13 (31.41)
SF	16.68 (0.23)	13.78 (0.13)	8.28	3.26 (0.09)	21.66	1,217.66 (194.25)

2.2. Gas emissions measurements during storage

Acidified and untreated slurries and their corresponding fractions were stored, in 5-liter jars, in the lab at room temperature for 60 days (temperature monitoring was performed as described by Regueiro et al., 2016). Each jar was filled with 1.500 g of liquid sample (raw slurry and liquid fraction) or with 800 g of solid fraction to maintain constant the head space in the jar. The gaseous emissions were detected through a dynamic chamber system, using an infrared photoacoustic monitor (IPD; 1412 Multi-gas Monitor, Innova® Air Tech Instruments) described by Berg et al. (2006). The emissions were monitored from the beginning of the storage every 24h for the first 2 weeks of storage and afterwards the measurement frequency was changed to three times per week. The measurement protocol is as described by Iria et al. (2016). Data were analyzed by analysis of variance procedure (ANOVA) followed by Tukey's post hoc test (with the significance level set at $P < 0.05$). The gaseous losses obtained are estimated as CO_2eq using the global warming potentials of 28 for CH_4 and 265 for N_2O, and considering the indirect NH_3 contribution to the N_2O emissions, estimated at 1% (IPPC, 2013).

2.3. Analytical methods

Dry matter (DM) content, presented as a percentage of wet weight, was measured, using a scale (Kern®, model ABS 220-4) after drying the fresh samples to a constant weight (24h at 105 °C). The volatile solids content (VS) was calculated as loss upon ignition at 550 °C for 5h (VDI 4630, 2006) and stated as percentage of dry matter. The pH of the slurry and liquids samples were measured directly using a glass electrode (Hanna instruments® electrode HI 1023). The pH of the solid samples was measured directly using a glass electrode for semi solid (Hanna instruments® electrode HI 1053B). Total nitrogen (N) and ammonium nitrogen (NH4-N) were measured according to the Kjeldahl method. Method used to measure total sulfur were UNI EN 13804 2013 + UNI EN 13805 2002 + EPA 6010C 2007.

3. Results and Discussion

3.1. Separation Test

Chemical characteristics of raw, solid and liquid fractions samples at the beginning of the experiments are shown in Table 1. Sulfur addition didn't affect the chemical properties of the raw slurry. From Separating a raw slurry with a DM content of 4.6% a solid fraction with a DM of approx. 17% was obtained. As previously highlighted by Hjorth et al. (2010) the total nitrogen and ammonia nitrogen content were are higher in the solid fraction than in the liquid fraction. The sulfur content in the raw slurry samples was about 10 times lower than that observed in the literature (Sørensen and Eriksen, 2009; Peu et al., 2012). Separation efficiency obtained for DM and VS was equal to 64% and 19%, respectively. These values are in accordance to those provided by Popovic et al. (2014).

3.2. Storage conditions

During the 60 days storage trial, the average temperature resulted 15.3 °C with a maximum value of 23.9°C and a minimum value of 13.9°C (Fig. 1). The temperature values recorded during the experiment can be considered representative of the outside spring condition in North Italy. Environmental temperature is well known to strongly affect NH_3 and CH_4 emissions (Kai et al., 2008, Dinuccio et al., 2008, Kaiying et al., 2014). Furthermore, Jaggi et al. (1999) found a strong influence of temperature on the rate of S oxidations.

Raw slurry (RS) pH (Fig. 2) remained higher than 7 during the experiment, while the liquid fraction (LF) was slightly more alkaline, with a pH level over 8. The solid fraction (SF) pH was lower for all the treatments and SF 0.5 reached a pH of 5.7. Samples RS 0.1 and LF 0.1 reached pH 7 after 30th day; samples SF 0.1, RS 0.5 and LF 0.5 reached pH 6.5. The effect of sulfur addition started from the 7th day as observed in a precedent study (Balsari et al., 2015). Several studies indicated pH 5.5 as an optimal level to achieve NH_3 emission reduction (Fangueiro et al., 2015), although the target pH should be defined considering also the economic costs of the treatment and the acidification efficiency. The efficiency of acidification with the objective of reducing NH_3 emissions depends on parameters such as the type of additive, target pH, manure type and step in the slurry management chain (Ndegwa et al., 2008). Reaching pH between 6 and 6.5 may allow to obtain abatements of NH_3 and CH_4 losses up to 40% (Kai et al., 2008; Berg et al., 2006, Kaiying et al., 2014; Lefcourt and Meisinger, 2001; Nyord et al., 2013; Balsari et al., 2015; Ottosen et al., 2009).

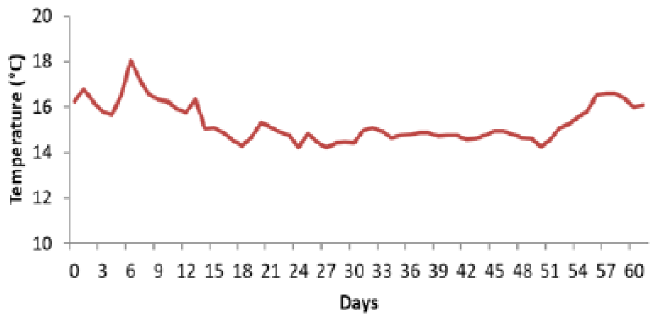


Figure 1. Air temperature trend measured during the test.

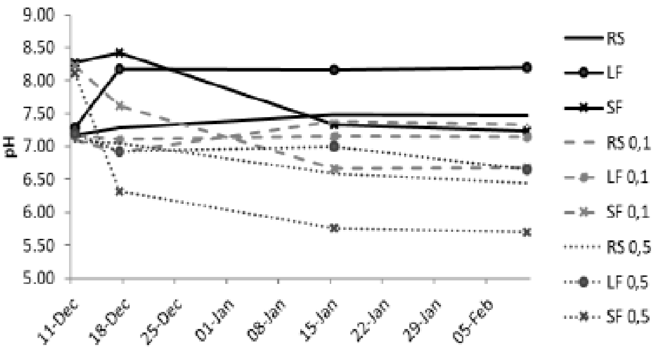


Figure 2. pH trend measured during the test.

3.3. Emissions of NH_3 and GHG

In the control samples the combined emissions (Fig. 3) measured from the storage of the liquid and solid fractions resulted in increased NH_3 losses compared with the storage of RS. This result is consistent with other studies (Amon et al., 2006; Dinuccio et al., 2008; Fangueiro et al., 2008). In contrast, in the acidified samples with lower S dose, the mechanical separation decreased significantly ($P < 0.05$) NH_3 losses (Fraction sum 0.1, Fig. 3a). For the slurry with the higher S application rate, instead, the separation did not significantly ($P > 0.05$) change the emissions amount (Fraction sum 0.5, Fig. 3a). The acidification S effect was more efficient for the liquid fraction. Specifically, LF 0.1 and LF 0.5 lost on average the 3.70 % of total initial nitrogen as ammonia compared to the 10% of LF. These percentages of N losses are lower than those recorded by Dinuccio et al. (2008) but consistent with Balsari et al. (2015).

Mechanical separation increased N_2O emissions from the separated fractions (Fig. 3b), similarly to what was reported in previous studies (Petersen S. O. and Sommer S.G., 2011; Amon et al., 2006). In general, N_2O emissions have been reduced by sulphur additions, with a reduction of the raw slurry emissions of 89% and 96% for RS 0.1 and for RS 0.5 respectively. For solid fractions, only the dose 0.5 has had a significant ($P < 0.05$) effect, with a N_2O emission reduction of 82% compared to the emission level of the control. The cumulative emission of N_2O was in the range of 0.02% (RS 0.5) to 0.08% (SF) of the initial total N content. All the 0.5 S samples emitted less than 0.1% N-N_2O/N content.

As expected, acidification altered methanogenic activity; CH_4 emissions were significantly reduced by sulphur acidification both in raw slurry and in separated fractions (Fig. 3c). The observed CH_4 emissions are in accordance with several researches (Martinez et al., 2003; Jiajun et al., 2010; Dong et al., 2011). C-CH4 emissions in raw slurry were reduced from 52% (S 0.1) to 91% (S 0.5). The emissions deriving from both separated fractions were also reduced by the sulfur treatment, although the effect of the two doses did not differ significantly ($P > 0.05$).

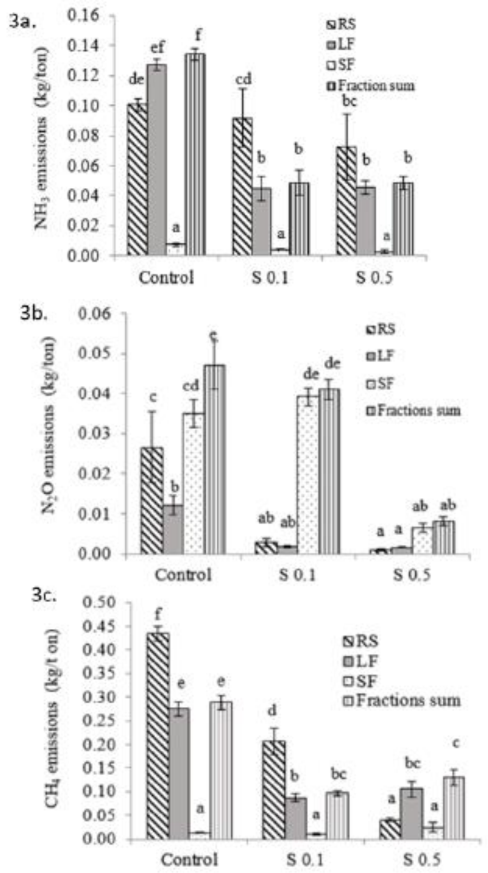


Fig. 3. Cumulative gaseous emissions of NH_3 (3a), N_2O (3b) and CH_4 (3c) during manure storage.

4. Conclusions

The addition of elementary S to slurry showed to be a reliable and effective slurry acidification method. Therefore, it can be considered as a valid alternative to the common sulfuric acid. Sulfur addition led to significant reduction of gaseous emissions (NH_3 and GHG) during storage. Ammonia emission rates from raw slurry and separate fractions were reduced on average by up to 28% and 49% respectively. GHG emissions were reduced by 79% and 53%, respectively for raw slurry and the sum of separate fractions.

According to these results, 0.1% S might be considered the best application rate, allowing an emission reduction in line with the current acidification technology performances.

Acknowledgements

This work has been realized within the project "Improvement and disclosure of efficient techniques for manure management towards a circular and sustainable agriculture (AGRICLOSE - LIFE17 ENV/ES/000439)".

References

Amon, B., Kryvoruchko, V., Amon, T., Zechmeister-Boltenstern, S., 2006. Methane, nitrous oxide and ammonia emissions during storage and after application of dairy cattle slurry and influence of slurry treatment. Agric. Ecosyst. Environ. 112, 153–162.

Balsari P., Cuk D., Dinuccio E., Gioelli F., Rollè L., 2015. Reduction of animal slurry gaseous emissions through its acidification with sulfur. AIIA 2015 International Mid-Term Conference, Naples, Italy.

Berg W., Brunsch R., Pazsiczki I., 2006. Greenhouse gas emissions from covered slurry compared with uncovered during storage. Agriculture, Ecosystem and Environment 112, 129–134.

Dinuccio E, Gioelli F, Balsari P, Dorno N., 2012. Ammonia losses from the storage and application of raw and chemo-mechanically separated slurry. Agriculture, Ecosystems and Environment 153 (2012) 16–23.

Dinuccio E., Berg W., Balsari P., 2008. Gaseous emissions from the storage of untreated slurries and the fractions obtained after mechanical separation. Atmospheric Environment 42 (2008) 2448–2459.

Dong H., Zhu Z., Zhou Z., Xin H., Chen X., 2011. Greenhouse gas emissions from swine manure stored at different stack heights. Animal Feed Science and Technology 166–167 (2011) 557–561

EC, 1996. Council directive 96/61/EC of 24 September 1996 concerning integrated pollution prevention and control. Official Journal L 257 , 10/10/1996 P. 0026 – 0040.

EEA, 2015. NEC Directive Status Report 2014. Technical report no. 7/2015. Available at: http://www.eea.europa.eu//publications/nec-directive-status-report-2014

Eriksen, J., Sorensen, P., Elsgaard, L., 2008. The fate of sulfate in acidified pig slurry during storage and following application to cropped soil. J. Environ. Qual. 37, 280–286.

Fangueiro D., Hjorth M., Gioelli F., 2015. Acidification of animal slurry - a review. Journal of Environmental Management 149 (2014) 46-56.

Fangueiro, D., Coutinho, J., Chadwick, D., Moreira, N., Trindade, H., 2008. Effect of cattle slurry separation on greenhouse gas and ammonia emissions during storage. J. Environ. Qual. 37, 2322–2331.

Hjorth, M., Christensen, K.V., Christensen, M.L., Sommer, S.G., 2010. Solid-liquid separation of animal slurry in theory and practice. A review. Agron. Sustain. Dev. 30, 153e180.

ISPRA, 2014. Italian Greenhouse Gas Inventory 1990–2012. Available at: http://www.sinanet.isprambiente.it/it/sia-ispra/serie-storiche-emissioni/serie-storiche-delle-emissioni-di-gas-serra-1990-2010/view

ISPRA, 2015. Italian Emission Inventory 1990–2013. Information inventory report 2015. Available at: http://www.isprambiente.gov.it/files/pubblicazioni/rapporti/R_223_15_IIR_2015.pdf

ISTAT, 2011. Istituto nazionale di statistica, 6° censimento generale dell'agricoltura.

Jaggi , R.C., Aulakh, M.S. Sharma,rR., 1999. Temperature effect on soil organic sulphur mineralization and elemental sulphur oxidation in subtropical soils of varying pH. Nutr. Cycl. Agroecosyst. 54, 175-182.

Jiajun W., Chiqing D., Yaqin J., Yichao S., 2010. Methane emissions during storage of different treatments from cattle manure in Tianjin. Journal of Environmental Sciences 2010, 22(10) 1564–1569.

Kai P., Pedersen P., Jensen J.E., Hansen M.N., Sommer S.G., 2008. A whole-farm assessment of the efficacy of slurry acidification in reducing ammonia emissions. European Journal of Agronomy, 28 (2), (2008) 148–154.

Kaiying W., Dandan H., Hongchuang Y., Haojie L., 2014. Effects of acidification during storage on emissions of methane, ammonia, and hydrogen sulfide from digested pig slurry. Biosystems Engineering 122, (2014) 23–30.

Lefcourt A.M., Meisinger J.J., 2001. Effect of adding alum or zeolite to dairy slurry on ammonia volatilization and chemical composition J. Dairy Sci., 84 (2001), pp. 1814–1821.

Martinez J., Guiziou F., Peu P., Gueutier V., 2003. Influence of Treatment Techniques for Pig Slurry on Methane Emissions during Subsequent Storage. Biosystems Engineering (2003) 85 (3), 347–354.

Møller, H. B., S. G. Sommer, and B. K. Ahring. 2002. Separation efficiency and particle size

Møller, H.B., Hansen, J.D., Sorensen, C.A.G., 2007. Nutrient recovery by solid liquid separation and methane productivity of solids. Trans. ASABE 50, 193-200.

Ndegwa P.M., Hristov A.N., Arogo J., Sheffield R.E., 2008. A review of ammonia emission mitigation techniques for concentrated animal feeding operations. Biosyst. Eng. 100, 453-469.

Nyord T., Liu D., Eriksen J., Adamsen A.P.S., 2013. Effect of acidification and soil injection of animal slurry on ammonia and odour emission Proceedings from the 15th RAMIRAN Conference, Versailles, France (2013)

Ottosen L.D.M., Poulsen H.V., Nielsen D.A., Finster K., Nielsen L.P., Revsbech N.P., 2009. Observations on microbial activity in acidified pig slurry. Biosystems Engineering, 102 (3), (2009) 291–297.

Petersen S. O., Andersen, J. A., & Eriksen, J., 2012. Effects of cattle slurry acidification on ammonia and methane evolution during storage. Journal of Environmental Quality, 41(1), 88-94.

Petersen S. O., Sommer S.G., 2011. Ammonia and nitrous oxide interactions: Roles of manure organic matter management. Animal Feed Science and Technology 166–167 (2011) 503–513.

Peu P., Picard S., Diara A., Girault R., Béline F., Bridoux G., Dabert P., 2012. Prediction of hydrogen sulphide production during anaerobic digestion of organic substrates. Bioresource Technology 121 (2012) 419–424

Popovic O., Gioelli F., Dinuccio E., Balsari P., 2014. Improved pig slurry mechanical separation using chitosan and biochar. Biosystems engineering 127 (2014) 115-124.

Regueiro I., Coutinho J., Gioelli F., Balsari P., Dinuccio E., 2016. Acidification of raw and co-digested pig slurries with alum before mechanical separation reduces gaseous emission during storage of solid and liquid fractions. Agriculture, Ecosystems and Environment 227 (2016), 42-51.

Schils, R.L.M., van der Meer, H.G., Wouters, A.P., Geurink, J.H., Sikkema, K., 1999. Nitrogen utilization from diluted and undiluted nitric acid treated cattle slurry following surface application to grassland. Nutr. Cycl. Agroecosyst. 53, 269–280.

Sørensen P., Eriksen J., 2009. Effects of slurry acidification with sulphuric acid combined with aeration on the turnover and plant availability of nitrogen Agriculture, Ecosystems and Environment 131 (2009) 240–246

4.3. ARTICLE VIII: *"Development and Testing of an Innovative System to Acidify Animal Slurry with Powdery Sulphur before Mechanical Separation"*

The results presented in Article VII had shown that slurry acidification wih powdery sulfur has good potential for reducing both NH_3 and greenhouse gases emissions. This second conference paper aims at presenting a full scale solution for implementing acidification with powdery sulfur and to test its operation parameters.

Proceedings of the AGENG 2021 Conference (Submitted)
<u>Authors:</u> Elio Dinuccio, Jacopo Maffia, Luca Rollé, Fabrizio Gioelli, Gianfranco Airoldi, Paolo Balsari

Abstract

Slurry acidification is one of the most efficient mitigation strategies to reduce atmospheric emissions of ammonia (NH_3) and greenhouse gases (GHG) from animal slurry. Powdery sulphur (S) has been proposed as an alternative to strong acids to achieve slurry acidification, avoiding safety risks and foam formation. In the context of the Agriclose LIFE Project, a set of lab-scale trials has been carried out to test the effect of S addition to raw pig slurry before mechanical separation on NH3 and GHG emission during storage of separated (liquid, solid) fractions. Powdery sulphur was added to fresh raw slurry in 2 doses: 0.1% (w/w) and 0.5% (w/w). Ammonia emission rates from raw slurry and separate fractions were reduced on average by up to 28% and 49% respectively. GHG emissions were reduced by 79% and 53%, respectively for raw slurry and the sum of separate fractions. On the basis of the results obtained from lab-scale tests, a full-scale prototype for acidification of pig slurry before mechanical separation has been designed, developed and tested. The prototype adopts a semi-continuous process and is composed of four main parts: a stainless-steel mixing tank provided with a rigid cover and filling sensors, an automatic system for mixing and dosing powdery S to slurry, a volumetric pump to transfer the acidified slurry to a screw press separator, and a control panel. The system automatically adds 0.2 to 1.5 kg S m-3 of slurry, allowing the separator to work at its full capacity (12-15 m3 h-1). The development of this prototype is a step forward to allow sulphur to be implemented at the farm level, achieving emission reduction and preserving nutrients.

Keywords: slurry treatment, acidification, ammonia emission, mitigation

1. Introduction

Acidification of animal slurry is one of the most promising mitigation strategies available to reduce emission of ammonia (NH_3), which is one of the main anthropogenic pollutant and it is almost entirely ascribable to the agricultural sector (up to 95%). In fact, NH_3 emissions are involved in the formation of particulate matter, water and soil acidification and water eutrophication (Bittman et al., 2014; Erisman & Schaap, 2004). Moreover, high ammonia concentration in barns represent a hazard for farmers and are detrimental for animal health (Baker et al., 2020). Many studies investigated the effects of acidification systems on slurry emissions, in all steps of the manure management chain: housing (Kai et al., 2008), storage (Misselbrook et al., 2016) and field spreading (Seidel et al., 2017). Most acidification systems rely on the use of strong acids, such as sulphuric acid and nitric acid, which are added and mixed into slurry tanks. that the addition of sulphuric acid to stored slurry allows to reduce NH_3 emission by 42-95 % (Seidel et al., 2017; Stevens et al., 1992). Alternative solutions to strong acids and milder acids were tested too (Eriksen et al., 2012; Lefcourt & Meisinger, 2001). In general, acidification of slurry should aim to lower the pH to a level of about 5-6, in order to achieve good emission mitigation results (Fangueiro et al., 2015).

