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CICLO: XXX

**Size fractionation and bioavailability
in the assessment of heavy metal contamination
of urban soils and road dust.**

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Abstract

Urban settlements host already the majority of the world population, and growing. The biggest urban growth is occurring in small and medium-sized cities and in peri-urban spaces. This urban sprawl is of serious concern, as city expansion in the surrounding countryside will cover both farmlands and soils affected by industrial legacies. The risk posed by this urbanization is soil and ecosystem degradation due to human activities and non-sustainable use of the land. All these activities, as construction, industry, traffic, waste disposal, could cause contamination, both organic and inorganic.

In literature, it is increasingly apparent that considerable areas in many parts of the world have already been contaminated by heavy metals and metalloids (HM), whose importance derives from their concentration and potential toxicity, amplified by their very long persistence in the environment.

This thesis was focused on unraveling the threat posed by HM in matrices highly impacted from human activities, such as roadside soils, playground sands and road dust (RD), a mixed matrix composed by soil, deposited dust from atmospheric pollution, vehicle exhaust and non-exhaust emissions (from brake, tire and road wear), and on the interaction of these matrices with the atmosphere.

Between contamination sources, long-term dust deposition is the most important diffuse source for soil, where deposited particles (mostly finer than 10 μm) can derive from short or long-range transport. Among localized contaminations, the most common sources are traffic, corrosion of metal structures, incorporation of man-made materials in the soil or dusts, paints, agricultural contaminants from the former use of the land and industrial wastes.

Heavy metal(loid)s contamination is generally defined basing on the total concentration. However, as the hazard derives from the interaction of the contaminated material with the population, the health risk could be very different in reason of the fraction that could be taken up by plants or absorbed by the human body. This bioavailable or bioaccessible (soluble in the gastrointestinal tract) fraction is related to the chemico-physical speciation of the HM-bearing particles but also to matrix properties.

As in urban environments the most important risk is considered in relation to human health, the second key feature determining the threat is the size of HM-bearing particles, as it controls the fraction of HM that could enter the human body, i.e. particles that can enter the respiratory system through inhalation or adhere to human hands and be incidentally ingested.

Considering this last pathway, the size fraction of particles that can adhere to human hands, especially of children, is commonly defined as particles <150 or <200 μm . Conversely, the size fraction of interest for the inhalation pathway belong to particles that could be resuspended and enter the human pulmonary tract, so particles <10 μm , reaching the thoracic region, and <2.5 μm , travelling deeply in lungs.

These resuspendable particles of RD have been found in various studies to be a major component of the coarse particulate matter (PM), thus influencing more the PM₁₀ than the PM_{2.5}. Their contribution is comparable to that of tailpipe emissions and can also be the first contributor to PM₁₀ concentration.

To understand the effect of size fractionation and bioaccessibility on the risk posed by HM we collected soil, RD and sand samples in Turin and Barcelona, and we carried out a review study to quantify the impact of road dust resuspension on the worldwide air quality parameters.

The observed concentrations of HM in RD and roadside soils in Turin were higher than reported in previous studies and above the legislative limits. Fine particles (<2.5 and 2.5 - 10 μm in size) were enriched for all HM except Cr and Ni, compared to the bulk samples, and the spatial variation was more pronounced for elements mostly emitted by traffic sources (Cu, Sb, Pb and Zn).

In the soil samples, the bioaccessibility of Fe, Mn, Cr and Ni increased in fine particles, likely due to their greater reactivity and the higher anthropic contribution with respect to coarser fractions, while Cu, Pb, Sb and Zn had almost constant bioaccessibility for all size fractions. In the RD samples, the bioaccessibility of fine particles was clearly greater than in soils for all metals. For Pb, Cu and Zn, the bioaccessible fraction reached 90% of the total concentration in the <2.5 μm fraction, which also showed the highest enrichment when compared to the earth's crust.

The literature review on the impact of non-exhaust emissions on air quality revealed that RD contributed 22%, as mean, to PM₁₀ concentrations, comparably to vehicle exhaust (21%) and sensibly higher than brake wear (7%) and tire wear (4%). In PM_{2.5}, the road dust contribution is still the highest among non-exhaust ones (mean of 11%), but sensibly lower than vehicle exhaust (24%).