The main issues encountered when applying manure acidification are related to safety concerns, since strong acids are hazardous substances and handling procedure are strictly regulated by national laws, which is one of the reasons why acidification is widely adopted only in certain European countries. Moreover, acid addition to animal slurry induces foam formation, causing handling difficulties.

This study aims to propose alternative acidification technique, relying on the use of powdery sulphur, a refinery industry by-product, to achieve acidification of slurry before its mechanical separation. A farm scale prototype for sulphur acidification was developed and its separation efficiency and working capacity were tested.

2. Materials and Methods

The experiments were carried out in two phases. In the first phase preliminary laboratory experiments were performed to test sulphur acidification mitigation potential, while in the second phase the farm scale prototype was developed and tested.

2.1. Preliminary tests and laboratory emission assessment

Pig slurry, collected from a commercial pig farm, was enriched with powdery sulphur 24 h before performing liquid solid separation in laboratory conditions. Two doses of sulphur were used: 0.1% (S 0.1) and 0.5% (S 0.5) on weight. Mechanical separation of slurry was performed using a lab-scale device, described in Popovic et al. (2017).

The raw slurry (RS), liquid (LF) and solid (SF) fractions were stored for 60 days, in 5 liters glass jars, at room temperature (15.3±2.1°C). The temperature value is comparable with usual outside spring condition in North Italy (temperature monitoring was performed with thermocouples; HOBO, OnSet).

Gaseous emissions during storage were monitored using a dynamic chamber system. Gas concentration measurement were performed using an infrared photoacoustic monitor (IPD; 1412 Multi-gas Monitor, Innova® Air Tech Instruments). The overall dynamic chamber system was described by (Berg et al., 2006). Emissions were monitored from the beginning of the storage period, every 24h for the first 2 weeks of storage and three times per week in the remaining period. The measurement protocol is as described by (Regueiro et al., 2016). Data were analyzed by analysis of variance procedure (ANOVA) followed by Tukey's post hoc test (with the significance level set at $P < 0.05$). The gaseous losses obtained are estimated as CO2eq using the global warming potentials of 28 for

CH_4 and 265 for N_2O, and considering the indirect NH_3 contribution to the N_2O emissions, estimated at 1% (Edenhofer et al., 2015).

2.2. Slurry characterisation

Chemical characteristics of RS, LF and SF at the start of the preliminary experiment and in all stages of the acidification prototype testing were analysed. Dry matter (DM) content, as a percentage of wet weight, was assessed with a precision scale (Kern®, model ABS 220-4) after drying the fresh samples (24h at 105 °C). The volatile solids content (VS) were calculated as loss upon ignition at 550 °C for 5h (VDI 4630, 2006). The pH of the slurry and liquids samples were measured directly using a glass electrode (Hanna instruments® electrode HI 1023). The pH of the solid samples was measured directly using a glass electrode for semi solid (Hanna instruments® electrode HI 1053B). Total nitrogen (N) and ammonium nitrogen (NH4-N) were measured according to the Kjeldahl method.

2.3. Farm scale prototype development and testing

The farm scale acidification prototype (Figure 1) developed for the Agriclose LIFE project is composed of three main stages: a raw slurry tank a batch acidification system and a screw-press separator. From the raw slurry tank with mixers (1), the slurry is conveyed to a smaller (7 m3) acidification tank (2), that works as a batch system and is provided with a sulphur dispenser (3) and mixers, finally a volumetric pump makes the acidified slurry flow to a screw-press separator (4), which divides SF and LF. The entire system is controlled from an electric panel.

Working as a batch system, the acidification tank requires a certain amount of time to fill up and perform the acidification before separation can start. The time required to acidify and separate 7 m3 of slurry was measured and compare with the normal screw-press separator work capacity. Moreover, the Sulphur dosing system (3) was calibrated and tested to evaluate the effect of cochlea rotation speed on sulphur flow rate and the influence of the discharge system opening (which was set to two difference levels: OL1 and OL2).

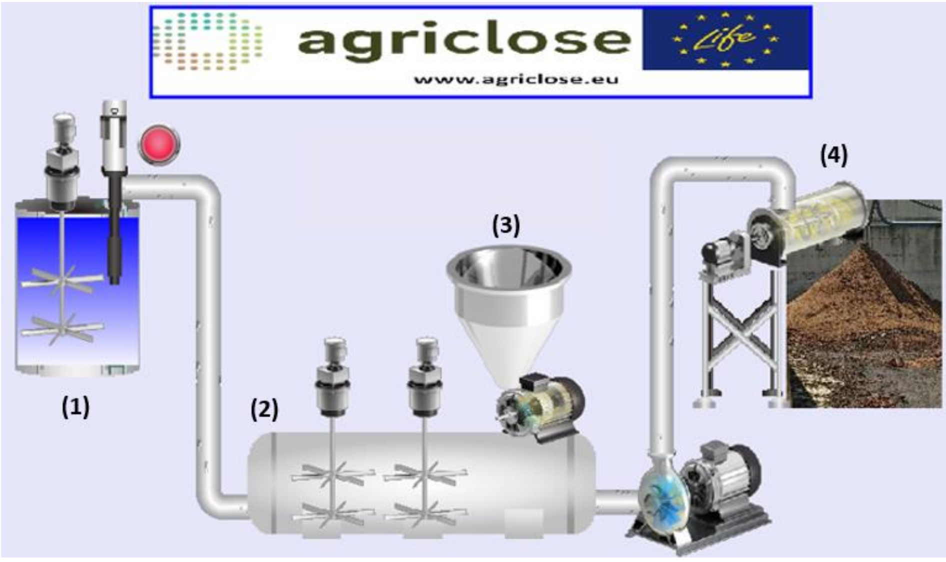


Figure 1. Acidification system prototype with (1) RS tank, (2) acidification tank, (3) sulphur dosing system, (4) screw-press separator.

2.4. Statistical analyses

Statistical analyses were performed using the R software (R core team, 2019). An ANOVA, followed by a Tuckey post hoc test was performed to evaluate differences among non-treated (NT) slurry and acidified ones (S 0.1 and S 0.5) in terms of atmospheric emissions and pH.

3. Results and Discussion

3.1. Slurry characteristics and pH

RS, LF and SF characteristics at the start of preliminary emission tests are presented in Table 1. It was observed that, apart from the difference in DM and VS among fractions, total nitrogen (Ntot) and ammonia nitrogen ($N\text{-}NH_3$) were more concentrated in SF, after separation. SF also had a higher starting pH. Figure 2 illustrates the pH variations during the experiment in all three thesis (NT, S 0.1 and S 0.5) and in combination with the three manure types. The S 0.5 dose effectively reduced pH for all manures until the end of the experiment, S 0.1, instead, had fewer effects on raw slurry, which was affected only in the first 20 days, and on SF, for which the effect of the S 0.5 dose was almost double the S 0.1 dose one. On LF, the S 0.1 and S 0.5 doses had similar effects. In general, the most promising pH reduction effects were observed on SF.

Slurry characteristics during prototype testing are presented in Table 2. SF DM content is higher than that observed in the preliminary trial, probably due to very low DM content of the slurry, which was three times less than the preliminary trial one.

Table 1. Initial slurry characteristics in the preliminary experiment.

	DM (% on wet mass)	VS (% on DM)	pH	N_{tot} (g kg^{-1})	N-NH_3 (%Ntot)
RS	4.62 ± 0.05	3.51 ± 0.03	7.18	1.12 ± 0.10	17.33
LF	2.15 ± 0.03	1.40 ± 0.01	7.29	0.70 ± 0.01	9.33
SF	16.68 ± 0.23	13.78 ± 0.13	8.28	3.26 ± 0.09	21.66

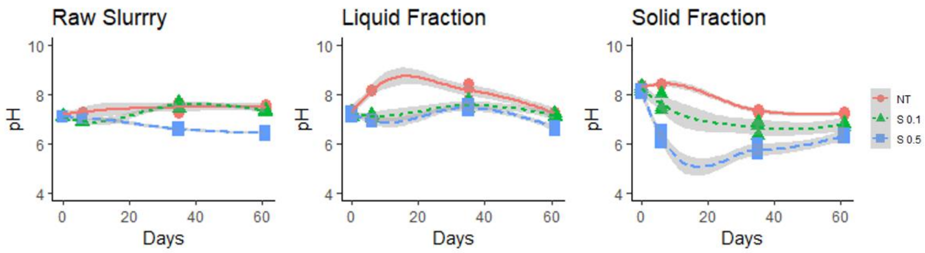


Figure 2. pH trend during simulated storage trial in all three manure types (grey areas indicate 75% confidence levels).

Table 2. Dry matter and Volatile solid content of slurries from prototype testing trial.

	DM (%on wet mass)	SV (% on DM)
RS	1.73 ± 0.01	59.65 ± 0.11
AS*	1.74 ± 0.02	58.24 ± 0.44
LF	1.47 ± 0.00	55.38 ± 0.67
SF	30.84 ± 0.15	83.25 ± 0.09

*Acidified slurry (sampled in the acidification tank).

3.2. Preliminary trial results

Ammonia and CO2eq emissions observed during the preliminary experiments are presented in Figure 3 and 4, while table 3 reports the results of the post hoc test on total emissions. For all slurry types NH_3 emission reduction were evident and were ascribable to lower emissions in the first 20-40 days of storage. Good mitigation effects were obtained with both S 0.1 and S 0.5 for LF, while in the RS thesis the S 0.1 dose caused a delay in the NH_3 emission but ended up recovering most of the emission potential in the last 20 days of storage. A good emission reduction trend was observed also for SF, but the final emission difference resulted being not significant. Similarly, good mitigation effects were observed for greenhouse gases (GHG) emissions (Figure 4), with both S 0.1 and S0.5 showing good results in RS (S 0.5 had better mitigation effects than S 0.1) and LF (S 0.5 and S 0.1 mitigation effects were statistically similar). For SF only the S 0.5 dose allowed a significant emission reduction. In general, sulphur acidification appears to be an effective mean for emission mitigation of both NH_3 and GHG during slurry storage.

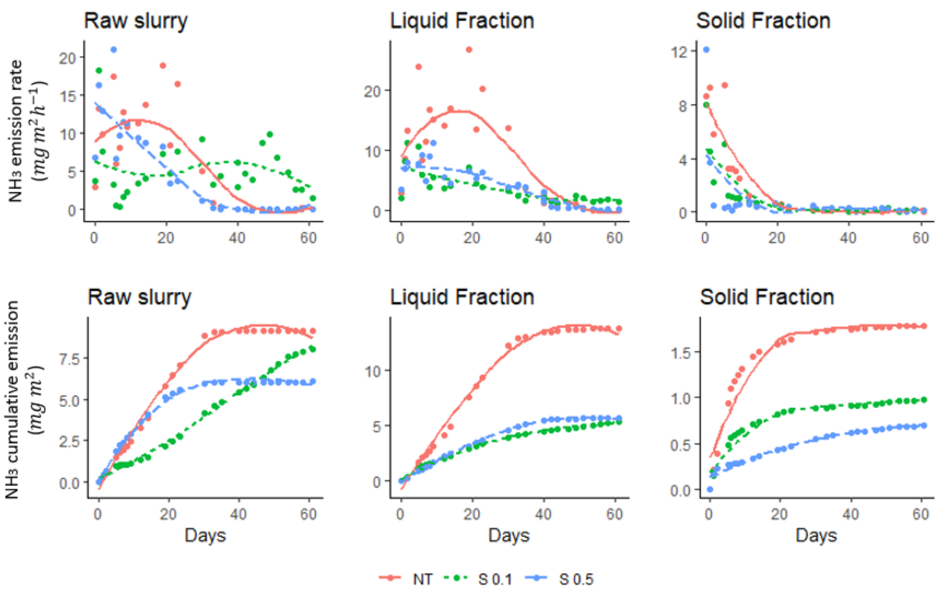


Figure 3. Daily emission trend and cumulative emissions of NH_3 during simulated storage experiment.

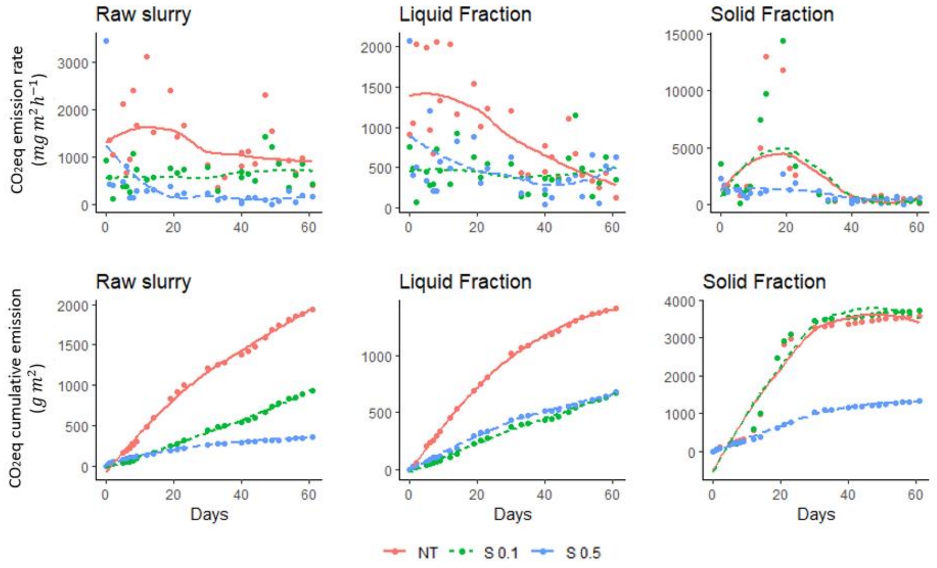


Figure 4. Daily emission trend and cumulative emissions of GHG (in CO2eq) during simulated storage experiment.

Table 3. Total NH_3 and GHG emissions occurred during simulated storage experiment (with Tukey's post hoc test results).

			Emissions ($g\ m^{-2}$)		SEM	N	P
NH_3	Liquid fraction	S 0.5	5.6	a	0.56	3	<0.001
		S 0.1	5.7	a			
		NT	13.3	b			
	Solid fraction	S 0.5	0.7	a			
		S 0.1	1.1	a			
		NT	1.9	a			
	Raw slurry	S 0.5	6.3	a			
		S 0.1	8	ab			
		NT	8.9	b			
CO_2eq	Liquid fraction	S 0.5	673	a	81.6	3	<0.001
		S 0.1	675	a			
		NT	1438	b			
	Solid fraction	S 0.5	1311	a			
		S 0.1	3677	b			
		NT	3573	b			
	Raw slurry	S 0.5	368	a			
		S 0.1	979	b			
		NT	2001	c			

3.3. Prototype performance and testing

The sulphur dosing mechanism was calibrated and tested to evaluate the rotation speed of cochlea needed to obtain the right S dosages (S 0.1 = 1 kg min-1; S 0.1 = 5 kg min-1), as well as evaluating the best opening level (OL) of the valve at the release point. Figure 5 presents the results of the calibration experiment. The sulphur flow rate increases linearly with incremental rotation speed. The OL2 allowed to reach the S 0.5 dosage in 1 min and, therefore, was chosen as more suited for operation.

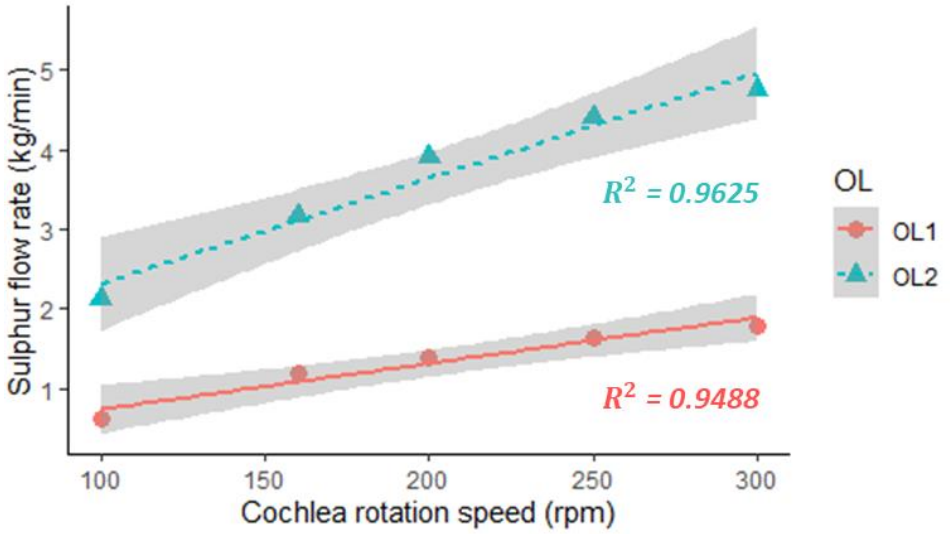


Figure 5. Linear regression lines for sulphur dosing calibration.

The DM content of SF was very high (~30 %), highlighting good separation performances. The time required by the prototype to fill the acidification tank with RS and perform the acidification was of 3 min and 50 ± 10 s, while the time required to separate the acidified slurry into SF and LF and was of 25 min and 8 ± 15 s. The work capacity of the system was calculated to be of 14.5 m3 h^{-1}, which is only slightly lower than the capacity of the solid-liquid separator itself (15.0 m3 h-1). The unit cost of sulphur is of about 0.6 € kg^{-1} and, consequently, the cost of the acidification procedure would be of 0.6 and 2.9 € m^{-3} of treated slurry with the S 0.1 and S 0.5 doses respectively. In conclusion, the prototype performed well and allowed to treat the slurry without increasing in a relevant way the separation times.

4. Conclusions

An acidification approach based on the use of powdery sulphur as a mean for slurry acidification was tested in laboratory, obtaining good mitigation results, both on NH_3 and GHG emissions. Moreover, a farm-scale prototype for sulphur acidification was developed and tested with good operational results. Sulphur acidification represents an intriguing novelty for manure emission mitigation and treatment, although more studies are needed to assess the possible effects of sulphur on soil and evaluate the economic and energetic feasibility of the system.

Acknowledgements

This work has been realized within the project "Improvement and disclosure of efficient techniques for manure management towards a circular and sustainable agriculture (AGRICLOSE - LIFE17 ENV/ES/000439)".

References

Baker, J., Battye, W. H., Robarge, W., Pal Arya, S., & Aneja, V. P. (2020). Modeling and measurements of ammonia from poultry operations: Their emissions, transport, and deposition in the Chesapeake Bay. Science of The Total Environment, 706, 135290. https://doi.org/10.1016/j.scitotenv.2019.135290

Berg, W., Brunsch, R., & Pazsiczki, I. (2006). Greenhouse gas emissions from covered slurry compared with uncovered during storage. Agriculture, Ecosystems & Environment, 112(2), 129–134. https://doi.org/10.1016/j.agee.2005.08.031

Bittman, S., Brook, J. R., Bleeker, A., & Bruulsema, T. W. (2014). Air Quality, Health Effects and Management of Ammonia Emissions from Fertilizers. In E. Taylor & A. McMillan (Eds.), Air Quality Management: Canadian Perspectives on a Global Issue (pp. 261–277). Springer Netherlands. https://doi.org/10.1007/978-94-007-7557-2_12

Edenhofer, O., Pichs-Madruga, R., Sokona, Y., Minx, J. C., Farahani, E., Kadner, S., Seyboth, K., Adler, A., Baum, I., Brunner, S., Eickmeier, P., Kriemann, B., Savolainen, J., Schlomer, S., Stechow, C. von, Zwickel, T., & Intergovernmental Panel on Climate Change (Eds.). (2015). Climate Change 2014: Mitigation of Climate Change ; Summary for Policymakers Technical Summary ; Part of the Working Group III Contribution to the Fifth Asessment Report of the Intergovernmental Panel on Climate Change. Intergovernmental Panel on Climate Change.

Eriksen, J., Andersen, A. J., Poulsen, H. V., Adamsen, A. P. S., & Petersen, S. O. (2012). Sulfur Turnover and Emissions during Storage of Cattle Slurry: Effects of Acidification and Sulfur Addition. Journal of Environmental Quality, 41(5), 1633–1641. https://doi.org/10.2134/jeq2012.0012

Erisman, J. W., & Schaap, M. (2004). The need for ammonia abatement with respect to secondary PM reductions in Europe. Environmental Pollution, 129(1), 159–163. https://doi.org/10.1016/j.envpol.2003.08.042

Fangueiro, D., Hjorth, M., & Gioelli, F. (2015). Acidification of animal slurry– a review. Journal of Environmental Management, 149, 46–56. https://doi.org/10.1016/j.jenvman.2014.10.001

Kai, P., Pedersen, P., Jensen, J. E., Hansen, M. N., & Sommer, S. G. (2008). A whole-farm assessment of the efficacy of slurry acidification in reducing ammonia emissions. European Journal of Agronomy, 28(2), 148–154. Scopus. https://doi.org/10.1016/j.eja.2007.06.004

Lefcourt, A. M., & Meisinger, J. J. (2001). Effect of Adding Alum or Zeolite to Dairy Slurry on Ammonia Volatilization and Chemical Composition. Journal of Dairy Science, 84(8), 1814–1821. https://doi.org/10.3168/jds.S0022-0302(01)74620-6

Misselbrook, T., Hunt, J., Perazzolo, F., & Provolo, G. (2016). Greenhouse Gas and Ammonia Emissions from Slurry Storage: Impacts of Temperature and Potential Mitigation through Covering (Pig Slurry) or Acidification (Cattle Slurry). Journal of Environmental Quality, 45(5), 1520–1530. https://doi.org/10.2134/jeq2015.12.0618

Popovic, O., Gioelli, F., Dinuccio, E., Rollè, L., & Balsari, P. (2017). Centrifugation of Digestate: The Effect of Chitosan on Separation Efficiency. Sustainability, 9(12), 2302. https://doi.org/10.3390/su9122302

Regueiro, I., Coutinho, J., Gioelli, F., Balsari, P., Dinuccio, E., & Fangueiro, D. (2016). Acidification of raw and co-digested pig slurries with alum before mechanical separation reduces gaseous emission during storage of solid and liquid fractions. Agriculture, Ecosystems & Environment, 227, 42–51. https://doi.org/10.1016/j.agee.2016.04.016

Seidel, A., Pacholski, A., Nyord, T., Vestergaard, A., Pahlmann, I., Herrmann, A., & Kage, H. (2017). Effects of acidification and injection of pasture applied cattle slurry on ammonia losses, N2O emissions and crop N uptake. Agriculture, Ecosystems & Environment, 247, 23–32. https://doi.org/10.1016/j.agee.2017.05.030

Stevens, R. J., Laughlin, R. J., Anderson, R., & Frost, J. P. (1992). Evaluation of separation plus acidification with nitric acid and separation plus dilution to make cattle slurry a balanced, efficient fertilizer for grass and silage. The Journal of Agricultural Science, 119(3), 391–399. Scopus. https://doi.org/10.1017/S0021859600012235

4.4. ARTICLE IX: *"Testing the Efficiency of a Passive Sampler for Ammonia Monitoring and Comparison with Alpha-Samplers"*

This article presents a methodological contribution to ammonia passive sampling practices, by testing the applicability of the diffusion passive sampler equation, as applied by Tang et al. (2014) to a very simple open sampler design. Moreover, a laboratory system has been built to test the sampler efficiency. Passive samplers, in fact, although being among the most convenient techniques for ammonia monitoring, present the substantial drawback of having less than optimal efficiency. Therefore, building a system able to identify the sampler's efficiency in different conditions could pose a solution to an unsolved problem. The results presented in the conference paper provide a first insight on this issue, while also comparing the tested sampler with a more commonly used one.

IEEE International Workshop on Metrology for Agriculture and Forestry, MetroAgriFor 2021 (Submitted)

Authors: Jacopo Maffia, Simone Pelissetti, Paolo Balsari, Elio Dinuccio, Dario Sacco

Abstract
Ammonia (NH_3) emissions from fertilizer and manure spreading pose several environmental issues, such as soil and water acidification, water eutrophication and fine particulate matter formation. Constant and diffuse monitoring of NH_3 concentrations is crucial to provide accurate emission estimation and understating of seasonal and spatial variation of NH_3 concentration. Passive sampling technique represent a good solution for long term and low-cost NH_3 monitoring campaigns, especially when covering large areas is necessary. Nonetheless, few studies evaluated the efficiency of passive samplers. This study aims to develop a laboratory system to assess the efficiency of a passive sampler with very simple design and to perform a field comparison with one of the most utilized passive samplers (alpha-samplers) for ammonia monitoring. The tested samplers showed capture efficiencies ranging from 49 to 89% and performed similarly to alpha-samplers in field conditions.

Keywords—ammonia, environmental monitoring, passive samplers,

1. Introduction

Ammonia (NH_3) emission after manure spreading in fields is one of the main issues related to nutrient management and environmental pollution in integrated crop-livestock systems. Ammonia volatilization, other than reducing the nitrogen efficiency of fertilizers (Jantalia et al., 2012), also contributes to several environmental impacts, such as soil and water acidification, water eutrophication and formation of fine particulate matter in the atmosphere (Anderson et al., 2003). Accurate estimation methods for ammonia losses from fields are of fundamental importance to gather information about current impacts and test proper mitigation measures. Several methods have been developed so far to estimate emissions from fields and can be distinguished in two main categories: enclosure methods and micrometeorological methods. The most diffuse enclosure methods are based on the use of open dynamic chambers, such as wind tunnels (Ryden and Lockyer, 1985). These systems are relatively expensive and are suited for evaluation of emission from small plots and the obtained Emission Factor (EF) are more suited to be used as comparative values than as absolute ones, also because they tend to underestimate or overestimate the emissions (Misselbrook et al., 2005; Sintermann et al., 2012). To overcome these limitations, the use of micrometeorological methods has become more common in recent years. Micrometeorological techniques are, in fact, suited for open field assessment of absolute emission values. Among the most common micrometeorological techniques is the Integrated Horizontal Flux (IHF) technique (Denmead, 1983; Misselbrook et al., 2005), which has long been considered the reference technique for open field ammonia emission assessment. The main drawbacks of this technique are the need to sample ammonia at many different heights and the fact that it is only suited for emission estimation from circular plots. To overcome the issue of concentration measurement at multiple heights, Wilson et al. (Wilson et al., 1982) proposed an alternative method (the Theoretical Profile Shape method, TSP), later verified (Wilson et al., 1983), which allows to calculate the emission flux from a circular plot by measuring concentration at just one height (the so called ZINST height). The same model used in the TSP method was later developed into a more advanced one (Flesch et al., 1995), which is Backward Lagrangian Stochastic model WindTrax. The use of the WindTrax model to estimate emissions allows to perform cost-effective (Vilms Pedersen, 2018) estimation of NH3 emissions from sources of different shapes (Crenna et al., 2008) and also to manage multi-plot source experiments (Gericke et al., 2011; Lavrsen Kure et al., 2018). Moreover, the model can be ran using time-averaged concentration data (Flesch et al., 2004), derived using low-cost passive samplers (Lavrsen Kure et al., 2018). The most widely used low-cost samplers for NH3 are Alpha samplers and Leuning samplers (Leuning et al., 1985; Tang et al., 2014). These two samplers are based on two very different principles. The alpha samplers, in fact, rely on the Fick's law of gas diffusion, while the Leuning samplers have a tube shape that pivots with the wind and aims to capture the horizontal NH3 flux over a catchment (Leuning samplers are often used with the IHF method). The aim of this study is to assess an alternative passive sampler (open acid samplers, OS), designed on the base of the calibrated samplers proposed by Pacholski et al. (Pacholski et al., 2006), which rely on a concentration estimation system similar to the one used by alpha samplers. The samplers were first tested in a laboratory trial and then compared with alpha samplers in a field experiment.

2. Materials and methods

2.1. Sampler design

The open acid samplers (OS) used for this study were designed after Pacholski et al. (Pacholski et al., 2006) and are shown in Fig. 1. OS are constituted by a rectangular plastic bottle, with circular holes, protected by a plastic mesh, at the 4 sides. The screw down lid on top is secured to a plastic roof with a metal stand, providing coverage for rain and securing the sampler at 30-50 cm from ground level, depending on the experimental needs. Inside the sampler, 20 ml of 0.05 N H2SO4 is placed at the start of the measurement trial and is collected at the end using a syringe or by pouring it carefully. The N-NH_3 content of the liquid is then determined by spectrophotometry (Crooke and Simpson, 1971). The air volume (V, m^3) passed through the sampler was measured as follows:

V=DAt/L

Where D is the diffusion coefficient (set to 2.09 x 10-5 m2 s^{-1}), A is the area (m^2) of the circular opening on the OS, t is the exposure time (s) and L is the distance (m) between the bottom of the circular opening and the free surface of the acid solution. The final concentration (C, µg m^{-3}) was then retrieved dividing the amount (µg) of NH_3 in the solution by V. The formula used were the same described for use in alpha-samplers (Tang et al., 2014).

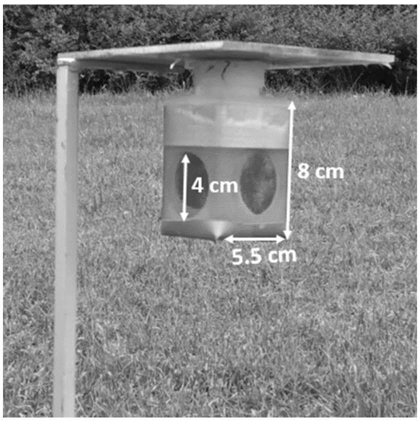


Figure 1. Photo of an Open Sampler (with main dimensions).

2.2. Laboratory testing system and experimental layout

A laboratory system was developed to test the capture efficiency of OS. The system (Fig. 2) relied on the use of a tracer gas, with known NH4 concentration, and a vacuum pump to ensure a correct mixing (in a mixing chamber) of ambient air and NH_3, in order to convey to the sampler a flux of air containing 3.5±0.3 or 9.5±0.2 mg m-3 of NH_3 (the concentrations were determined by placing the photoacoustic monitor in the same spot as the OS sampler. A further sampling chamber was added to the system to enable a control of the actual concentration of incoming air at the time of measurement, which was done using a photoacoustic sampler (INNOVA, 1412). OS were tested with two ammonia concentrations (3.5 mg m^{-3}, 9.5 mg m^{-3}) and with three different flow levels (low = 5 l min^{-1}, medium =10 l min^{-1} and high = 15 l min^{-1}). The concentrations are higher than those normally found in field conditions; this is due to the fact that the sampler exposure time in the laboratory test was way lower than field exposure time. Sampling testing period was of 15 min for each of configuration (air flow | concentration) and three experimental replicas were made. The capture efficiency was determined as the ratio among the observed concentration (with OS and photoacoustic) and the expected one. It was chosen to use the expected concentration as reference, since the concentrations contemporarily measured by the photoacoustic instrument could have been influenced by the different sampling position.

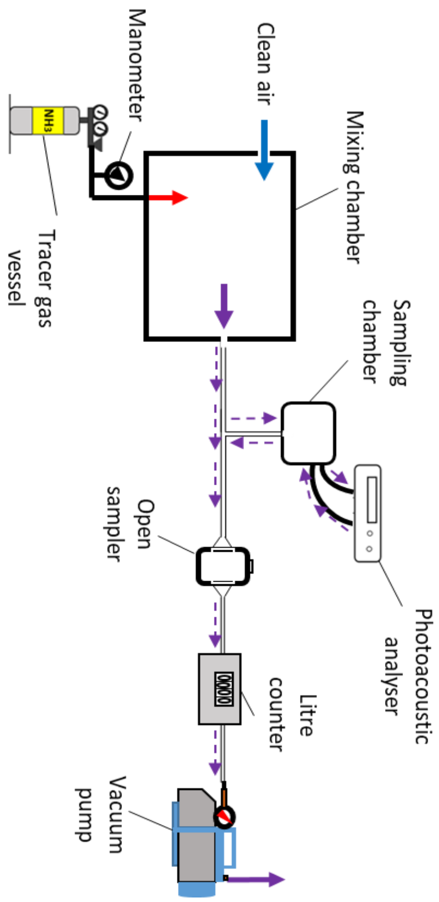


Figure 2. Scheme of the laboratory sampling system for OS efficiency testing.

2.3. Field comparison with alpha-samplers

A field comparison trial was performed to compare OS samplers with the alpha samplers, which are considered one of the state of the art devices for passive monitoring of NH_3. The field experiment set up was composed by a circular emitting surface (pig slurry was spread evenly on a circular grass catchment with 4 m ray; Fig. 3). Three OS and three alpha-samplers were placed at the center of the plot and wind conditions were continuously monitored with a sonic 3D anemometer (GILL, WindMaster). The samplers were left in the field for 24 h in total, divided in three sampling period (t1, t2 and t3). Fig. 4 shows the duration of the three sampling intervals, after which the solution (for OS) and acid filters (for alpha-samplers) were replaced. Sampling period t2 is longer and occurred during night time. The samplers were placed at ~0.5 m from ground level.

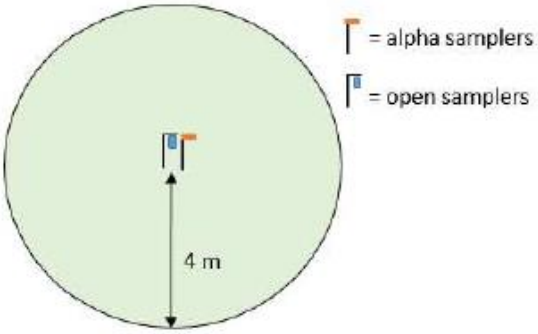


Figure 3. Field trial scheme

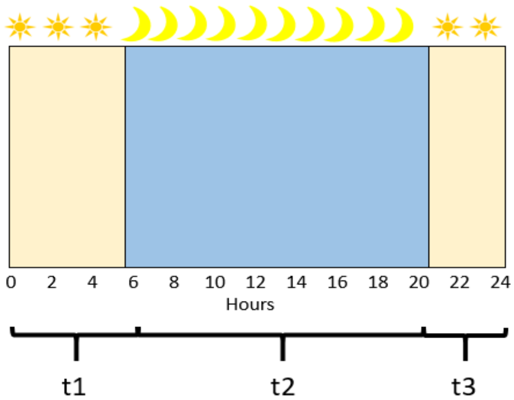


Figure 4. Field trial sampling intervals duration (in hours).

2.4. Statistical analysis

An ANOVA analysis, followed by a Tukeys post-hoc test, was performed to assess significant differences among OS and alpha-samplers concentrations during the field trial. Similarly, an ANOVA test was performed to identify differences in OS capture efficiencies with low and high concentration levels during the laboratory experiment. The analysis were performed using R statistical software (R core team, 2019).

3. Results and discussion

3.1. Laboratory test results

The laboratory trial allowed to evaluate the OS capture efficiency at low (3.5 mg m^{-3}) and high (9.5 mg m^{-3}) concentrations and at all three flow levels (low = 5 l min^{-1}, medium = 10 l min^{-1} and high = 15 l min^{-1}). The test results are summarized in Fig. 5, presenting the concentrations retrieved by OS and photoacoustic analyzer, and Table 1, presenting OS capture efficiency results.

Concentrations observed with the photoacoustic instrument were in good agreement with the expected concentration levels, meaning that the sampling chamber control system was effective in allowing to check the system performance during the test. The concentrations observed with the OS sampler, instead, were always lower than the expected ones, especially when tested at the higher concentration level. Flux intensity effect on concentration was less evident. Results in Table 1 further highlight the difference among OS efficiency with low and high NH_3 concentration streams, with the efficiency being higher with low concentration (~85%) than high one (~40%). This difference was significant for both the high and medium flow rate tests, while no efficiency difference among low and high concentration was observed in the low flow rate test.
The higher efficiency generally observed at low concentration levels is probably due to the fact that, when NH_3 levels are too high, the acid solution is not capable to adsorb it at a sufficient rate and, therefore, the air exiting the OS still contains a relatively high amount of NH_3. As for the lower efficiency observed in the low flow rate test, this could be attributed to the less turbulent flow and poor mixing conditions that derive from the lower air flow.

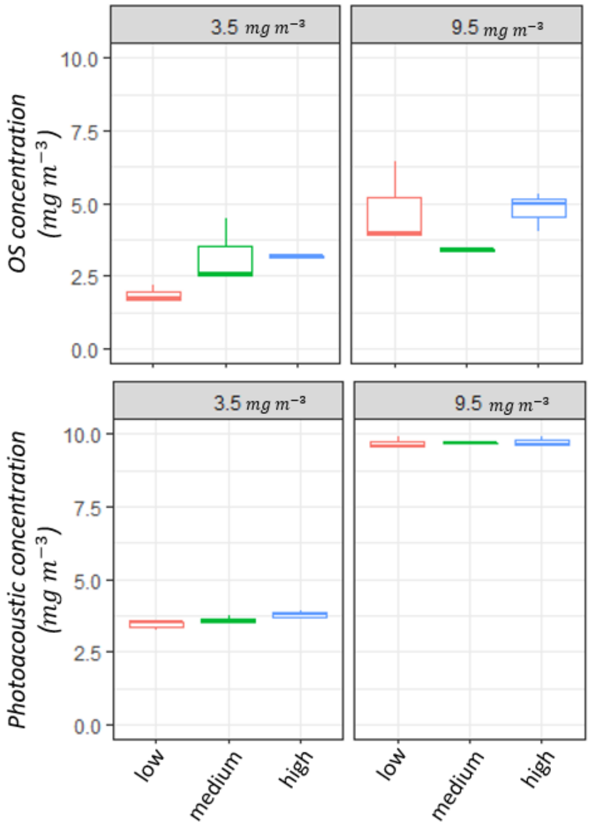


Figure 5. Boxplot graph of NH3 concentration retrieved by OS and photoacoustic instrument at varius concentration and flow levels.

Table 1. Capture efficiency of OS for the different flows and ammonia concentrations (means followed by the same letter do not differ statistically; P>0.05).

Flow	Concentration	Capture efficiency (%)	N[a]	LCL[b]	UCL[b]
High	low	83.9 b	3	64.1	103.7
	high	35.0 a	3	15.2	54.8
Medium	low	88.6 b	3	68.8	108.4
	high	49.3 a	3	29.5	69.1
Low	low	53.5 a	3	33.7	73.3
	high	49.4 a	3	29.6	69.2

3.2. Field comparison with alpha-samplers

The field experiment allowed a comparison among OS and alpha samplers over three sampling intervals. The concentrations observed during the trial and the post-hoc test results highlighting significant difference among samplers are summarized in Fig. 6. The concentrations retrieved by the two samplers were similar in all three intervals. In particular, concentrations from OS and alpha-samplers in t1 and t3 did not differ statistically, while in t2 there was a significant difference, with higher concentration of NH_3 from OS than from the alpha-sampler. This difference occurred during the night time sampling interval, when atmospheric conditions are generally different (stable atmosphere; Hoolohan et al., 2018). In fact, during t2 wind speed (WS) was lower than in t1 and t3.

In general, results derived with OS and alpha-samplers were consistent. Nonetheless, considering the results of the laboratory trial and the fact that OS data presented in Fig. 6 were not corrected by the sampler efficiency (Table 1), some doubts arise on the validity of the passive sampling methodology for absolute value emission determination. In fact, if the efficiency of OS during the field trial was around 80-85 %, as the lab scale trial suggests, an underestimation of the actual NH_3 concentration is expected. Nonetheless, the widely utilized alpha samplers performed no better than OS, giving even lower values in t2 (although the numerical difference was small). Moreover, it must be noted that the concentrations observed here are way lower than those observed during the lab trial, although the total amounts of NH_3 accumulated over the sampling time is similar. This difference could have caused samplers efficiency to increase slightly; future trials should address this issue.

A further observation can be made on the confidence intervals of retrieved data. In fact, OS data varied less than alpha samplers ones. Thus, it can be said that, in this trial OS precision (the closeness of measures to each other) in determining NH_3 concentration was higher than the alpha-samplers. As for the samplers accuracy, instead, some doubts arise due to lab trial efficiency testing.

The overall field trial results seem to suggest that the alpha-samplers methodology to estimate NH_3 concentration can be applied to samplers with very different designs, if all parameter are accurately set.

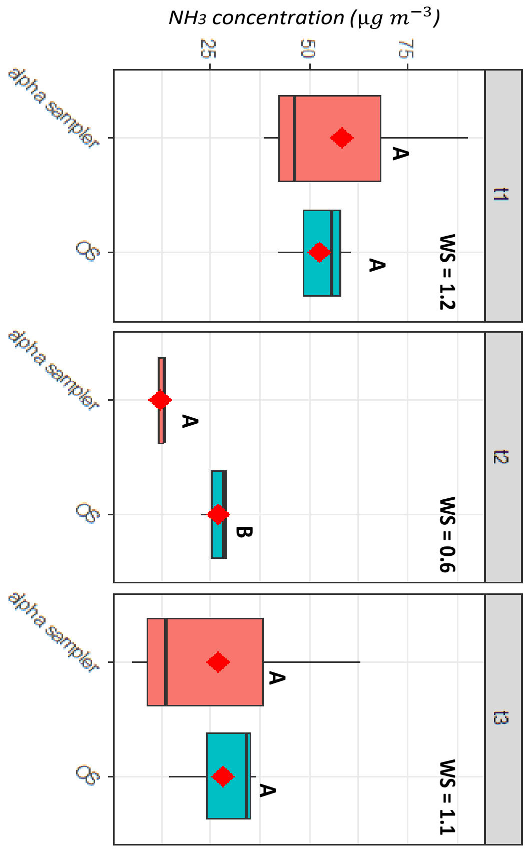


Figure 6. Boxplot graph of NH3 concentration retrieved by OS and alpha samplers during the field trial (rhobuses indicate mean values; means associated with the same letter do not show significant difference for P<0.05).