We observed an increasing contribution (in % of PM₁₀) of RD from rural to traffic locations, with the highest step from sub-urban to urban locations. A climate-dependence was also found for RD, with the highest contributions relatively to exhaust emissions in Mediterranean and Tropical-Monsoon climates. Further research is still necessary to better separate individual contributions from road dust resuspension, brake, tire and road wear, given that the relative toxicity and mitigation measures are different.

In the cities of Turin and Barcelona we explored the influence of road characteristics (macro-texture, traffic intensity and distance from the braking zone) on the RD fraction that can be mobilized and resuspended. Our results allowed building an empirical model able to predict resuspendable RD based on the aforementioned road data. This model can significantly improve bottom-up emission inventory for spatial allocation of emissions and air quality management (helping select those roads with higher emissions for the application of mitigation measures).

The characterization of the sands used in the public playgrounds of the city of Barcelona improved our understanding of their potential risk in case of ingestion by toddlers and inhalation. The fraction of particles below 10, 2.5 and 1 μm represented a low percentage of the volume, but increasing every year by an 18%, 5% and 2%, respectively. Concerning HM, only Sb and As resulted to be sensibly enriched with respect to the upper continental crust. Both showed a high spatial variation, attributed to anthropogenic sources from the PMF analysis. The suggested main sources of Sb were road traffic and industry, while harbor and industry for As. Bioaccessibility was higher for the carbonate-bearing particles and for the anthropic emitted metals, being more than 50% of the bioaccessible fraction of Ba, Cu, K, Pb and Zn due to the anthropogenic source.

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1. Introduction

1.1 Heavy metals and metalloids in urban matrices

Urban areas host already 50 per cent of the world population, and projections show that this proportion will increase to 66% by 2050 (United Nations, 2015). Much of the expected urban growth will take place in peri-urban spaces, which are increasing at a faster rate than traditional core cities (European Commission, 2011). Thus, the management of urban and peri-urban areas will be one of the major goals in next years, as urban sprawl will increase contamination sources and influence the surrounding environments.

In densely populated metropolitan regions, an important legacy of urban sprawl is soil, air and ecosystem degradation due to human activities and non-sustainable use of the land. All these activities, as construction, industry, traffic, waste disposal, could cause contamination, both organic and inorganic. Soil contamination has been listed by the European Commission (2012) as one of the major threat to urban soils, together with soil organic matter loss, erosion, compaction and sealing. In literature it is increasingly apparent that considerable areas of soil in many parts of the world have been contaminated by heavy metals and metalloids (Ajmone Marsan and Biasioli, 2010; Alloway, 2013). This could become a serious threat to human health, if not properly managed.

The term heavy metals and metalloids (heavy metal(loid)s, or HM) has been initially used to refer to elements of high atomic mass ($>5 \text{ g cm}^{-3}$), that could pose toxicity hazards. Currently, it is a category used to identify the most important environmentally elements and it normally includes: arsenic (As), cadmium (Cd), chromium (Cr), cobalt (Co), copper (Cu), mercury (Hg), lead (Pb), manganese (Mn), nickel (Ni) and zinc (Zn); but also antimony (Sb), barium, (Ba), molybdenum (Mo), tin (Sn) and vanadium (V) are increasingly studied and included in the classification (Alloway, 2013). Some of these elements have been studied not only for their toxicity, but also for their importance as plant nutrients, as for Zn, Cu and Mn, others for their wide use and, therefore, pollution.

Heavy metal(loid)s are also significant natural components of various urban matrices (soil, sand, road dust, atmospheric particulate matter (PM)) and could be present in the mineral fraction, comprising potentially-mobile metal species in clays, minerals and oxides, or in the organic fraction, frequently as bound forms (Violante et al., 2010). Their importance derives from their concentration, that could vary widely, and from their potential toxicity, amplified by their very long persistence in the environment as, contrarily to organic contaminants, HM do not

undergo microbial or chemical degradation and persist in soil for a long time after their introduction (Bolan et al., 2014).