4. Conclusions

The results of the field and laboratory trials suggested that passive samplers of different designs can be used as an alternative to alpha-samplers by adopting the same diffusion principle, with almost no significant difference in results. Nonetheless, the laboratory trial highlighted that sampler efficiency strongly decreases when NH_3 concentrations are high (~9.5 mg m^{-3}). This result does not hinder the possibility of applying the samplers for environmental monitoring, since concentrations retrieved in fields are substantially lower. Nonetheless, the observed capture efficiencies confirm the hypothesis that passive samplers are more suited for studying variations in emission concentrations over long periods of time and to address seasonality. In general, although micrometeorological methods are the best option to determine absolute value EFs, when those are coupled with passive samplers, a thorough calibration with more accurate measurement systems (e.g. optical sensors) should be performed to avoid underestimating EFs.

Aknowledgements

Dedicated to the memory of Prof. Dario Sacco, who supervised this research work.

References

Anderson, N., Strader, R., Davidson, C., 2003. Airborne reduced nitrogen: ammonia emissions from agriculture and other sources. Environ Int 29, 277–286. https://doi.org/10.1016/S0160-4120(02)00186-1

Crenna, B.P., Flesch, T.K., Wilson, J.D., 2008. Influence of source–sensor geometry on multi-source emission rate estimates. Atmospheric Environment 42, 7373–7383. https://doi.org/10.1016/j.atmosenv.2008.06.019

Crooke, W.M., Simpson, W.E., 1971. Determination of ammonium in Kjeldahl digests of crops by an automated procedure. Journal of the Science of Food and Agriculture 22, 9–10. https://doi.org/10.1002/jsfa.2740220104

Denmead, O.T., 1983. Micrometeorological methods for measuring gaseous losses of nitrogen in the field, in: Freney, J.R., Simpson, J.R. (Eds.), Gaseous Loss of Nitrogen from Plant-Soil Systems, Developments in Plant and Soil Sciences. Springer Netherlands, Dordrecht, pp. 133–157. https://doi.org/10.1007/978-94-017-1662-8_5

Flesch, T.K., Wilson, J.D., Harper, L.A., Crenna, B.P., Sharpe, R.R., 2004. Deducing Ground-to-Air Emissions from Observed Trace Gas Concentrations: A Field Trial. J. Appl. Meteor. 43, 487–502. https://doi.org/10.1175/1520-0450(2004)043<0487:DGEFOT>2.0.CO;2

Gericke, D., Pacholski, A., Kage, H., 2011. Measurement of ammonia emissions in multi-plot field experiments. Biosystems Engineering 108, 164–173. https://doi.org/10.1016/j.biosystemseng.2010.11.009

Hoolohan, V., Tomlin, A.S., Cockerill, T., 2018. Improved near surface wind speed predictions using Gaussian process regression combined with numerical weather predictions and observed meteorological data. Renewable Energy 126, 1043–1054. https://doi.org/10.1016/j.renene.2018.04.019

Jantalia, C.P., Halvorson, A.D., Follett, R.F., Rodrigues Alves, B.J., Polidoro, J.C., Urquiaga, S., 2012. Nitrogen Source Effects on Ammonia Volatilization as Measured with Semi-Static Chambers. Agronomy Journal 104, 1595–1603. https://doi.org/10.2134/agronj2012.0210

Lavrsen Kure, J., Krabben, J., Vilms Pedersen, S., Carozzi, M., Sommer, S., 2018. An Assessment of Low-Cost Techniques to Measure Ammonia Emission from Multi-Plots: A Case Study with Urea Fertilization. Agronomy 8, 245. https://doi.org/10.3390/agronomy8110245

Leuning, R., Freney, J.R., Denmead, O.T., Simpson, J.R., 1985. A sampler for measuring atmospheric ammonia flux. Atmospheric Environment (1967) 19, 1117–1124. https://doi.org/10.1016/0004-6981(85)90196-9

Misselbrook, T.H., Nicholson, F.A., Chambers, B.J., Johnson, R.A., 2005. Measuring ammonia emissions from land applied manure: an intercomparison of commonly used samplers and techniques. Environmental Pollution, The National Atmospheric Depostition PRogram (25th Anniversary) and Ammonia Workshop 135, 389–397. https://doi.org/10.1016/j.envpol.2004.11.012

Pacholski, A., Cai, G., Nieder, R., Richter, J., Fan, X., Zhu, Z., Roelcke, M., 2006. Calibration of a simple method for determining ammonia volatilization in the field – comparative measurements in Henan Province, China. Nutr Cycl Agroecosyst 74, 259–273. https://doi.org/10.1007/s10705-006-9003-4

R core team, 2019. R: A language and environment for statistical computing.

Ryden, J.C., Lockyer, D.R., 1985. Evaluation of a system of wind tunnels for field studies of ammonia loss from grassland through volatilisation. Journal of the Science of Food and Agriculture 36, 781–788. https://doi.org/10.1002/jsfa.2740360904

Sintermann, J., Neftel, A., Ammann, C., Häni, C., Hensen, A., Loubet, B., Flechard, C.R., 2012. Are ammonia emissions from field-applied slurry substantially over-estimated in European emission inventories? Biogeosciences 9, 1611–1632. https://doi.org/10.5194/bg-9-1611-2012

Tang, Z., Wen, C., Li, P., Wang, T., Zhou, Y., 2014. Effect of Zinc-Bearing Zeolite Clinoptilolite on Growth Performance, Nutrient Retention, Digestive Enzyme Activities, and Intestinal Function of Broiler Chickens. Biological Trace Element Research 158, 51–57. https://doi.org/10.1007/s12011-014-9900-3

Vilms Pedersen, S., 2018. Evaluation of a simple, small-plot meteorological technique for measurement of ammonia emission. American Society of Agricultural and Biological Engineers. Transactions 61, 103–115. https://doi.org/10.13031/trans.12445

Wilson, J.D., Catchpoole, V.R., Denmead, O.T., Thurtell, G.W., 1983. Verification of a simple micrometeorological method for estimating the rate of gaseous mass transfer from the ground to the atmosphere. Agricultural Meteorology 29, 183–189. https://doi.org/10.1016/0002-1571(83)90065-1

Wilson, J.D., Thurtell, G.W., Kidd, G.E., Beauchamp, E.G., 1982. Estimation of the rate of gaseous mass transfer from a surface source plot to the atmosphere. Atmospheric Environment (1967) 16, 1861–1867. https://doi.org/10.1016/0004-6981(82)90374-2

4.5. ARTICLE X: *"Clinoptilolite (E567), a natural zeolite, inclusion in heavy-pig diets: effect on the productive performance and gaseous emissions during fattening and manure storage"*

This article addresses emissions from pig houses and aims to avaluate the use of zeolite as a feed additive to reduce ammonia and greenhouse gases emissions. The interest for natural zeolite was determined by its many application for animal well-being and digestive health and by the interesting effects on meat productions shown by previous studies (Cevolani et al., 2010; Mumpton and Fishman, 1977). In fact, although there are many solutions to reduce emissions from animal houses, very few of those solutions provide improvements other than the emission reduction itself. Finding solutions that provide compelling advantages from the productive point of view, as well as from the environmental one, is one way of ensuring their future use in commercial farms. Many mitigation options, in fact, may be seen as nuisance from farmers, since they require additional costs or work, but do not supply any economical advantage. Moreover, the simplicity of use of feed additives as mitigation solutions, makes them particularly interesting for real world applications.

Journal of Agricultural Engineering (JAE), eISSN 2239-6268 (Submitted)

Authors: Elio Dinuccio, Jacopo Maffia, Carla Lazzaroni, Gianfranco Airoldi, Paolo Balsari, Davide Biagini

Abstract

Intensive pig rearing systems produce several air pollutant emissions, mainly associated with housing and slurry storage. Dietary strategies based on the use of feed additives can be effective in mitigating such impacts. This work has been aimed at evaluating the effectiveness of dietary zeolites in mitigating ammonia (NH_3), carbon dioxide (CO_2), methane (CH_4) and nitrous oxide (N_2O) emissions from piggery and slurry storage on finishing pig farms. An experimental trial, in which three groups of approximately 500 pigs each were reared, has been carried out on a commercial pig farm. The three groups were fed the same diet, with the addition of 0 g/kg (Z0, control), 10 g/kg (Z1) and 20 g/kg (Z2) of micronized clinoptilolite (E567), respectively. The emissions from housing facilities, as well as the live and slaughtering animal performances were assessed. In addition, manure samples were collected during the rearing period to evaluate, at a laboratory-scale, the NH_3, CO_2, CH_4 and N_2O emission potential during the subsequent slurry storage phase prior to land application. The results have shown that the addition of dietary zeolite can be considered a valid strategy to reduce gaseous emissions from pig houses, without affecting animal performances or the overall productivity of the system. Treatment Z2 gave the best results, and resulted in a 25% and 36% reduction of NH_3 and CO_2 equivalent emission fluxes, respectively, compared to those recorded for the control. The laboratory-scale experiment has revealed no significant effect of dietary clinoptilolite inclusion on NH_3 or on the greenhouse gas (GHG) emission potential during slurry storage.

Keywords: Pig; Ammonia; Greenhouse gases; Zeolite; Slurry storage.

Abbreviations

ADF, acid detergent fibre; ADG, average daily gain; Al_2O_3, aluminium oxide; aNDF, neutral detergent fibre; BW, body weight; CaO, calcium oxide; CH_4, methane; CO_2, carbon dioxide; CO_2eq, CO_2 equivalent; CP, crude protein; DM, dry matter; EE, ether extract; F, net emission flux; FCR, feed conversion rate; Fe_2O_3, ferric oxide; GHG, greenhouse gases; H_2O, water; K_2O, potassium oxide; MgO, magnesium oxide; Na_2O, sodium oxide; N_2O, nitrous oxide; NE, net energy; NH^+, ammonium cation; NH_3, ammonia; NH_3-N, ammonia nitrogen; NO_3, nitrates; PDO, protected designation of origin; SD, standard deviation; SEM, standard error of the mean; SiO_2, silicon dioxide; Sp, gas sampling points; TiO_2, titanium dioxide; TN, total nitrogen; VS, volatile solid; WB, wet basis; ZeoS, commercial clinoptilolite supplement used in the experiment; Z0, diet with the addition of 0 g/kg of ZeoS; Z1, diet with the addition of 10 g/kg of ZeoS; Z2, diet with the addition of 20 g/kg of ZeoS.

1. Introduction

The management of pig wastes, such as slurry and manure, produces ammonia (NH_3) emissions and greenhouse gases (carbon dioxide, CO_2; methane, CH_4; nitrous oxide, N_2O) (IPCC, 2014; Steinfeld et al., 2006). Ammonia is one of the environmental pollutants of greatest concern, as it is responsible for the formation of airborne particulate matter, the acidification of soils and water eutrophication

(Davidson et al., 2005; Philippe et al., 2011; Philippe and Nicks, 2015). Furthermore, a high concentration of NH_3 inside pig production buildings has negative effects on animal and human health (Michiels et al., 2015). Greenhouse gas (GHG) emissions are also of great concern, not only because of their effect on global warming, but also because the rise in the average temperatures, as a result of high GHG concentrations, could lead to an increase in NH_3 emissions from pig houses, thereby neutralising some of the efforts made to mitigate them (Schauberger et al., 2018). The proposed solutions for the abatement of polluting gas emissions from pig farms include a combination of nutrition strategies, techniques for treating the air against pollutants within buildings (e.g., an air scrubbing technology, bio-filters) and improved manure management practices.
The aim of this work has been to evaluate the efficacy of the addition of a zeolite (clinoptilolite type) to pig growing and fattening diets as a technique to mitigate gaseous emissions from pig houses and slurry storage. Zeolites are crystalline aluminosilicate minerals, which are characterised by a high porosity and the ability to exchange cations (Mumpton and Fishman, 1977; Reháková et al., 2004). Among the many different types of zeolites, clinoptilolite has been widely used in animal husbandry as a feed additive (Mumpton and Fishman, 1977) because of its strong exchange capacity with ammonium and its deodorising effect. Interest in this technique is due to the better efficiency in feed utilisation and the lower incidence of intestinal disease (Cevolani, 2010) that has been observed. The adsorption capacity of zeolites leads to a reduction in the intestinal concentration of ammonia, which is then slowly released during digestion, thereby promoting a better utilisation of feed nitrogen, a lower nitrogen excretion and, in turn, lower NH_3 emissions (Mercurio et al., 2016; Mumpton and Fishman, 1977). The capacity of zeolites of binding ammonia and, therefore, of reducing NH_3 emissions has been confirmed by many authors (Fokas et al., 2004; Milić et al., 2006; Poulsen and Oksbjerg, 1995). However, the information about the effects of zeolite integration on animal performances is contrasting, since some authors have observed practically no effects or even slightly worse performances (Fokas et al., 2004; Poulsen and Oksbjerg, 1995), while others have reported substantial improvements (Leung et al., 2007; Yannakopoulos et al., 2000). Furthermore, there is still a lack of information on the influence of such a dietary strategy on GHG emissions from pig houses and manure management.

2. Materials and methods

All the procedures involving animals were conducted according to the Italian Law that regulates animal welfare in scientific experiments (Legislative Decree DLgs 146/2001).

2.1. Clinoptilolite characteristics

Clinoptilolite is a natural form of zeolite (empirical formula: $(Ca, K_2, Na_2, Mg)_4\ Al_8\ Si_{40}\ O_{96}\cdot 24H_2O$). The zeolitic material used in the experiment (ZeoS: feed additive E567, produced by Zeocem, Bystré, Prešov region, the Slovak Republic) had a particle size of 50 μm, an average specific weight of 2320 kg/m^3 and contained clinoptilolite (875 g/kg), plagioclasi (95 g/kg) and illite (40 g/kg). The chemical composition was 684 g/kg silicon dioxide (SiO_2), 124 g/kg aluminium oxide (Al_2O_3), 39 g/kg calcium oxide (CaO), 28 g/kg potassium oxide (K_2O), 12 g/kg ferric oxide (Fe_2O_3), 8 g/kg magnesium oxide (MgO), 7 g/kg sodium oxide (Na_2O), 2 g/kg titanium dioxide (TiO_2) and 96 g/kg water (H_2O). The maximum total cation exchange capacity of the material was 1.5 mol/kg and the ammonium cation (NH^+) substitution capacity was 8500 mg/kg.

2.2. Animals: housing and diets

The experimental trial was conducted on a commercial fattening pig farm on the Po plain in North West Italy (Genola, Cuneo, Italy; 44°34′53″N, 7°39′08.4″E, at 340 m a.s.l.) which produces "Prosciutto di Parma" cured pork ham for the protected designation of origin (PDO) supply chain.

During a fattening period that lasted about 5 months (from 31 May to 27 October), an initial group of 1550 pigs (commercial hybrid L 1050, by PIC Italy, Perugia, both females and castrated males in an average 1:1 ratio) was reared inside a north-south oriented building with a total area of 1928.0 m^2 (120.5 m length x 16.0 m width), a height of 3.5 m at the eaves, and 6.5 m at the roof ridge. The building was made up of three consecutives rooms, which were separate from each other. Each room, used for one different treatment, was provided with mechanical ventilation and had 28 pens (2.80 x 6.50 m), while the floor was totally slatted. The ventilation system consisted of two series of 2 fans (EOLOSTAR ES-120, GigolA®, Brescia, Italy) installed on the two opposite sides of each room. Fresh air entered each room through openable windows located along the eaves. The ventilation system was equipped with automatic controls to provide an appropriate level of air exchange through the rooms and to limit rises in temperature in the facility during the summer. The opening of the windows was adjusted automatically to maintain a negative pressure of approx. 20 Pa between the inside of each room and the outside. The pits in the three rooms were also independent of each other and were equipped with a vacuum system to remove the slurry.

The animals were randomly assigned to each room and treatment, maintaining the 1:1 sex ratio, on arrival at the farm. The animal density inside the pens (18.4 pig/pen, at least 1 m^2 per pig at the end of the fattening period taking into account pig mortality) complies with the specific European Law requirements (European Council Directive 2008/120/EC) for the protection of pigs. The three animal groups were fed a wet diet based on whey and two commercial feedstuffs (M-90 and M-120, Martini SpA, Longiano, FC, Italy) containing corn, triticale, wheat bran, dehulled soybean, peas, calcium carbonate and sodium chloride, according to a two-phase diet programme (the first phase lasted 76 days, from 50 till 120 kg of average bodyweight, BW, and the second one lasted 73 days till slaughtering, at about 170 kg of average BW). The whey addition ranged between 2:1 to 3:1 on weight basis of feedstuff given according to the animal weight. After a 30-day adaptation period, the feedstuff was integrated with the addition of 0 g/kg (control diet, Z0), 10 g/kg (Z1) and 20 g/kg (Z2), of ZeoS, on a wet basis before whey addition, with a total cost (purchase plus delivery to the farm) of 0.305 €/kg. The feed characteristics given by the feedstuff company are reported in Table 1. The feed was sampled monthly after whey addition to verify the diet composition, determined according to the following AOAC (2006) methods: preparation of an analytical sample (950.02 method), dry matter (DM) content (934.01); total ash (942.05 method); crude protein (CP) content (984.13 method); ether extract (EE) content (2003.05 method); neutral detergent fibre (aNDF) content (2002.04 method); acid detergent fibre (ADF) content (973.18 method). The net energy (NE) of feed was calculated on the basis of the caloric content of the nutritional components detected with the chemical analysis.

Table 1. Composition and mineral-vitamin-enzymatic supplementation per kg as fed of feedstuff

	first phase (until 120 kg BW)	**second phase (until slaughter)**
Crude protein (g)	133	110
Ether extract (g)	42	43
Crude cellulose (g)	40	29
Ash (g)	42	34
Lysine (g)	8	5.9
Methionine (g)	2.1	1.8
Ca (g)	0.54	0.47
P (g)	0.39	0.33
Na (g)	0.20	0.20
Vitamin A (U.I.)	6500	5200
Vitamin D3 (U.I.)	1500	1200
Vitamin E (mg)	55	44
Biotin (mg)	0.10	0.08
Vitamin K3 (mg)	4.0	3.2
Niacin (mg)	30	24

Folic acid (mg)	0.80	0.64
Vitamin B1 (mg)	2.5	2.0
Vitamin B2 (mg)	5.0	4.0
Vitamin B6 (mg)	3.8	3.0
Vitamin B12 (mg)	0.030	0.024
6-phyitase (FYT)	1000	1000

2.3. Live and slaughtering performances

The initial and final BW (kg) of the pigs, as well as the feed intake, were recorded by trained operators during the experimental period. The pigs were weighed individually, using platform scales (Model EC2000, Tru-Test Limited, Auckland, New Zealand) to determine the initial and final BW. The feed intake was recorded per pen, the distributed feed was weighed and its total consumption verified. The average daily gain (ADG, kg/d) and feed conversion rate (FCR, kg WB/kg BW) were calculated on the basis of these data.

At the end of the fattening period, the pigs were slaughtered in an authorised slaughterhouse. The carcass weight, the dressing percentage, the rib muscle thickness, the back fat depth and the EUROP carcass grade were determined at slaughtering, using an online weight scales and a Fat-O-Meat'er II^{TM} instrument (Frontmatec, Kolding, Denmark), according to the European Commission Implementing Decision 2014/38/EU.

Since slaughtering was performed without detachment of some anatomical parts (e.g. flare fat, kidneys and diaphragm), the carcass weight was corrected according to the European legislation (attachment V part B Council Regulation (EC) 1234/2007) to obtain the standard carcass weight.

2.4. Evaluation of the emissions derived from the housing facilities

In order to evaluate the gaseous emissions from the pig house rooms, weekly measurements of the environmental concentrations of CO_2, CH_4, N_2O and NH_3 were carried out using an infrared photoacoustic multi-gas analyser (INNOVA 1412, AirTech Instruments, Ballerup, Denmark). Seven gas measuring points were identified in each room in order to obtain a representative dataset of the gaseous emission rates: four (Sp_{1-4}) for the inlet gas concentrations and three (Sp_{5-7}) for the outlet ones. The Sp_{1-4} sampling points were located outside, close to the air inlets, and were arranged symmetrically (two on each side of the room). The Sp_{5-7} sampling points were inside the room, and were spaced equally along the longitudinal symmetry line at the same height as the rotation axis of the ventilation fans.

Before starting each measurement, the flow rate of the fans was measured using a vane type anemometer (Model 416, Testo Ltd, Alton, Hampshire, UK)

connected to a Testo 400 data logger. The multi-gas analyzer simultaneously measured the concentration of the target gases (CO_2, CH_4, N_2O and NH_3) plus relative humidity (RH) in air samples. The air temperature inside each room was also detected during each measurement, using temperature data loggers (Model U12-014, HOBO, Onset Computer Corporation, Bourne, MA, USA).
The detected NH_3 and GHG concentrations (mg/m^3) were related to the air ventilation rate and expressed on a per pig basis. The net emission flux of each gas (*F*, mg/h/head) was calculated as follows:

where *Cout* is the outlet gas concentration (mg/m^3), *Cin* is the air inlet gas concentration (mg/m^3), *Q* is the air flow rate (mg/h) and *n* is the number of animals housed in the room at the time of each measurement.
The total NH_3, CO_2, CH_4, and N_2O (*Ec*, kg/head) emitted during the fattening period were estimated as follows:

where *Fm* is the average net emission flux value (mg/h/head) of two consecutive measurements; *n* is the number of measurements carried out during the trial; *t* is the duration of the time-lapse between two measurements (h). The CO_2 equivalent (CO_2eq) emissions were calculated by multiplying the CO_2, CH_4 and N_2O emissions by their 100 year global warming powers (1, 28 and 265, respectively), as suggested by IPCC (2014).

2.5. Evaluation of the emission potential during slurry storage

In order to evaluate whether the dietary addition of ZeoS could influence NH_3 and GHG emissions during storage, a laboratory experiment was carried out on slurry samples collected during pig rearing. Slurry sub-samples were taken monthly; this involved inserting a specific slurry sampler into an inspection well when the pit was being emptied. The inspection well was placed on the pipeline connecting the under-floor slurry pit of each room to the storage tank outside the building. The collected slurry sub-samples were stored at +4 °C in sealed plastic barrels and were used to produce three composite slurry samples (one per treatment) for the storage trial.
Before starting the trial, the composite slurry samples were analysed to determine the dry matter content (DM; g/kg on a wet basis, WB), volatile solid content (VS; g/kg on DM), the total nitrogen content (TN; g/kg on WB, the 984.13 method in AOAC, 2006), the ammonia nitrogen content (NH_3-N; g/kg on WB, the 941.04 method in AOAC, 2006) and pH. The DM of the slurries was determined by drying weighed slurry samples in an oven (Model ABS 220-4, Kern & Sohn gmbH, Balingen, Germany) at 105 °C for 24 h. The volatile solid content was determined by igniting the weighed slurry samples in a muffle furnace (Model TCN115, Argo Lab, Carpi, MO, Italy) at 450 °C for 4 hours. The pH was determined using a pH-meter (Model HI 9026, Hanna Instruments Italia srl, Ronchi di Villafranca Padovana, PD, Italy).
During the laboratory test, three 4 L homogeneous slurry aliquots of each treatment were stored, for a thirty-day period, in nine experimental 5 L capacity

glass jars. The storage was performed at room temperature (17.01±2.2 °C). Gaseous emissions were measured by means of a ventilated chamber system and using an infrared photoacoustic multi-gas analyser (INNOVA 1412, AirTech Instruments, Ballerup, Denmark), as described by Dinuccio et al. (2008, 2011, 2019).
The emission fluxes (F, mg/h/m^2) of NH_3 and GHG from each jar were calculated according to the following formula:

where i is the gas concentration detected by the photoacoustic analyser in mg/m^3; Q is the air exchange rate inside the jars (0.06 m^3/h); S is the free slurry surface area (m^2).
The average daily emission rates (Er, mg/m^2/d^1) were then calculated as follows:

where Fv is the average emission flux value (mg/h/m^2) between two consecutive measurements; n is the number of measurements carried out during the trial; t is the number of hours that elapsed between two measurements; d is the overall duration of the storage period (days).
The CO_2eq emissions were estimated as described in the section above (2.4).

2.6. Statistical analysis
The collected data were analysed by statistical means, using the GLM (IBM SPSS, 2017) procedure. The data related to the initial BW (kg) of the animals, to environmental condition of the fattening rooms (temperature and relative humidity) and to the gas emissions, from both housing (kg/pig) and storage (g/m^2/d), were assessed, after testing their normal distribution and their heteroscedasticity (Shapiro-Wilk test and Levene test), using the GLM ANOVA procedure (IBM SPSS, 2017), according to the following model:
$y = \mu + \alpha_i + \varepsilon_{ij}$
where μ is the general mean value; α_i is the ZeoS integration effect; ε_{ij} is the random error effect.
Moreover, given that the three groups of animals had a different average initial and final BW, the data related to the live and slaughtering performances were tested using the GLM ANCOVA procedure (IBM SPSS, 2017), according to the following model:
$y = \mu + \alpha_i + \beta(x_{ij}-x) + \varepsilon_{ij}$
where μ is the general mean value; α_i is the ZeoS integration effect; $\beta(x_{ij}-x)$ is the effect linearly associated with the initial BW (for live performances) and with the final BW (for slaughtering performances); ε_{ij} is the random error effect.
Differences in the mean values were tested, by means of the Duncan test, using a first class error α = 0.05 to accept the differences as significant.

3. Results
3.1. Effects on animal performances
During the experimental period diets composition used for the different animal groups (Table 2) showed no differences between the three groups for both the two feeding phases. The live and slaughtering performances of the three tested animal

groups are shown in Table 3. After the weaning phase, the animals were divided into the experimental groups on arrival at the fattening farm. At the beginning of the experimental period, the Z0 group showed a slightly higher initial BW than the other groups (P<0.05). Although the three experimental groups did not result balanced in terms of weight, in order to avoid increasing the stress conditions among the piglets, which could have affected the live performance of some subjects (feed consumption, weight gain, etc.), it was decided not to move the animals at this stage. This decision allowed any uncontrollable variables to be eliminated. The GLM ANCOVA analysis revealed that the final BW, the weight gain and ADG had higher estimated means in the Z0 and Z2 groups than in Z1 (P<0.05), whereas the Z2 group showed the most favourable FCR (P<0.05).
As far as the slaughtering performance is concerned, the Z0 group showed higher dressing percentages and carcass weights than the Z1 and Z2 groups (P<0.01). The treatment did not affect the rib muscle thickness, but the back fat depth was greater in the Z0 and Z2 groups than in the Z1 group (P<0.01). Consequently, the carcass grade was also affected, and the Z0 and Z2 groups had more carcasses classified as E and U than the Z1 group, and therefore a higher lean meat yield.

Table 2. Diet composition in the two feeding phases for the three groups of pigs.

	first phase (until 120 kg BW)					**second phase (until slaughter)**				
	Z0	**Z1**	**Z2**	**SEM**	***P***	**Z0**	**Z1**	**Z2**	**SEM**	***P***
DM (g/kg)	192.15	193.83	199.26	3.143	.636	172.17	171.41	175.83	1.122	.279
Ash (g/kg DM)	63.76	64.76	66.05	.349	.053	72.80	74.44	76.48	.911	.304
CP (g/kg DM)	152.66	153.50	152.15	1.096	.881	133.13	132.18	131.37	1.226	.844
EE (g/kg DM)	43.28	39.20	41.31	.951	.246	43.23	47.49	44.23	.652	.061

aNDF (g/kg DM)	136.25	136.43	137.66	1.510	.917	112.89	118.56	119.09	2.163	.463
ADF (g/kg DM)	49.12	51.83	51.86	.688	.209	44.17	47.01	48.07	2.017	.725
NE (MJ/ kgDM)	8.84	8.78	8.78	.020	.382	8.90	8.90	8.81	.031	.372

BW, body weight; DM, dry matter; CP, crude protein; EE, ether extract; aNDF, neutral detergent fibre; ADF, acid detergent fibre; NE, net energy; Z0, control diet with 0 g/kg of ZeoS; Z1, diet with the addition of 10 g/kg of ZeoS; Z2, diet with the addition of 20 g/kg of ZeoS; SEM, standard error of the mean (calculated on 6 replicates).

Table 3. Live performances (adjusted for an initial BW = 51.69) and slaughtering performances (adjusted for a final BW = 175.65) for the three groups of pigs.

	Z0		Z1		Z2		SEM	*P*
Live performances								
Initial BW (kg)	54.43	a	50.38	b	50.46	b	0.567	0.013
Final BW (kg)	177.16	a	173.53	b	176.25	a	0.455	0.024
Weight gain (kg)	125.46	a	121.83	b	124.55	a	0.455	0.024
ADG (kg/d)	0.80	a	0.78	b	0.80	a	0.003	0.024
FCR (kg WB/kg BW)	3.33	a	3.35	a	3.25	b	0.013	0.011
Slaughtering performances								
Carcass yield (kg/100 kg BW)	84.81	A	83.94	B	83.36	C	0.067	<0.001

Hot standard carcass weight (kg)	144.30	A	142.85	B	141.85	C	0.112	<0.001
Cold standard carcass weight (kg)	141.42	A	139.99	B	139.02	C	0.110	<0.001
Back fat depth (mm)	36.08	A	37.46	B	35.86	A	0.229	0.009
Rib muscle thickness (mm)	68.81		69.29		70.41		0.290	0.066
Carcass classification (1E-5P)	2.62	B	2.79	A	2.60	B	0.024	0.002

BW, body weight; ADG, average daily gain; FCR, feed conversion rate; WB, wet basis; Z0, control diet with 0 g/kg of ZeoS; Z1, diet with the addition of 10 g/kg of ZeoS; Z2, diet with the addition of 20 g/kg of ZeoS; SEM, standard error of the mean (calculated on 28 and 252 replicates for live performances and slaughtering performances respectively). Treatment means with the same letter are not significantly different (P>0.05).

3.2. Effects of housing on the emissions

Temperature and relative humidity trends during fattening are presented in Fig. 1. The average air temperatures measured inside the rearing facility during the trial were 26.41 ± SD 3.18, 26.55 ± SD 3.00 and 26.25 ± SD 2.65 °C for Z0, Z1 and Z2, respectively, with no significant difference (P>0.05) between the three rooms. Average relative humidity was equal to 74.8 ± SD 6.36, 76.4 ± SD 6.78 and 74.9 ± SD 5.76 % in Z0, Z1 and Z2, respectively, with no significant difference (P>0.05) between the three rooms. Similarly, no statistically different average air flow rates (P>0.05) were recorded during the gas emission measurements, which ranged from 157 to 173 m^3/head/h, between the control room (Z0) and the treatment pig-rearing rooms (Z1, Z2). Therefore, it was possible to make a meaningful comparison between the emission rates in the three rooms.

As can be seen in Table 4, the addition of ZeoS to the diets led to significantly (P<0.05) lower cumulated NH_3 emissions in the Z1 and Z2 groups than in the control group (Z0). The greenhouse gas emissions were also significantly reduced, and in particular the CO_2 and CH_4 emission levels, which were lowered by 18% and 12% (in the Z1 group) and by 51% and 31% (in the Z2 group), respectively. The cumulated N_2O emissions were found to only be affected slightly, with a significant (P<0.05) 5.13% reduction in the Z2 group. The total GHG emission reductions in the Z1 and Z2 groups, in terms of CO_2 equivalents, were equal to 13% and 36%, respectively.

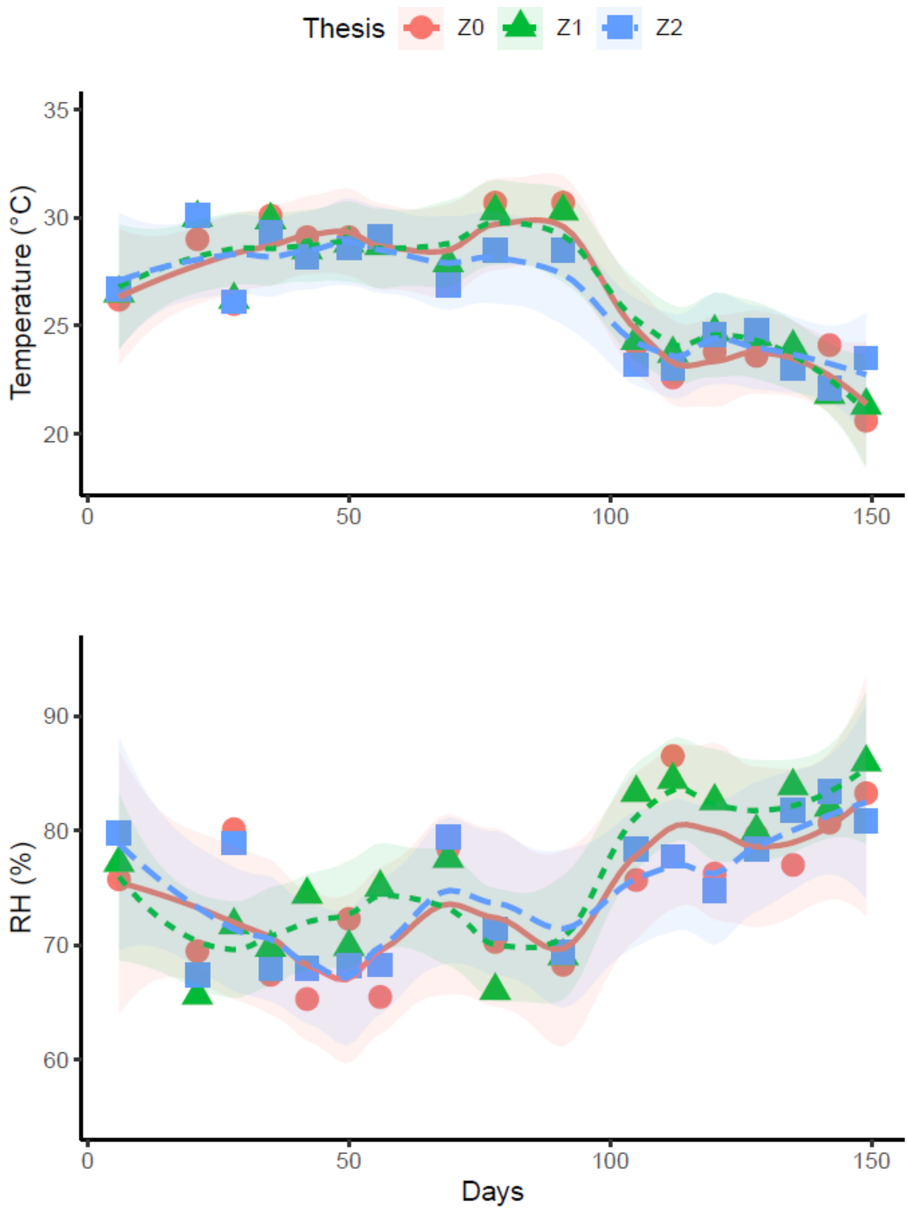


Fig. 1. Temperature and relative humidity (RH) trends during fattening (each point represents the T and RH value averaged over three sampling points, with 10 measures per point, in each chamber; n = 30); graphs are obtained using ‘geom_smooth’ function of R package ggplot2 and adopting a “loess” smoothing method (Wickham, 2016; R core team, 2019)

Table 4. Total gaseous emissions from pig houses for the three groups of pigs.

	Z0		Z1		Z2		SEM	*P*
NH_3 (kg/pig)	1.79	a	1.62	b	1.34	c	0.019	<0.001
CO_2 (kg/pig)	1358.00	a	1194.90	b	934.80	c	30.670	<0.001
CH_4 (kg/pig)	25.39	a	20.79	b	12.43	c	0.848	<0.001
N_2O (kg/pig)	0.39	a	0.38	a	0.37	b	0.004	0.006
CO_2eq (kg/pig)	2172.76	a	1878.41	b	1379.86	c	53.801	<0.001

NH_3, ammonia; CO_2, carbon dioxide; CH_4, methane; N_2O, nitrous oxide; CO_2eq, carbon dioxide equivalent; Z0, control diet with 0 g/kg of ZeoS; Z1, diet with the addition of 10 g/kg of ZeoS; Z2, diet with the addition of 20 g/kg of ZeoS; SEM: standard error of the mean (calculated on 3 replicates).
Treatment means with the same letter are not significantly different (P>0.05).

3.3. Effects on the slurry composition and emission potential during storage
The composition of the control slurry (Z0) and the slurries from the treated groups (Z1, Z2) are shown in Table 5. Comparisons of the mean values of the measured slurry parameters exhibited significant (P<0.05) variations with respect to DM, VS and pH. The DM content varied from 50.70 g/kg in Z2 to 50.30 g/kg in Z0 and 42.70 g/kg in Z1. At the same time, the VS/DM ratio was equal to 0.65 in Z0, 0.64 in Z2 and 0.64 in Z1. The pH, on average, was equal to 7.47, and was higher for Z0 than for Z1 and Z2. Nevertheless, there was no significant difference (P>0.05) between treatments, in terms of TN and NH_3-N content, with overall means of 4.40 and 2.30 g/kg, respectively, for all the slurries. Similarly, the GHG and NH_3 emissions that occurred during slurry storage did not vary significantly (P>0.05) for the three treatments (Table 5).

Table 5. Main slurry characteristics for the three groups of pigs.

	Z0		Z1		Z2		SEM	*P*
DM (g/kg)	50.27	b	42.74	c	50.70	a	0.642	<0.001
VS (g/kg WB)	32.87	a	27.14	c	32.59	b	0.548	0.010
TN (g/kg WB)	4.55		4.19		4.52		0.009	0.063
NH_3-N (g/kg WB)	2.32		2.24		2.30		0.006	0.597
pH	7.55	a	7.47	b	7.39	c	0.007	0.021

DM, dry matter; VS, volatile solids; TN, total nitrogen; WB, wet basis; NH_3-N, ammonia nitrogen; Z0, control diet with 0 g/kg of ZeoS; Z1, diet with the addition of 10 g/kg of

ZeoS; Z2, diet with the addition of 20 g/kg of ZeoS; SEM, standard error of the mean (calculated on 3 replicates).
Treatment means with the same letter are not significantly different (P>0.05).

4. Discussion

In spite of the addition of ZeoS, that according to the experimental plan is 10-20 g/kg of feedstuff before the whey addition (and therefore corresponding only to 2-4 g/kg of DM increment to the final diet), the ash content of the different diets did not change significantly between groups and phases (Table 2). Moreover, the regulation of the PDO (which pigs are intended) recommended a diet ash content in the second phase feed between 4 and 8% on DM. The commercial feedstuff of the first and second phases had an ash content of 4.2 and 3.5% as fed respectively, but the whey (varying composition according to the lot supplied) had higher ash concentration (about +2%) in the last period than in the first one and this affected the total ash content of the diet determined by analysis. The addition of clinoptilolite to the diet slightly affected the live performance of the pigs, albeit only slightly (Table 2). The Z2 group showed the same live performances as the Z0 one, except for the FCR. Although zeolite, and clinoptilolite in particular, is usually added to animal feeds at a level of 20–25 g/kg (Fokas et al., 2004), the 20 g/kg of zeolite supplementation used in our trial may have been too low to trigger an improvement in animal performances. Fokas et al. (2004), conducted a study on the effects of the addition of 20 g/kg zeolite to the diet of pigs and did not find any significant effect on the live performances of the animals. On the other hand, a study in which a higher concentration of zeolites (50 g/kg) had been used (Mumpton and Fishman, 1977), showed some improvements in terms of weight gain. Similarly, Yannakopoulos et al. (2000) observed improvements in weight gain and FCR after adding 60 g/kg of clinoptilolite-rich tuff to finishing pig diets. Moreover, it should be noted that in our study the ZeoS inclusion only pertained to the growing and finishing phases. This could have affected the obtained results. In fact, Alexopoulos et al. (2007) found that the long-term dietary use of clinoptilolite, at an inclusion of 20 g/kg, appeared to enhance the performance of growing and fattening pigs without adversely affecting their health status. They already recorded a higher weight gain during the weaning stage (70 days), which also affected the performance of the whole growing period. Prvulovic et al. (2007) found that, during the first 90 days of an experiment with a diet inclusion of 5 g of clinoptilolite per kilogram of feed in growing pigs, the treated group showed a higher body weight gain than with the control one, and the growth parameters were significantly lower in the finishing phase (-4.8%), results that would seem to confirm our results. The observed variations in slaughtering performance (Table 3) did not affect the quantity or quality of the obtained productions to any great extent. To the best of our knowledge, this is the first study to have reported the effect of zeolite addition to the diet on the slaughtering performance of heavy-pigs. Further studies should include this aspect, particularly as regard the carcass grade, a key parameter for the production of PDO ham in Italy.
The cumulated NH_3 and GHG emissions from the housing facilities resulted to be influenced to a great extent by the addition of ZeoS to the diets (Table 4).