Each matrix contains HM in different chemical forms and concentrations because, in urban environments, HM can derive from a range of sources. Apart from soil, in some cases, the major share of HM arises from anthropogenic activities. Contamination can be either extensive (affecting large areas) or localized. Extensive contaminations common to all the urban sites are atmospheric deposition and flooding or sediment deposition (Alloway, 2013). Atmospheric deposition is a major source of road dust but lead, also, to long-term pollution of soils, as deposition rates are the lowest among transport mechanisms, while flooding or landslides could lead to large pollution areas, e.g. in case of mining areas. Conversely, localized, or site-related pollution of air and soils could arise from traffic, industrial sites, and agricultural practices or from unwanted release of technogenic materials.

Until recent years, HM contamination was defined basing on the total concentration, measured through the total or partial dissolution of the matrix in a strong extractant (e.g. hot acids). However, as the hazard derives from the interaction of the contaminated material with the population, the health risk could be very different in reason of the contaminant fraction that could be taken up by plants or absorbed by the human body.

This fraction is often named as *bioavailable* or *bioaccessible*, depending on the receptor (e.g. plants, animals, individuals) and on the research field, as it is related to the chemical speciation of the HM but also to matrix properties, such as texture, organic matter content, Fe, Al and Mn oxide content, but also pH, redox potential and others (Basta et al., 2005; Ming et al., 2012). In the urban environment, the most important risk is considered in relation to human health, so the concern goes to the fraction of HM that could enter the human body, i.e. fine particles of PM, soil or dust that can enter the respiratory system, or adhere to human hands and be incidentally ingested. Instead, from a different point of view, the important fraction could be the HM species that can be absorbed or enter the circulatory system after the ingestion, thus using solutions that mimic the human gastro-intestinal tract.

In this work, different urban matrices have been considered, trying to have an overview of the interactions between them and of the impact of HM pollution. In particular, the work was focused on unraveling the threat posed by HM in matrices highly impacted from human activities, such as roadside soils, playground soils and road dust, a mixed matrix composed by soil, deposited dust from atmospheric pollution, traffic abrasion and exhaust products, and on the interaction of these compartments with the atmosphere.

1.1.1 Urban soils and soil-like materials

In the urban environment, soil is a substantial compartment and, differently from natural and agricultural areas, it acquires supplementary functions, as it contributes to the general quality of life (van Kamp et al. 2003). In particular, together with technosols, such as deposited soils in parks, playgrounds and restored areas, and soil-like materials, such as playground sands, it has an esthetical and recreational function.

Due to these different functions, to the anthropic activities and the land use changes during urbanization history, urban soils have highly heterogeneous physical and chemical properties (Madrid et al., 2006), with amplified spatial variations with respect to natural areas (e.g. for the incorporation of carbonates from concrete debris or for compaction and sealing processes) (Biasioli et al., 2006). These same activities can provoke HM contamination, with their unpredictable and diffuse pattern enhancing the risk to population.

The prevailing sources of urban soil pollution have been well studied in last years (Ajmone Marsan and Biasioli, 2010; Meuser, 2010; Werkenthin et al., 2014) and, normally, a single source does not explain the anomalously high MH concentrations found in a urban area, apart from point contaminations normally found, for example, in industrial polluted soils. If we consider diffuse contamination sources, dust deposition is of primary importance and, in particular where a strong industrialization developed, long-term dust deposition can cause a vast accumulation of HM. Deposited particles can derive from short or long-range transport and could, therefore, carry coarser or finer particles depending on the source. However, the size of transported PM mostly belong to the fraction finer than 10 μm , designated as the most dangerous for human health (Brunekreef and Holgate, 2002). These particles have been shown to accumulate the contaminants, due to their enhanced sorption capacity, and retained HM could be more available and reactive (Ajmone Marsan et al., 2008; Bi et al., 2015).

In urban locations, the most common localized sources are traffic, corrosion of metal structures, incorporation of man-made materials in the soil or in dusts, paints, agricultural contaminants from the former use of the land and industrial wastes, dumpsites (from a former use) or dust (Alloway, 2013).

Due to the long persistence of these contaminations and to the non- degradability of HM, the remediation of matrices contaminated by toxic HM can only work on the displacement of the particles from the matrix (through digging, plant uptake, leaching or volatilization), or on chemical immobilization (through sorption, precipitation, and complexation reactions), to reduce their availability.

1.1.2 Road dust

The road dust (RD) is a complex environmental medium at the interface between the soil and the atmosphere; therefore, could be a temporary source or a sink of pollutants for both, as it is continuously produced or removed from the road surface and can be washed off or accumulated. The major sources of RD include particles from soil and atmospheric deposition, but also vehicle exhaust and non-exhaust emissions, such as brake, tire and road particles, and industrial activities are very important sources (Thorpe and Harrison, 2008; Pant and Harrison, 2013; Amato et al., 2014).

Most of the studies in last years focused on the RD characterization with regard to organic and inorganic constituents in the bulk material and in size fractions (Charlesworth and Lees, 1999; Sternbeck et al. 2002; McKenzie et al., 2008; Acosta et al., 2011). Source apportionment studies started later and were focused, in particular, in distinguishing the fraction deriving from traffic non-exhaust sources (Amato et al., 2009, 2014; Aimar et al., 2012; Kumar et al., 2013). In fact, due to the increasing restrictions in the legislation on vehicle exhaust emissions, the non-exhaust fraction has been increasing in importance.

However, the mineral sources of road dust (particles arising from soil and road surface erosion, mainly) have been poorly studied (Amato et al., 2013; Pietrodangelo et al., 2013; Kupiainen et al., 2016). This is probably the result of the difficulty to separate soil-derived RD from other mineral sources, such as road wear and wind-transported particles, due to the lack of univocal source profiles and chemical tracers. Indeed, soils have a very large variability in chemical features and, for each study area, it would be necessary to build up specific source profiles to separate different mineral sources.

Conversely, traffic-related sources of RD have been identified in last years, including brake wear, tire wear, vehicle exhaust, asphalt and lubricating oil (Sternbeck et al, 2002; Adaichi and Tainosho, 2004; Gietl et al., 2010) due to the more unique chemical signatures; for example, brake particles have particular HM ratios depending on the brake type from which they can be traced (Grigoratos and Martini, 2015).

Based on HM variability and particle size distribution, in the last years various source apportionment tools have been used to identify RD sources and the share of each to the total HM concentrations (Amato et al., 2011; Kupiainen et al., 2016; Pant et al., 2015).

Concerns over elevated HM concentrations in RD started in the 1980s, as dust ingestion and storm-water runoff from streets were recognized as a threat (Harrison et al, 1981). RD can contain a large palette of HM and organic pollutants, due to the various sources and, in general, the concentrations found are usually

comparable with urban polluted soils. However, differently from soils, an emission control regulation could be possible, as from a better source identification of particles could originate HM concentration limits and different chemical formulations for brake, tire or road materials.

Road dust, as soil particles, can also be easily re-suspended by vehicles or wind, resulting in an important source of atmospheric particulate matter (PM), significant mostly in highly urbanized areas. In recent years, concerns over its contribution to PM grown due to the lack of legislation for all non-exhaust sources (Amato et al., 2014; Denier van der Gon et al., 2013; Kousoulidou et al., 2008). With the continuous reduction of exhaust emissions (until the endpoint of electric vehicles), non-exhaust particles, such as RD, will increase their share of the total particulate matter and may become dominant over the coming years.

1.2 Importance of size fractionation

As outlined above, the particle size distribution of soil and RD and the associated HM content is of primary importance in assessing their impact on urban population. Various studies have proven in the last years that fine particles (e.g $<10\ \mu\text{m}$) have higher concentrations of HM than coarser ones due to their larger surface area, higher clay minerals and organic matter content and to the presence of Fe and Mn oxides, promoting the HM accumulation owing to adsorption, physical occlusion and complexation processes (Charlesworth and Lees, 1999; Ajmone Marsan et al., 2008; Acosta et al., 2011; Sutherland et al., 2012). This behavior in urban areas is worsened from anthropic processes, which tend to generate finer particles compared to natural ones.