As expected, the ammonia emissions were reduced ($P<0.05$) in the Z1 and Z2 groups, by 9% and 25%, respectively, compared to the control group (Z0). This result is similar to the one obtained by Milić et al. (2006), who observed a 33% NH_3 emission reduction in piglets, after implementing an integration of 20 g/kg of zeolite integration in their diet. Similarly, the CO_2 and CH_4 emission levels (Table 4) resulted significantly ($P<0.05$) higher for Z0 than for Z1 and Z2 groups. Although little information is currently available in literature on dietary clinoptilolite supplementation as a GHG emission mitigation technique on pig farms, the adsorption properties of clinoptilolite, with respect to CO_2 and CH_4, has been well documented (Arefi Pour et al., 2015; Hao et al., 2018; Kennedy et al., 2019), thus making it a potential tool for gas purification. The adsorption effect of clinoptilolite on CH_4 could have been exerted both during the digestion phase, by reducing the enteric CH_4 production, and on the CH_4 produced by anaerobic microbial degradation of the slurry organic matter in the slurry pit (Philippe and Nicks, 2015). Moreover, the capacity of clinoptilolite to adsorb CH_4 is related to its surface area and pore volume (Arefi Pour et al., 2015) and to the specific ions that clinoptilolite is cation-exchanged with (Kennedy et al., 2019); it therefore depends on the particular type of clinoptilolite that is used.
The net NH_3 emission fluxes recorded during the rearing period (Table 4) for the Z0 group were 0.53 mg/h/head^{-1} on average, which is equivalent to an annual amount of 3.81 kg/head/year. The latter figure falls within the range of those given for typical heavy-pig rearing systems in Italy, that is, ranging from 1.7 (Guarino et al., 2003) to 6.29 (Costa, 2017) kg/pig/year. However, the average annual N_2O (0.832 kg/pig) and CH_4 (54.2 kg/pig) EFs estimated in this study were 2.9 and 3.2 times higher than those reported by Costa and Guarino (2009) for fattening pigs with more than 110 kg of live weight. The higher N_2O and CH_4 emissions found in our study could be attributed to several factors, including differences in diet composition and housing conditions (Philippe and Nicks, 2015). Moreover, the measurements in our study were performed under summer-autumn conditions, with an average internal temperature ranging from 20.6 to 30.7 °C, while the EFs reported by Costa and Guarino (2009) were based on measurements performed in three different periods of the year, including winter conditions (room temperature ranging from 15.0 to 21.0 °C). The presence of a forced ventilation system (instead of a natural one) could also have determined higher gaseous emissions, as pointed out in previous studies (Gallmann et al., 2003; Philippe et al., 2007; Blanes-Vidal et al., 2008).
The GHG and NH_3 emissions that occurred during slurry storage did not vary significantly for the three treatments (Table 6). This absence of variation, especially in terms of NH_3 emissions, could be attributed to the low concentration of ZeoS in the slurry biomass. Considering that the ZeoS in the diets did not accumulate in the animal bodies and the total mass of slurry produced during the rearing cycle (about 1.5 m^3/head), which was estimated using the reference guideline values reported in the Piedmont region regulations (DPGR 10/R, 2007), the concentration of ZeoS in the stored slurry was calculated to be approximately 0.17% (on WB). This concentration is lower than the one adopted by Lefcourt and Meisinger (2001), who observed an NH_3 emission reduction in dairy slurry

of about 50% as a result of adding 6.25% of zeolites. Moreover, the capacity of ZeoS to mitigate NH_3 and GHG emissions could have been depleted during housing, thereby having no further effect in the subsequent phases. On the other hand, there seems to have been an increasing CH_4 emission trend (even though no significant variation was detected) as the zeolite concentration was increased. Therefore, it could be hypothesised that the adsorption of CH_4 during housing can lead to an increase in storage CH_4 emissions due to a delayed release of the pollutant.

5. Conclusions

The dietary addition of ZeoS, at both 10 and 20 g/kg, was able to reduce NH_3, and GHG emissions from pig houses. Of the two ZeoS concentrations that were tested, the 20 g/kg one resulted in a higher mitigation effect, reducing NH_3 and GHG emissions by about 25% and 36%, respectively. The increase in the feeding cost per head, as a result of a 20 g/kg supplementation in the diet, can be calculated as approximately € 0.02 per day, that is, about 1.5% of the current selling price of heavy-pigs in Italy. This cost could be acceptable at a farm level, but this depends on the general production costs and on the sale price of the pigs, which vary over time according to market dynamics. Nevertheless, the manure storage trial showed an increasing trend in CH_4 emissions as ZeoS concentration in the diet was increased, thus suggesting that the adsorption of CH_4 during housing could lead to an increase in storage CH_4 emissions due to a delayed release of the pollutant. Therefore, ZeoS could be a valid tool to mitigate CH_4 emissions during housing, but only if coupled with other mitigation strategies (such as covering the storage tank) to prevent the loss of saved CH_4 in the subsequent phases of the manure management cycle.

Conflict of Interest

None.

Acknowledgments

This work has been realised within the “Strategie innovative per la riduzione dell'impatto ambientale e l'incremento delle performance produttive negli allevamenti suinicoli (Innovative strategies for reducing environmental impact and increasing production performance on pig farms)” project, funded by the Fondazione Cassa di Risparmio di Torino (CRT foundation) [grant numbers 2016.2508].

References

Alexopoulos C, Papaioannou DS, Fortomaris P, Kyriakis CS, Tserveni-Goussi A, Yannakopoulos A, Kyriakis SC, 2007. Experimental study on the effect of in feed administration of a clinoptilolite-rich tuff on certain biochemical and hematological parameters of growing and fattening pigs. Livest. Sci. 111, 230–241. https://doi.org/10.1016/j.livsci.2007.01.152

AOAC International, 2006. Official methods of analysis of the Association of Official Analytical Chemists, 18th ed. Association of Official Analytical Chemists, Gaithersburg, MD, USA.
Arefi Pour A, Sharifnia S, NeishaboriSalehi R, Ghodrati M, 2015. Performance evaluation of clinoptilolite and 13X zeolites in CO_2 separation from CO_2/CH_4 mixture. J. Nat. Gas Sci. Eng. 26, 1246–1253. https://doi.org/10.1016/j.jngse.2015.08.033
Blanes-Vidal V, Hansen MN, Pedersen S, Rom HB, 2008. Emissions of ammonia, methane and nitrous oxide from pig houses and slurry: effects of rooting material, animal activity and ventilation flow. Agric. Ecosyst. Environ. 124, 237–244. https://doi.org/10.1016/j.agee.2007.10.002
Cevolani D, 2010. Prontuario degli alimenti per il suino. Edagricole, Bologna, Italy.
Commission Implementing Decision of 24 January 2014 authorising methods for grading pig carcases in Italy (notified under document C(2014) 279) (Only the Italian text is authentic) (2014/38/EU); ELI: http://data.europa.eu/eli/dec_impl/2014/38/2014-01-01
Costa A, 2017. Ammonia concentrations and emissions from finishing pigs reared in different growing rooms. J. Environ. Qual. 46, 255–260. https://doi.org/10.2134/jeq2016.04.0134
Costa A, Guarino M, 2009. Definition of yearly emission factor of dust and greenhouse gases through continuous measurements in swine husbandry. Atmos. Environ. 43, 1548–1556. https://doi.org/10.1016/j.atmosenv.2008.11.009
Council Directive 2008/120/EC of 18 December 2008 laying down minimum standards for the protection of pigs (Codified version) OJ L 47, 18.2.2009, p. 5–13. ELI: http://data.europa.eu/eli/dir/2008/120/oj
Council Regulation (EC) No 1234/2007 of 22 October 2007 establishing a common organisation of agricultural markets and on specific provisions for certain agricultural products (Single CMO Regulation) OJ L 299, 16.11.2007, p. 1–149 ELI: http://data.europa.eu/eli/reg/2007/1234/oj
Davidson CI, Phalen RF, Solomon PA, 2005. Airborne particulate matter and human health: A review. Aerosol Sci. Technol. 39, 737–749. https://doi.org/10.1080/02786820500191348
Dinuccio E, Berg W, Balsari P, 2008. Gaseous emissions from the storage of untreated slurries and the fractions obtained after mechanical separation. Atmos. Environ. 42, 2448-2459. https://doi.org/10.1016/j.atmosenv.2007.12.022
Dinuccio E, Berg W, Balsari P, 2011. Effects of mechanical separation on GHG and ammonia emissions from cattle slurry under winter conditions. Anim. Feed Sci. Technol. 166-167, 532-538. https://doi.org/10.1016/j.anifeedsci.2011.04.037
Dinuccio E, Biagini D, Rosato R, Balsari P, Lazzaroni C, 2019. Organic matter and nitrogen balance in rabbit fattening and gaseous emissions during manure storage and simulated land application. Agric. Ecosyst. Environ. 269, 30–38. https://doi.org/10.1016/j.agee.2018.09.018

DLgs 146/2001. Decreto Legislativo 26 marzo 2001, n. 146 "Attuazione della direttiva 98/58/CE relativa alla protezione degli animali negli allevamenti", Gazzetta Ufficiale n. 95 del 24 aprile 2001, 21-25, Italia.

DPGR 10/R, 2007. Regolamento regionale recante: "Disciplina generale dell'utilizzazione agronomica degli effluenti zootecnici e delle acque reflue e programma di azione per le zone vulnerabili da nitrati di origine agricola (Legge regionale 29 dicembre 2000, n. 61)". Bollettino Ufficiale Regione Piemonte, Italia, n. 44, 31/10/2007. http://www.regione.piemonte.it/governo/bollettino/abbonati/2007/44/siste/00000001.htm.

Fokas P, Zervas G, Fegeros K, Zoiopoulos P, 2004. Assessment of Pb retention coefficient and nutrient utilization in growing pigs fed diets with added clinoptilolite. Anim. Feed Sci. Technol. 117, 121–129. https://doi.org/10.1016/j.anifeedsci.2004.06.005

Gallmann E, Hartung E, Jungbluth T, 2003. Long-term study regarding the emission rates of ammonia and greenhouse gases from different housing systems for fattening pigs-final results. In: Commission Internationale de Génie Rural (Ed.), Proceedings of the International Symposium on Gaseous and Odour Emissions from Animal Production Facilities, Danish Institute for Agricultural Sciences Foulum, Denmark, pp. 122–130.

Guarino M, Fabbri C, Navarotto P, Valli L, Mascatelli G, Rossetti M, Mazzotta V, 2003. Ammonia, methane and nitrous oxide emissions and particulate matter concentrations in two different buildings for fattening pig. In: Commission Internationale de Génie Rural (Ed.), Proceedings of the International Symposium on Gaseous and Odour Emissions from Animal Production Facilities, Danish Institute for Agricultural Sciences Foulum, Denmark, pp. 140–149.

Hao X, Hu H, Li Z, Wu L, Liu X, Zhang Y, 2018. Adsorption properties of modified clinoptilolite for methane and nitrogen. Materials 11, 2024, 12 pp. https://doi.org/10.3390/ma11102024

IBM SPPS, 2017. IBM SPSS Statistics 25.0. SPSS Inc., Chicago, USA.

IPCC Intergovernmental Panel on Climate Change, 2014. Climate Change 2014 Mitigation of Climate Change: Working Group III Contribution to the Fifth Assessment Report of the Intergovernmental Panel on Climate Change. Cambridge University Press, Cambridge. https://doi.org/10.1017/CBO9781107415416

Kennedy DA, Mujčin M, Abou-Zeid C, Tezel FH, 2019. Cation exchange modification of clinoptilolite – thermodynamic effects on adsorption separations of carbon dioxide, methane, and nitrogen. Micropor. Mesopor. Mat. 274, 327–341. https://doi.org/10.1016/j.micromeso.2018.08.035

Lefcourt AM, Meisinger JJ, 2001. Effect of adding alum or zeolite to dairy slurry on ammonia volatilization and chemical composition. J. Dairy Sci. 84, 1814–1821. https://doi.org/10.3168/jds.S0022-0302(01)74620-6

Leung S, Barrington S, Wan Y, Zhao X, El-Husseini B, 2007. Zeolite (clinoptilolite) as feed additive to reduce manure mineral content.

Bioresour. Technol. 98, 3309–3316. https://doi.org/10.1016/j.biortech.2006.07.010
Mercurio M, Cappelletti P, de Gennaro B, de Gennaro M, Bovera F, Iannaccone F, Grifa C, Langella A, Monetti, V, Esposito L, 2016. The effect of digestive activity of pig gastro-intestinal tract on zeolite-rich rocks: An in vitro study. Micropor. Mesopor. Mat. 225, 133–136. https://doi.org/10.1016/j.micromeso.2015.11.039
Michiels A, Piepers S, Ulens T, Van Ransbeeck N, Del Pozo Sacristán R, Sierens A, Haesebrouck F, Demeyer P, Maes D, 2015. Impact of particulate matter and ammonia on average daily weight gain, mortality and lung lesions in pigs. Prev. Vet. Med. 121, 99–107. https://doi.org/10.1016/j.prevetmed.2015.06.011
Milić D, Tofant A, Vučemilo M, Venglovsky J, Ondrašovič O, 2006. The performance of natural zeolite as a feed additive in reducing aerial ammonia and slurry ammonium ion concentration in the pig farm nursery. Folia Vet. 49, 23–25.
Mumpton FA, Fishman PH, 1977. The application of natural zeolites in animal science and aquaculture. J. Animal Sci. 45, 1188–1203. https://doi.org/10.2527/jas1977.4551188x
Philippe F-X, Laitat M, Canart B, Vandenheede M, Nicks B, 2007. Comparison of ammonia and greenhouse gas emissions during the fattening of pigs, kept either on fully slatted floor or on deep litter. Livest. Sci. 111, 144–152. https://doi.org/10.1016/j.livsci.2006.12.012
Philippe F-X, Cabaraux J-F, Nicks B, 2011. Ammonia emissions from pig houses: Influencing factors and mitigation techniques. Agric. Ecosyst. Environ. 141, 245–260. https://doi.org/10.1016/j.agee.2011.03.012
Philippe F-X, Nicks B, 2015. Review on greenhouse gas emissions from pig houses: Production of carbon dioxide, methane and nitrous oxide by animals and manure. Agric. Ecosyst. Environ. 199, 10–25. https://doi.org/10.1016/j.agee.2014.08.015
Poulsen HD, Oksbjerg N, 1995. Effects of dietary inclusion of a zeolite (clinoptilolite) on performance and protein metabolism of young growing pigs. Anim. Feed Sci. Technol. 53, 297–303. https://doi.org/10.1016/0377-8401(94)00744-T
Prvulovic D, Jovanovic-Galovic A, Stanic B, Popovic M, Grubor-Lajsic G, 2007. Effects of a clinoptilolite supplement in pig diets on performance and serum parameters. Czech J. Anim. Sci. 52, 159-166.
Reháková M, Čuvanová S, Dzivák M, Rimár J, Gaval'ová Z, 2004. Agricultural and agrochemical uses of natural zeolite of the clinoptilolite type. Curr. Opin. Solid St. M. Science 8, 397–404. https://doi.org/10.1016/j.cossms.2005.04.004
Schauberger G, Piringer M, Mikovits C, Zollitsch W, Hörtenhuber SJ, Baumgartner J, Niebuhr K, Anders I, Andre K, Hennig-Pauka I, Schönhart M, 2018. Impact of global warming on the odour and ammonia emissions of livestock buildings used for fattening pigs. Biosyst. Eng. 175, 106–114. https://doi.org/10.1016/j.biosystemseng.2018.09.001

Steinfeld H, Gerber P, Wassenaar T, Castel V, Rosales M, de Haan C, 2006. Livestock's long shadow: environmental issues and options. FAO, Rome, 416 pp. http://www.fao.org/docrep/010/a0701e/a0701e.pdf

Yannakopoulos A, Tserveni-Gousi A, Kassoli-Fournaraki A, Tsirambides A, Michailidis K, Filippidis A, Lutat U, 2000. Effects of dietary clinoptilolite-rich tuff on the performance of growing-finishing pigs. pp. 471–481. In: C. Coela, F.A. Mumpton (Eds.), Natural Zeolites for the Third Millenium, De Frede Editore, Napoli, Italia, pp. 471–481.

5. CONCLUSIONS

5.1. Particulate matter emissions from agricultural activities

The research experiences presented in this thesis allow to cover only partially the existing gap of knowledge on the topic of PM emissions from agriculture, providing insights on land preparation operation in northern Italy, specific PM emission properties of North Italian soils and on outdoor hens rearing operation (in the Netherlands). For all topics the works performed met the double goal of providing new information (EFs development and evaluation of mitigation measures) and of developing and validating (when necessary) the measurement methods and equipment used.

Emissions from land operation activities were addressed in the works presented in paragraphs 3.2 and 3.5. The two works allowed to identify preliminary EFs for tilling operations in Northern Italy, where the atmospheric conditions are very different from those of Northern European or US environment were of the currently available EFs were derived. The Alpine and Sub-Alpine weather typical of the areas of the Piedmont region where the experiments were performed, is in fact, characterized by low wind speeds and unstable atmospheric stability conditions, which influences the emissions of PM from sources such as tillage.

The developed EFs are still insufficient, since there are no sufficient data to account for the weather and soil variability of the region. Nonetheless, the results are consistent with those of previous studies and provide a first reference. Further developing of EFs and accounting for other operations will be crucial for assessing the contribution of outdoor agricultural operations to the overall emissions from agriculture. A first approximation can be made to address the contribution of tillage practices to the total PM emissions in Italy (using the EFs developed in this thesis). In fact, a gross estimation can be made by assuming that the entire surface invested with annual crops in Italy in 2010 (1,201,366 ha; ISTAT, 2010) is tilled once per year; considering that the total anthropogenic PM_{10} emissions in that same year, accounted for by ISPRA (2021), were of 234 Gg (9.6 % of which from agricultural origin), the contribution of land preparation activities represents 0.8 % of the total and around 8% of the agricultural sector contribution to it. This figure may seem quite low, but it refers to a small part of the total emission deriving from crop production systems, which entail several other operations, including cultivation, harvesting and post-harvesting activity. Moreover, these operations are performed on large areas in relatively short time periods, corresponding to the sowing of crops, resulting in potential haze for residents in sub-urban areas (Chen et al., 2017). Another important perspective is the operator safety during soil tillage.

As for the specific characteristics of dust produced during tillage, the article presented in paragraph 3.3 provides a better understanding of contaminants present in soil derived PM, particularly of trace elements and heavy metals. In this regard, it was observed that trace elements are most concentrated in the finest soil fractions and, therefore, the PM_{10} emitted from soil has higher trace elements concentrations (concentrations are exceeding the ones in soil by up to 20 times)

than the soil itself. This entails a possible increase of health risks related to PM emissions from tillage operation, due to the exposure to toxic elements.
The research presented in chapter 3.3 provides a valuable method to address the effect of soil moisture and characteristics on the emissions, with the introduction of a mixed (field and laboratory) approach for EF determination, that could strongly simplify the future EF estimation studies, increasing their cost effectiveness.
Moreover, the research work in chapter 3.5 allowed to provide a first evaluation of reduced tillage practices (minimum and strip tillage) as mitigation measures for PM emissions from land preparation. The outcome of the study presented in paragraph 3.5 highlighted the potential of minimum tillage as a mitigation tool for soil PM.

5.1.1. General considerations and future perspectives

This thesis allowed to cover some aspects linked with particulate matter emissions from agriculture, especially from open field cropping operations. Very few studies were previously available on this topic, especially in the European area, and the contribution of these emissions is roughly estimated in national inventories. Since the cropping activities, working conditions, crop types and mechanical implements are many and are combined differently in real world scenarios, a great deal of work and research must still be performed to provide a comprehensive figure of the emissions. Moreover, the information available on characteristics and size of particles produced from tilling and harvesting operations is also insufficient and future work should be performed on the subject. Tilling emissions contribute for a good share to total PM emissions from agriculture (Sharratt and Auvermann, 2014). Globally, there is an open discussion on traditional tillage practices, which have been recognized as possible causes of land degradation, loss of soil organic matter and structure and disturbance for soil microbial activities, especially with certain soil types and climates (Schneider et al., 2017; Derpsch, 2003). As a consenquence, conservantion tillage techniques, that were originally developed to contrast erosion under very specific environmental conditions, are gaining traction and starting to be applied on an increasing share of land worldwide. This tendendency could positively impact PM emissions from soil, not only for the lower direct emission of minimum tillage as compared to traditional one, but also for the lower exposure of soil to wind, which as been shown to reduce fugitive PM emissions during intercropping periods and fallows (Singh et al., 2012; Sharratt et al., 2006; Derpsch, 2003). Moreover, different implements can be used for implementing minimum, strip tillage or sod seeding techniques with potentially different effects on PM emissions. Globally, few reseaches addressed and compared emissions observed with different tilling setups and future research should address this topic, due to the increasing importance of minimum and no tillage, in order to properly quantify the mitigation potential of different practices. Moreover, the issue of toxic elements in soil derived dust, such as heavy metals, is almost unstudied. Since there are many studies which pointed out the widespread presence of contaminated soils in certain regions of the world and in Europe (Panagos et al., 2013), addressing the issue of fugitive emissions from these soils represents an interesting research topic that should be developed further by future studies.

Harvesting emissions were not included in this thesis, since field experiments are still in progress. Nonetheless, the future activities planned by the research group in Turin will address emissions from Maize harvesting to complete the assessment of emissions from the Maize production system. Globally, emissions from harvesting operations were addressed by few studies (Faulkner et al., 2009; Wanjura et al., 2007; Cassel et al., 2003). Moreover, a more thorough investigation is due to characterize the particles emitted from a biological point of view. In fact, particles from harvesting are very different from those generated by tillage, being finer and potentially linked with inflammatory responses, as shown from studies performed on working hazard for cereal receiving facilities. Moreover, some studies have highlighted the presence of mycotoxins (durin plant harvesting period) in particulate matter in indoor and outdoor environments (Tang et al., 2020; Buiarelli et al., 2015). The actual emission of mycotoxyns should, therefore, be measured at the source and, to do so, a methology should be developed, since the amounts of PM that can be collected during harvesting are very low and, therefore, hardly meeting LOD quantities for mycotoxin determination (Buiarelli et al., 2015). A further step would be that of implementing mitigation strategies and low emission combines for the most important crops such as Maize. In fact, similar equipments have been developed and tested for hazelnut and almonds, since harvesting these crops produces very high number of fine particles (Baticados et al., 2019; Pagano et al., 2011). To achieve reduction of overall PM emission from agriculture, crops such as Maize and Wheat should be addressed as well.

Globally, cropping activities and residue burning emissions have been shown to cause PM concentration levels all over specific countries or regions for limited periods of time. In fact, the peculiarity of tilling, harvesting and residue burning emissions as compared to other PM sources, is to be diffuse area sources that emit only in coincidence with seasonal sowing or harvesting periods. Nonetheless, in Europe the effect of harvesting and tilling periods on PM concentration on the regional scale has not been studied. Future research should implement new methodologies, adopting remote sensing and dispersion models to identify sources and emission periods to estimate concentrantion increases in urban and rural areas, and compare them with monitoring observations. This step should lead to results similar to those obtained by Hill et al. (2019), who modelled agricultural PM all over the United States and derived information on the risk for residents in different areas.

In general, a great deal of research activities is still needed to fill information gaps on angricultural PM, its sources, effects and possibilities of mitigation.

5.2. Ammonia emissions from agricultural activities

The issue of ammonia emissions from agricultural activities was addressed in the works performed during these years, by focusing mainly on specific mitigation measures and on their potential for emission reduction.

Article VII and VIII focused on the use of powdery sulphur as and acidifying agent during manure storage. The purpose of using powdery sulphur was to provide a valid alternative to strong acids for slurry acidification, since strong acids cause safety concerns and are bound by regulation restrictions, while also leading to foam formation when mixed with slurry. Powdery sulphur showed good results in terms of emission reduction (NH_3 emissions from solid fraction of pig slurry were abated to 49%). Moreover, a full-scale system for sulphur acidification system was built and tested on a farm, resulting in good operational capacity (Article VIII). Nonetheless, aspects linked with the economical sustainability of this solution are still to be addressed. Moreover, some concerns may arise with the amount of powdery sulphur that must be added to obtain satisfactory results, which may lead to high raw material, transportation and handling costs. A further aspect to be addressed in future works is the potential impact of sulphur on soil after spreading, as well as the emission of hydrogen sulfide (H_2S) during storage, that may be increased by sulphur addition (Clanton & Schmidt, 2000).

Article VI addressed the issue of NH_3 and N_2O emissions after slurry injection. There appears to be, in fact, a trade off among reduced NH_3 emissions and increased N_2O ones, when incorporating slurry into soil. This article proposed the first results of a trial aiming to assess the use of a nitrification inhibitor (nitapyrin) to solve this issue while improving nitrogen availability. The first trial highlighted good results on the N_2O emissions with reductions of up to 79%. Future studies should better investigate the economic viability of the technique by evaluating its positive effect on nitrogen availability, which was suggested by a previous study (Burzaco et al., 2014). Moreover, future studies should also address the potential effects of nitrapyrin on aquatic animals and its accumulation in soil (Woodward et al., 2021). Recent studies conducted by Woodward et al. (2019, 2021) in Midwerstern US, where nitrapyrin based inhibitors are widely used, reported notable concentrations of nitrapyrin in surface streams, but concentrations were, in almost all reported cases, lower than the toxicity tresholds for acquatic animals. Therefore, more comprehensive studies should be performed to address the effects of nitrapyrin on different environmental compartments and, eventually, the environmental opportunity of implementing this technique on a larger scale could be addressed with a LCA study.

Article IX is a standalone article, which diverged from the topic of mitigation measures. It mainly aimed to test the implementation of an easy to build passive sampler with open design. The most interesting contribution of this paper to the subject is probably the proposition of a laboratory system to test samplers efficiency. Passive samplers are, in fact, widely used for ammonia emission monitoring, but they have less than optimal efficiencies and need calibration to reduce errors (Noordijk et al., 2020; Pacholski et al., 2006). Nonetheless, performing calibration in field is costly and time consuming. Future studies should push forward the idea of building a more sophisticated laboratory systems to address samplers efficiency in different conditions, in order to build efficiency curves to adjust for concentration ranges and environmental parameters.

Article X addressed clinoptilolite use as feed additive to reduce NH_3 and GHG emissions from pig houses. The study resulted in encouraging NH_3 and GHG emission reductions from barns. Nonetheless, the zeolite addiction did not influence pigs fattening and slaughtering performances, hindering its economic viability. This was probably due to the dosages, that were not high enough to induce improvements in pig performances. Future studies may address other type of zeolites or study the implications of zeolite addition to pig diets before finishing phase.

The experience acquired from the research performed led to highlight that the main issue, when it comes to mitigate NH_3 emissions, is not the absence of technically viable solutions but the economical and logistic aspects. It is, in fact, important to focus on solutions that are economically viable and that do not imply an over-complication of farming activities, since those two aspects are crucial to achieve real world implementation of mitigation measures.

5.2.1. General considerations and future perspectives

Ammonia emissions have been assessed from a wide range of sources (EEA, 2019; Santonja et al., 2017) and using a variety of different methodologies (Sommer & Misselbrook, 2016). Recently, new technologies for ammonia monitoring and sensing have been developed, which allow for lower detection limits and finer temporal definition. This improved technologies, such as mid-infrared fiber laser (Woodward et al., 2019), quartz enhanced photoacoustic spectroscopy (Ma et al., 2017), cavity enhanced and cavity ring-down spectroscopy (Bielecki et al., 2020), represent a novelty for ammonia monitoring in the agricultural field and will help provide a better understanding of emission sources. Nonetheless, a recent review from Insausti et al. (2020) has highlighted the importance of having access to sensors for ammonia monitoring that should be low cost and user friendly. Achieving such a goal would in fact allow for more diffuse monitoring of the emissions and possibly to detect the most detrimental emission source at the single farm level, allowing intervention. Another important trend that may revolutionize the current understanding of ammonia emissions and its interactions in the atmosphere is the use of Unmanned Aerial Vehicles, which opens up new frontiers for air quality studies in general (Lambey & Prasad, 2021). These advances may also help in better defining the actual contribution of NH_3 emissions to $PM_{2.5}$ formation. It would, in fact, be very useful to deepen the knowledge about NH_3-$PM_{2.5}$ convertion, especially for inventory purposes. Currently, in fact, evaluations on this topic are made through modeling of atmospheric dispersion and chemical interaction, using models such a GEOS-CHEM (Tian et al., 2021), but there is a lack of conversion factors or figures allowing for a quick, even if approximated, understanding of the total conversion figure and the timeframe in which these chemical reactions occur. The most easy-to-use conversion factor was developed by de Leeuw (2002), who proposed the

a PM_{10} equivalent factor for NH_3 emissions (similar, in concept, to CO_2eq for GHG, made available through IPCC guidelines); new studies updating this information and, possibly, relating to different geographical and seasonal scales (e.g. winter-summer time), would be a useful contribution to provide reference figures to researchers working in emission assessment or inventorying and to policy-makers.Researches published in the last decade provided and consolidated several ammonia mitigation techniques, which represent a valid solution for containing NH_3 losses in the three main stages (houses, manure storage and land spreading). A recent review paper from Sajeev et al. (2018) highlighted the importance of adopting whole management chain approaches to mitigation, considering the different steps and mitigation strategies in terms of priorities. This aspect is crucially important, partially because mitigation of ammonia emissions should always follow a "bottom up" approach, securing first the containement of emissions from manure spreading and then in previous stages, since most of the emission reduction achieved during rearing or storage can be lost by increased emissions from fields. Morever, it is necessary to consider mitigation measures also in terms of their advantages towards other gas species (e.g. acidification also reduces GHG; ARTICLE VII), and with respect to possible trade offs. In fact, certain mitigation strategies may cause increases in N_2O emissions or N losses through leaching, as it can occur after slurry injection (Sajeev et al., 2018). To account for this issue, it is necessary to look at NH_3 losses as one aspect of the Nitrogen cycle and focus on the overall nutrient imbalances at farm and regional scale. In fact, NH_3 emission mitigation is not only achieved through direct emission reduction but also, for example, from strategies allowing to relocate excess nitrogen on larger territories and to reduce inputs of nitrogen fertilizers or other external nutrient sources. In this sense, treatment techniques such as solid-liquid separation and composting are key to enable manure transport off-site and should be subject to further studies and implementantions (Flotats et al., 2009)
When proposing solutions for integrated manure management, it is important to take into consideration the broad environmental and economical aspects that define the opportunity of implementing them, considering their economical and environmental sustainability both at regional and farm levels.

5.3. Closing remarks

This thesis allowed to cover some aspects linked with particulate matter emissions from agriculture, especially from open field cropping operations. Very few studies were previously available on this topic, especially in the European area, and the contribution of these emissions is roughly estimated in national inventories. Since the cropping activities, working conditions, crop types and mechanical implements are many and are combined differently in real world scenarios, a great deal of work and research must still be performed to provide a comprehensive figure of the emissions. Moreover, the information available on characteristics and size of particles produced from tilling and harvesting operations is also insufficient and future work should be performed on the subject.

Particularly, the issue of toxic elements in agricultural dust, such as heavy metals (from soil) and mycotoxins (from plant harvesting) should be explored.
Future studies should also address mitigation measures, to reduce the emission from cropping activities and limit farmers exposure.
For what concerns ammonia emissions, some interesting solutions for mitigating emissions from barns, manure storage and land spreading were tested and proved to be viable options. Future studies should address not only the technical but also the economic viability and the ease of implementation of the suggested mitigation measures, since these aspects are fundamental for solutions to be adopted by farmers.

References

Aarnink, A.J.A., Hol, A.M.G., Beurskens, A.G.C., 2006. Ammonia emis-sion and nutrient load in outdoor runs of laying hens. Neth. J. Agric. Sci. 54, 223–234.

Aarnink, A.J.A., Swierstra, D., Van den Berg, A.J. and Speelman, L., 1997. Effect of type of slatted floor and degree of fouling of solid floor on ammonia emission rates from fattening piggeries. Journal of agricultural engineering research, 66(2), pp.93-102.

Andretta, I., Pomar, C., Rivest, J., Pomar, J. and Radünz, J., 2016. Precision feeding can significantly reduce lysine intake and nitrogen excretion without compromising the performance of growing pigs. Animal, 10(7), pp.1137-1147.

Aneja, V. P., Rogers, H. H., & Stahel, E. P., 1986. Dry deposition of ammonia at environmental concentrations on selected plant species. Journal of the Air Pollution Control Association, 36(12), 1338-1341.

Aphekom Proceedings, 2011. Aphekom – Improving knowledge and communication for decision making on air pollution in Europe. Proceedings Final Stakeholders Meeting, 2 March 2011. Institut de veille sanitaire, Saint-Maurice, France.

Baldini, C., Borgonovo, F., Gardoni, D. and Guarino, M., 2016. Comparison among NH3 and GHGs emissive patterns from different housing solutions of dairy farms. Atmospheric environment, 141, pp.60-66.

Balsari, P., Dinuccio, E. and Gioelli, F., 2006, July. A low cost solution for ammonia emission abatement from slurry storage. In International Congress Series (Vol. 1293, pp. 323-326). Elsevier.

Barzeghar, V., Sarbakhsh, P., Hassanvand, M.S., Faridi, S., Gholampour, A., 2020. Long-term trend of ambient air PM10, PM2.5, and O3 and their health effects in Tabriz city, Iran, during 2006–2017. Sustain. Cities Soc. 54, 101988. https://doi.org/10.1016/j.scs.2019.101988

Baticados, E.J.N., Capareda, S.C. and Maglinao, A.L., 2019. Particulate matter emission factors using low-dust harvesters for almond nut-picking operations. Journal of the Air & Waste Management Association, 69(11), pp.1304-1311.

Behera, S.N., Sharma, M., Aneja, V.P., Balasubramanian, R., 2013. Am-monia in the atmosphere: a review on emission sources, atmospher-ic chemistry and deposition on terrestrial bodies. Environ. Sci. Pol-lut. Res. 20, 8092–8131. https://doi.org/10.1007/s11356-013-2051-9

Bielecki, Z., Stacewicz, T., Smulko, J. and Wojtas, J., 2020. Ammonia gas sensors: Comparison of solid-state and optical methods. Applied Sciences, 10(15), p.5111.

Brunekreef, B., Forsberg, B., 2005. Epidemiological evidence of effects of coarse airborne particles on health. Eur. Respir. J. 26, 309 – 318. https://doi.org/10.1183/09031936.05.00001805

Buiarelli, F., Di Filippo, P., Riccardi, C., Pomata, D., Rumolo, E., Giannetti, L. and Neri, B., 2015. Analytical method for the determination of mycotoxins in indoor/outdoor airborne particulate matter by HPLC-MS-MS. International Journal of Environmental Analytical Chemistry, 95(8), pp.713-729.
Burzaco, J.P., Ciampitti, I.A. and Vyn, T.J., 2014. Nitrapyrin impacts on maize yield and nitrogen use efficiency with spring ‐ applied nitrogen: Field studies vs. meta ‐ analysis comparison. Agronomy Journal, 106(2), pp.753-760.
Cambra-López, M., Aarnink, A.J.A., Zhao, Y., Calvet, S., Torres, A.G., 2010. Airborne particulate matter from livestock production sys-tems: a review of an air pollution problem. Environ. Pollut. Barking Essex 1987 158, 1–17. https://doi.org/10.1016/j.envpol.2009.07.011
Cambra-López, M., Winkel, A., Van Harn, J., Ogink, N. W. M., & Aarnink, A. J. A., 2009. Ionization for reducing particulate matter emissions from poultry houses. Transactions of the ASABE, 52(5), 1757-1771.
Carozzi, M., Ferrara, R.M., Fumagalli, M., Sanna, M., Chiodini, M., Perego, A., Chierichetti, A., Brenna, S., Rana, G. and Acutis, M., 2012. Field-scale ammonia emissions from surface spreading of dairy slurry in Po Valley. Italian Journal of Agrometeorology, 4, pp.25-34.
Carozzi, M., Ferrara, R.M., Rana, G., Acutis, M., 2013. Evaluation of miti-gation strategies to reduce ammonia losses from slurry fertilisation on arable lands. Sci. Total Environ. 449, 126 – 133. https://doi.org/10.1016/j.scitotenv.2012.12.082
Cassel, T., Trzepla-Nabaglo, K. and Flocchini, R., 2003, April. PM10 emission factors for harvest and tillage of row crops. In 12th International Emission Inventory Conference, San Diego, CA.
Chen, W., Tong, D.Q., Dan, M., Zhang, S., Zhang, X., Pan, Y., 2017. Typi-cal atmospheric haze during crop harvest season in northeastern China: A case in the Changchun region. J. Environ. Sci. 54, 101 – 113. https://doi.org/10.1016/j.jes.2016.03.031
Clanton, C.J. and Schmidt, D.R., 2000. Sulfur compounds in gases emitted from stored manure. Transactions of the ASAE, 43(5), p.1229.
De Lange, C.F.M., Pluske, J., Gong, J. and Nyachoti, C.M., 2010. Strategic use of feed ingredients and feed additives to stimulate gut health and development in young pigs. Livestock Science, 134(1-3), pp.124-134.
de Leeuw, F.A., 2002. A set of emission indicators for long-range transboundary air pollution. Environmental Science & Policy, 5(2), pp.135-145.
Derpsch, R., 2003. Conservation tillage, no-tillage and related technologies. In Conservation agriculture (pp. 181-190). Springer, Dordrecht.
Dinuccio, E., Gioelli, F., Balsari, P., Dorno, N., 2012. Ammonia losses from the storage and application of raw and chemo-mechanically separated slurry.

Agric. Ecosyst. Environ. 153, 16 – 23. https://doi.org/10.1016/j.agee.2012.02.015

EEA, European Environmental Agency 2015. NEC Directive Status Report 2014. Technical report no. 7/2015. Available at: http://www.eea.europa.eu//publications/nec-directive-status-report-2014

EEA, European Environmental Agency, 2012. EEA Technical report No. 8/2012, European Union emission inventory report 1990 – 2010 un-der the UNECE Convention on Long-range Transboundary Air Pol-lution (LRTAP). European Environmental Agency. ISSN 1725-2237

EEA, European Environmental Agency, 2019. EEA Report No 08/2019, European Union emission inventory report 1990-2017 under the UNECE Convention on Long-range Transboundary Air Pollution (LRTAP). ISSN 1994-2019

EEA, European Environmental Agency, 2021. Air quality status 2021 brief-ing. European Environmental Agency. https://www.eea.europa.eu/publications/air-quality-status-2021

Erisman, J.W., Schaap, M., 2004. The need for ammonia abatement with respect to secondary PM reductions in Europe. Environ. Pollut. 129, 159–163. https://doi.org/10.1016/j.envpol.2003.08.042

Fang, Z., Deng, W., Zhang, Y., Ding, X., Tang, M., Liu, T., Hu, Q., Zhu, M., Wang, Z., Yang, W., Huang, Z., Song, W., Bi, X., Chen, J., Sun, Y., George, C., Wang, X., 2017. Open burning of rice, corn and wheat straws: primary emissions, photochemical aging, and second-ary organic aerosol formation. Atmospheric Chem. Phys. 17, 14821 – 14839. https://doi.org/10.5194/acp-17-14821-2017

Fangueiro, D., Hjorth, M. and Gioelli, F., 2015. Acidification of animal slurry–a review. Journal of environmental management, 149, pp.46-56.

Faulkner, W.B., 2013. Harvesting equipment to reduce particulate matter emissions from almond harvest. J. Air Waste Manag. Assoc. 63, 70–79. https://doi.org/10.1080/10962247.2012.738625

Faulkner, W.B., Goodrich, L.B., Botlaguduru, V.S., Capareda, S.C. and Parnell, C.B., 2009. Particulate matter emission factors for almond harvest as a function of harvester speed. Journal of the Air & Waste Management Association, 59(8), pp.943-949.

Feng, J.L., Guo, Z.G., Zhang, T.R., Yao, X.H., Chan, C.K., Fang, M., 2012. Source and formation of secondary particulate matter in PM2.5 in Asian continental outflow. J. Geophys. Res. Atmospheres 117. https://doi.org/10.1029/2011JD016400

Flotats, X., Bonmatí, A., Fernández, B. and Magrí, A., 2009. Manure treatment technologies: on-farm versus centralized strategies. NE Spain as case study. Bioresource Technology, 100(22), pp.5519-5526.

Fratianni, S., Cagnazzi, B., Cremonini, R., Bosco, F., Gai, V., 2007. Il vento in Piemonte. Torino : Arpa Piemonte ; Torino; Università di Torino. Dipartimento di scienze della terra.

Giannadaki, D., Lelieveld, J., Pozzer, A., 2016. Implementing the US air quality standard for PM2.5 worldwide can prevent millions of premature deaths per year. Environ. Health 15, 88. https://doi.org/10.1186/s12940-016-0170-8

Gioelli, F., Dinuccio, E. and Balsari, P., 2011. Residual biogas potential from the storage tanks of non-separated digestate and digested liquid fraction. Bioresource technology, 102(22), pp.10248-10251.

Gong, L., Lewicki, R., Griffin, R.J., Tittel, F.K., Lonsdale, C.R., Stevens, R.G., Pierce, J.R., Malloy, Q.G.J., Travis, S.A., Bobmanuel, L.M., Lefer, B.L., Flynn, J.H., 2013. Role of atmospheric ammonia in particulate matter formation in Houston during summertime. Atmos. Environ. 77, 893–900. https://doi.org/10.1016/j.atmosenv.2013.04.079

Guo, L., & Maghirang, R. G., 2012. Numerical simulation of airflow and particle collection by vegetative barriers. Engineering Applications of Computational Fluid Mechanics, 6(1), 110-122.

Hafidawati, Lestari, P., Sofyan, A., 2018. Assesment of PM 2.5 emission from corn stover burning determining in chamber combustion. IOP Conf. Ser. Mater. Sci. Eng. 345, 012048. https://doi.org/10.1088/1757-899X/345/1/012048

Halek, F., Kianpour-Rad, M., Kavousirahim, A., 2010. Seasonal variation in ambient PM mass and number concentrations (case study: Teh-ran, Iran). Environ. Monit. Assess. 169, 501–507. https://doi.org/10.1007/s10661-009-1192-2

Hayes, E.T., Curran, T.P., Dodd, V.A., 2006. Odour and ammonia emis-sions from intensive poultry units in Ireland. Bioresour. Technol. 97, 933–939. https://doi.org/10.1016/j.biortech.2005.04.024

Hernández, F., López, M., Martínez, S., Megías, M.D., Catalá, P. and Madrid, J., 2012. Effect of low-protein diets and single sex on production performance, plasma metabolites, digestibility, and nitrogen excretion in 1-to 48-day-old broilers. Poultry Science, 91(3), pp.683-692.

Hill, J., Goodkind, A., Tessum, C., Thakrar, S., Tilman, D., Polasky, S., Smith, T., Hunt, N., Mullins, K., Clark, M. and Marshall, J., 2019. Air-quality-related health damages of maize. Nature Sustainability, 2(5), pp.397-403.

Hoek, G., Kos, G., Harrison, R., de Hartog, J., Meliefste, K., ten Brink, H., Katsouyanni, K., Karakatsani, A., Lianou, M., Kotronarou, A., Ka-vouras, I., Pekkanen, J., Vallius, M., Kulmala, M., Puustinen, A., Thomas, S., Meddings, C., Ayres, J., van Wijnen, J., Hameri, K., 2008. Indoor – outdoor relationships of particle number and mass in four European cities. Atmos. Environ. 42, 156 – 169. https://doi.org/10.1016/j.atmosenv.2007.09.026

Hristov, A.N., 2011. Technical note: Contribution of ammonia emitted from livestock to atmospheric fine particulate matter (PM2.5) in the United States. J. Dairy Sci. 94, 3130−3136. https://doi.org/10.3168/jds.2010-3681
Insausti, M., Timmis, R., Kinnersley, R. and Rufino, M.C., 2020. Advances in sensing ammonia from agricultural sources. Science of The Total Environment, 706, p.135124.
Jackman, J.A., Boyd, R.D. and Elrod, C.C., 2020. Medium-chain fatty acids and monoglycerides as feed additives for pig production: towards gut health improvement and feed pathogen mitigation. Journal of animal science and biotechnology, 11(1), pp.1-15.
Jaworski, N. A., 1981. Sources of nutrients and the scale of eutrophication problems in estuaries. In Estuaries and nutrients (pp. 83-110). Humana Press.
JRC (Joint Research Center), 2020. European Commission, Joint Research Centre (EC-JRC)/Netherlands Environmental Assessment Agency (PBL). Emissions Database for Global Atmospheric Research (EDGAR), release EDGAR v5.0 (1970 - 2015) of April 2020.
Kai, P., Pedersen, P., Jensen, J.E., Hansen, M.N. and Sommer, S.G., 2008. A whole-farm assessment of the efficacy of slurry acidification in reducing ammonia emissions. European Journal of Agronomy, 28(2), pp.148-154.
Kelly, F.J., Fussell, J.C., 2012. Size, source and chemical composition as determinants of toxicity attributable to ambient particulate matter. Atmos. Environ. 60, 504 − 526. https://doi.org/10.1016/j.atmosenv.2012.06.039
Koerkamp, P. G., Metz, J. H. M., Uenk, G. H., Phillips, V. R., Holden, M. R., Sneath, R. W., ... & Wathes, C. M., 1998. Concentrations and emissions of ammonia in livestock buildings in Northern Europe. Journal of Agricultural Engineering Research, 70(1), 79-95.
Lambey, V., & Prasad, A. D., 2021. A review on air quality measurement using an unmanned aerial vehicle. Water, Air, & Soil Pollution, 232(3), 1-32.
Liu, Y., Espinosa, C.D., Abelilla, J.J., Casas, G.A., Lagos, L.V., Lee, S.A., Kwon, W.B., Mathai, J.K., Navarro, D.M., Jaworski, N.W. and Stein, H.H., 2018. Non-antibiotic feed additives in diets for pigs: A review. Animal nutrition, 4(2), pp.113-125.
Ma, Y., He, Y., Tong, Y., Yu, X. and Tittel, F.K., 2017. Ppb-level detection of ammonia based on QEPAS using a power amplified laser and a low resonance frequency quartz tuning fork. Optics Express, 25(23), pp.29356-29364.
Mar, T.F., Ito, K., Koenig, J.Q., Larson, T.V., Eatough, D.J., Henry, R.C., Kim, E., Laden, F., Lall, R., Neas, L., Stölzel, M., Paatero, P., Hop-ke, P.K., Thurston, G.D., 2006. PM source apportionment and health effects. 3. Investigation of inter-method variations in associa-tions between estimated source contributions of PM2.5 and daily mortality in Phoenix,

AZ. J. Expo. Sci. Environ. Epidemiol. 16, 311 – 320. https://doi.org/10.1038/sj.jea.7500465
Massé, D.I., Talbot, G. and Gilbert, Y., 2011. On farm biogas production: A method to reduce GHG emissions and develop more sustainable livestock operations. Animal feed science and technology, 166, pp.436-445.
Mercurio, M., Cappelletti, P., de Gennaro, B., de Gennaro, M., Bovera, F., Iannaccone, F., Grifa, C., Langella, A., Monetti, V. and Esposito, L., 2016. The effect of digestive activity of pig gastro-intestinal tract on zeolite-rich rocks: An in vitro study. Microporous and mesoporous materials, 225, pp.133-136.
Misselbrook, T., Hunt, J., Perazzolo, F., Provolo, G., 2016. Greenhouse Gas and Ammonia Emissions from Slurry Storage: Impacts of Temperature and Potential Mitigation through Covering (Pig Slurry) or Acidification (Cattle Slurry). J. Environ. Qual. 45, 1520 – 1530. https://doi.org/10.2134/jeq2015.12.0618
Misselbrook, T.H., Nicholson, F.A., Chambers, B.J., Johnson, R.A., 2005. Measuring ammonia emissions from land applied manure: an inter-comparison of commonly used samplers and techniques. Environ-mental Pollution, The National Atmospheric Depostition PRogram (25th Anniversary) and Ammonia Workshop 135, 389 – 397. https://doi.org/10.1016/j.envpol.2004.11.012
Mohankumar Sajeev, E.P., Winiwarter, W. and Amon, B., 2018. Greenhouse gas and ammonia emissions from different stages of liquid manure management chains: abatement options and emission interactions. Journal of Environmental Quality, 47(1), pp.30-41.
Noordijk, H., Braam, M., Rutledge-Jonker, S., Hoogerbrugge, R., Stolk, A.P. and van Pul, W.A.J., 2020. Performance of the MAN ammonia monitoring network in the Netherlands. Atmospheric Environment, 228, p.117400.
Orellano, P., Reynoso, J., Quaranta, N., Bardach, A., Ciapponi, A., 2020. Short-term exposure to particulate matter (PM10 and PM2.5), nitro-gen dioxide (NO2), and ozone (O3) and all-cause and cause-specific mortality: Systematic review and meta-analysis. Environ. Int. 142, 105876. https://doi.org/10.1016/j.envint.2020.105876
Ortega-Rosas, C.I., Meza-Figueroa, D., Vidal-Solano, J.R., González-Grijalva, B., Schiavo, B., 2021. Association of airborne particulate matter with pollen, fungal spores, and allergic symptoms in an arid urbanized area. Environ. Geochem. Health 43, 1761 – 1782. https://doi.org/10.1007/s10653-020-00752-7
Pacholski, A., 2016. Calibrated Passive Sampling - Multi-plot Field Measure-ments of NH3 Emissions with a Combination of Dynamic Tube Meth-od and Passive Samplers. J Vis Exp. https://doi.org/10.3791/53273
Pacholski, A., Cai, G., Nieder, R., Richter, J., Fan, X., Zhu, Z. and Roelcke, M., 2006. Calibration of a simple method for determining ammonia

volatilization in the field–comparative measurements in Henan Province, China. Nutrient Cycling in Agroecosystems, 74(3), pp.259-273.
Pagano, M., Fanigliulo, R., Tomasone, R., Cedrola, C., Recchi, P.F., Colorio, G., 2011. Mechanical hazelnut harvesting: First results of a pickup prototype for a low environmental impact. Acta Horticulturae 919, 139 – 146. https://doi.org/10.17660/ActaHortic.2011.919.17
Pahl, O., Williams, A.G. and Sneath, R.W., 2002. Reduction of ammonia and odour emissions from pig slurry under slats using oil and foam layers. Environmental Technology, 23(4), pp.395-403.
Panagos, P., Van Liedekerke, M., Yigini, Y. and Montanarella, L., 2013. Contaminated sites in Europe: review of the current situation based on data collected through a European network. Journal of Environmental and Public Health, 2013.
Papaioannou, D.S., Kyriakis, C.S., Alexopoulos, C., Tzika, E.D., Polizopoulou, Z.S. and Kyriakis, S.C., 2004. A field study on the effect of the dietary use of a clinoptilolite-rich tuff, alone or in combination with certain antimicrobials, on the health status and performance of weaned, growing and finishing pigs. Research in Veterinary Science, 76(1), pp.19-29.
Philippe, F.-X., Cabaraux, J.-F., Nicks, B., 2011. Ammonia emissions from pig houses: Influencing factors and mitigation techniques. Agriculture, Ecosystems & Environment 141, 245 – 260. https://doi.org/10.1016/j.agee.2011.03.012
Polichetti, G., Cocco, S., Spinali, A., Trimarco, V., Nunziata, A., 2009. Ef-fects of particulate matter (PM10, PM2.5 and PM1) on the cardio-vascular system. Toxicology 261, 1–8. https://doi.org/10.1016/j.tox.2009.04.035
Pope, C.A., 1996. Adverse health effects of air pollutants in a nonsmoking population. Toxicology, Risk Assessment Issues for Sensitive Hu-man Populations 111, 149 – 155. https://doi.org/10.1016/0300-483X(96)03372-0
Pope, C.A., 2007. Mortality Effects of Longer Term Exposures to Fine Par-ticulate Air Pollution: Review of Recent Epidemiological Evidence. Inhal. Toxicol. 19, 33–38. https://doi.org/10.1080/08958370701492961
Pope, C.A., Dockery, D.W., Spengler, J.D., Raizenne, M.E., 1991. Respira-tory Health and PM10 Pollution: A Daily Time Series Analysis. Am. Rev. Respir. Dis. 144, 668 – 674. https://doi.org/10.1164/ajrccm/144.3_Pt_1.668
Pope, C.A., Schwartz, J., Ransom, M.R., 1992. Daily Mortality and PM10 Pollution in Utah Valley. Arch. Environ. Health Int. J. 47, 211−217. https://doi.org/10.1080/00039896.1992.9938351
Santonja, G.G., Georgitzikis, K., Scalet, B.M., Montobbio, P., Roudier, S. and Sancho, L.D., 2017. Best available techniques (BAT) reference document for the intensive rearing of poultry or pigs. EUR 28674 EN.

Schneider, F., Don, A., Hennings, I., Schmittmann, O. and Seidel, S.J., 2017. The effect of deep tillage on crop yield–What do we really know?. Soil and tillage research, 174, pp.193-204.
Sharma, M., Kishore, S., Tripathi, S.N., Behera, S.N., 2007. Role of atmos-pheric ammonia in the formation of inorganic secondary particulate matter: A study at Kanpur, India. J. Atmospheric Chem. 58, 1 – 17. https://doi.org/10.1007/s10874-007-9074-x
Sharratt, B., Auvermann, B., 2014. Dust Pollution from Agriculture, in: Van Alfen, N.K. (Ed.), Encyclopedia of Agriculture and Food Systems. Academic Press, Oxford, pp. 487–504. https://doi.org/10.1016/B978-0-444-52512-3.00089-9
Sharratt, B., Zhang, M. and Sparrow, S., 2006. Twenty years of tillage research in subarctic Alaska: I. Impact on soil strength, aggregation, roughness, and residue cover. Soil and Tillage Research, 91(1-2), pp.75-81.
Shepherd, T.A., Xin, H., Stinn, J.P., Hayes, M.D., Zhao, Y. and Li, H., 2017. Ammonia and carbon dioxide emissions of three laying-hen housing systems as affected by manure accumulation time. Transactions of the ASABE, 60(1), pp.229-236.
Singh, P., Sharratt, B. and Schillinger, W.F., 2012. Wind erosion and PM10 emission affected by tillage systems in the world's driest rainfed wheat region. Soil and Tillage Research, 124, pp.219-225.
Sommer, S.G. and Misselbrook, T.H., 2016. A review of ammonia emission measured using wind tunnels compared with micrometeorological techniques. Soil Use and Management, 32, pp.101-108.
Sommer, S.G., Christensen, B.T., Nielsen, N.E. and Schjφrring, J.K., 1993. Ammonia volatilization during storage of cattle and pig slurry: effect of surface cover. The Journal of Agricultural Science, 121(1), pp.63-71.
Sousa, S.I.V., Martins, F.G., Pereira, M.C., Alvim-Ferraz, M.C.M., Ribeiro, H., Oliveira, M., Abreu, I., 2008. Influence of atmospheric ozone, PM10 and meteorological factors on the concentration of airborne pollen and fungal spores. Atmos. Environ. 42, 7452 – 7464. https://doi.org/10.1016/j.atmosenv.2008.06.004
Tang, Q., Huang, K., Liu, J., Shen, D., Dai, P., Li, Y. and Li, C., 2020. Seasonal variations of microbial assemblage in fine particulate matter from a nursery pig house. Science of The Total Environment, 708, p.134921.
Tao, R., Li, J., Hu, B. and Chu, G., 2021. Mitigating N2O emission by synthetic inhibitors mixed with urea and cattle manure application via inhibiting ammonia-oxidizing bacteria, but not archaea, in a calcareous soil. Environmental Pollution, 273, p.116478.
Thomsen, I.K., Pedersen, A.R., Nyord, T. and Petersen, S.O., 2010. Effects of slurry pre-treatment and application technique on short-term N2O emissions as determined by a new non-linear approach. Agriculture, ecosystems & environment, 136(3-4), pp.227-235.

Tian, R., Ma, X., Sha, T., Pan, X. and Wang, Z., 2021. Exploring dust heterogeneous chemistry over China: Insights from field observation and GEOS-Chem simulation. Science of The Total Environment, 798, p.149307.

Tong, R., Liu, J., Wang, W., Fang, Y., 2020. Health effects of PM2.5 emis-sions from on-road vehicles during weekdays and weekends in Bei-jing, China. Atmos. Environ. 223, 117258. https://doi.org/10.1016/j.atmosenv.2019.117258

US-EPA, US Environmental Protection Agency, 2021. Particulate Matter (PM) Basics. US Environmental Protection Agency (Consulted on 26th Sept 2021). https://www.epa.gov/pm-pollution/particulate-matter-pm-basics

Vecchi, R., Marcazzan, G., Valli, G., Ceriani, M., Antoniazzi, C., 2004. The role of atmospheric dispersion in the seasonal variation of PM1 and PM2.5 concentration and composition in the urban area of Milan (Italy). Atmos. Environ. 38, 4437 – 4446. https://doi.org/10.1016/j.atmosenv.2004.05.029

Wanjura, J.D., Shaw, B.W., Parnell, C.B., Capareda, S.C. and Faulkner, W.B., 2007. A preliminary particulate matter emission factor from cotton harvesting.

Wathes, C. M., Demmers, T. G., & Xin, H., 2003. Ammonia concentrations and emissions in livestock production facilities: guidelines and limits in the USA and UK. In 2003 ASAE Annual Meeting (p. 1). American Society of Agricultural and Biological Engineers.

Webb, J., Menzi, H., Pain, B. F., Misselbrook, T. H., Dämmgen, U., Hen-driks, H., & Döhler, H., 2005. Managing ammonia emissions from livestock production in Europe. Environmental pollution, 135(3), 399-406.

WHO, World Health Organization, 2006. Air quality guidelines: global up-date 2005: particulate matter, ozone, nitrogen dioxide, and sulfur dioxide. World Health Organization.

Williams, R., Creason, J., Zweidinger, R., Watts, R., Linda Sheldon, Shy, C., 2000. Indoor, outdoor, and personal exposure monitoring of particulate air pollution: the Baltimore elderly epidemiology-exposure pilot study. Atmos. Environ. 34, 4193 – 4204. https://doi.org/10.1016/S1352-2310(00)00209-0

Winkel, A. (2016). Particulate matter emission from livestock houses: measurement methods, emission levels and abatement systems (Doctoral dissertation, Wageningen University).

Winkel, A., Mosquera, J., Aarnink, A. J., Koerkamp, P. W. G., & Ogink, N. W., 2017. Evaluation of manure drying tunnels to serve as dust filters in the exhaust of laying hen houses: Emissions of particulate matter, ammonia, and odour. Biosystems Engineering, 162, 81-98.

Winkel, A., Van Riel, J. W., Van Emous, R. A., Aarnink, A. J. A., Koerkamp, P. G., & Ogink, N. W. M., 2016. Abatement of particulate matter emission from experimental aviary housings for laying hens by spraying rapeseed oil. Poultry science, 95(12), 2836-2848.

Womiloju, T.O., Miller, J.D., Mayer, P.M., Brook, J.R., 2003. Methods to determine the biological composition of particulate matter collected from outdoor air. Atmos. Environ. 37, 4335 – 4344. https://doi.org/10.1016/S1352-2310(03)00577-6

Wood, D. J., & Van Heyst, B. J., 2014. Assessment of sprinklers on the removal efficiency of ammonia and particulate matter in a commercial broiler facility. In 2014 Montreal, Quebec Canada July 13–July 16, 2014 (p. 1). American Society of Agricultural and Biological Engineers.

Woodward, E.E., Edwards, T.M., Givens, C.E., Kolpin, D.W. and Hladik, M.L., 2021. Widespread Use of the Nitrification Inhibitor Nitrapyrin: Assessing Benefits and Costs to Agriculture, Ecosystems, and Environmental Health. Environmental Science & Technology, 55(3), pp.1345-1353.

Woodward, E.E., Kolpin, D.W., Zheng, W., Holm, N.L., Meppelink, S.M., Terrio, P.J. and Hladik, M.L., 2019. Fate and transport of nitrapyrin in agroecosystems: Occurrence in agricultural soils, subsurface drains, and receiving streams in the Midwestern US. Science of the Total Environment, 650, pp.2830-2841.

Wulanningtyas, H.S., Gong, Y., Li, P., Sakagami, N., Nishiwaki, J. and Komatsuzaki, M., 2021. A cover crop and no-tillage system for enhancing soil health by increasing soil organic matter in soybean cultivation. Soil and Tillage Research, 205, p.104749.

Zhang, T., Wooster, M.J., Green, D.C., Main, B., 2015. New field-based agricultural biomass burning trace gas, PM2.5, and black carbon emission ratios and factors measured in situ at crop residue fires in Eastern China. Atmos. Environ., Interdisciplinary Research Aspects of Open Biomass Burning and its Impact on the Atmosphere 121, 22–34. https://doi.org/10.1016/j.atmosenv.2015.05.010

Zhang, Y., West, J.J., Mathur, R., Xing, J., Hogrefe, C., Roselle, S.J., Bash, J.O., Pleim, J.E., Gan, C.-M., Wong, D.C., 2018. Long-term trends in the ambient PM2.5- and O3-related mortality burdens in the United States under emission reductions from 1990 to 2010. At-mospheric Chem. Phys. 18, 15003–15016. https://doi.org/10.5194/acp-18-15003-2018

ZhiLing, G., Mauder, M., Desjardins, R.L., Flesch, T.K., Haarlem, R.P. van, 2009. Assessment of the backward Lagrangian Stochastic disper-sion technique for continuous measurements of CH4 emissions. Agric. For. Meteorol. 149, 1516–1523.

Zhu, X., Burger, M., Doane, T. A., & Horwath, W. R., 2013. Ammonia oxidation pathways and nitrifier denitrification are significant sources of N2O and NO under low oxygen availability. Proceedings of the National Academy of Sciences, 110(16), 6328-6333.

AKNOWLEDGEMENTS

I would like to thank Prof. Paolo Balsari and Prof. Elio Dinuccio, for their patience and support during my research and for always believing in my capabilities to face the challenges I encountered during these years.
I am also grateful to Luca Rollé for his outstanding support in lab work and field experimentations and for teaching me many essential things.
Special thanks go to Prof. Dario Sacco, who taught me much and transmitted me the passion for statistics.
I would also like to thank Dr. André Aarnink and Ing. Hilko Ellen for giving me the opportunity to work with them in Wageningen, for my abroad semester. It was an outstanding experience for me and I am very grateful for all the things they and the other colleagues in Wageningen taught me.
Finally, I would like to thank all the colleagues at DISAFA, who always provided a light and supportive atmosphere. I will miss the jokes and laughs we shared during launch and coffee breaks.
I would finally like to express my deepest gratitude to my partner Gloria and my parents who helped me overcome many insecurities and always supported me in this three-year journey.