When assessing the risk from HM in urban environments, ingestion and inhalation exposure are the most important pathways for both soil and RD, as found from various studies (Ferreira-Baptista and De Miguel, 2005; Zheng et al., 2010; Li et al., 2013; Kong et al., 2012), while the contribution of dermal absorption is essentially negligible. In spite of the increasing interest in inhalation risk assessment, ingestion still appear to be the major route of exposure, with inhalation risk being 2–4 orders of magnitude lower than ingestion (Shi et al., 2011; Kong et al., 2012).

Considering the ingestion pathway, particles are considered to derive primarily from incidental ingestion (U.S. EPA, 2011). This type of ingestion is largely the result of hand-to-mouth contact, while other actions, such as ingestion of soil particulates adhering to vegetables or inhalation of soil particulates, contribute minimally. Consequently, considering the HM exposure risk we have to consider the size fraction that can adhere to human hands, especially of children, as for adults soil ingestion is considered to be lower (Yamamoto et al., 2006; U.S. EPA, 2011).

Various studies have been conducted to assess the particle size of relevance in assessing incidental oral exposure to HM, although a definitive upper size cutoff has not yet been defined (Yamamoto et al., 2006; Siciliano et al., 2009; Ruby and Lowney, 2012). As soil texture directly influences dust adherence to hands different studies achieved different cutoff sizes, ranging from 50 to 250 μm (Driver et al., 1989; Edwards et al., 1999; Yamamoto et al., 2006; Ruby and Lowney, 2012), and the most common size is <150 or <200 μm .

The size fractions of interest for the inhalation pathway belong to particles that could be resuspended and enter the human body. Although particles with aerodynamic diameter (D_{ae}) up to 100 μm could, potentially, be suspended and travel some distances (in some cases termed as inhalable particles) (Brown et al., 2013), they mostly reach nose and mouth, and thus they undergo ingestion, while particles finer than 10 μm could reach the thoracic region (Dockery and Pope, 1994; Kastury et al., 2017). After inhalation, a relevant part of the coarsest particles (between 2.5 and 10 μm), are deposited in the pharyngeal and tracheal region, where a fraction of HM can be dissolved before particles are removed by the so-called mucociliary clearance, and are mainly swallowed, ending up in the gastrointestinal tract (Snipes, 1989; Mukhtar and Limbeck, 2013), while <2.5 μm particles can travel deeply in lungs. However, both particle sizes have been demonstrated to lead to adverse responses in the lungs, while specific effects are different (Dockery and Pope, 1994; Brunekreef and Holgate, 2002; Brunekreef and Forsberg, 2005).

Thus, most of the studies adopt the U.S. EPA classification of respirable PM, divided either in PM₁₀ (particles with $D_{ae} <10$ μm) and PM_{2.5} (<2.5 μm) or in coarse PM (10-2.5 μm) and fine PM (<2.5 μm).

1.2.1 Interaction with atmospheric particulate matter

Soil and RD particles finer than 10 μm are considered as *resuspendable*, so they could contribute to the air quality impairment in a very important share, in particular in developing countries, where non-paved streets are common also in urban areas, or in arid environments, where wind can suspend soil and dusts. In most of the studies, RD is found to be a major component of the coarse PM (Chan et al., 2008; Karanasiou et al., 2009; Achilleos et al., 2016), thus influencing more the PM₁₀ than the PM_{2.5}, since finer particles are formed more during combustion process, while coarser from mechanic processes (like wear of vehicle components and road, as above-outlined).

Worldwide, RD has been identified to contribute up to 76% of the total PM₁₀ concentration, maximum share found in winter in Stockholm due to the use of studded tires (Denby et al., 2013), with mean contributions around 20%, identifying

RD as a major source of PM (Marcazzan et al., 2003; Zhao et al., 2006; Kupiainen et al., 2016). This contribution is comparable to that of tailpipe emissions (Querol et al., 2004) and can raise due to also be the first contributor to urban PM10 concentration (Amato et al., 2014; Denier van der Gon et al., 2013).

However, RD is a quite generic term, sometimes used only to describe resuspended particles from road, other times to describe any particle coming from non-exhaust vehicle emission (including brake/tire wear). In this work we will use the term to designate all the particles deposited on the road surface and potentially suspendable or leachable.

Soil resuspension is expected to have a large role windy climates or where unpaved roads are present, but further research is necessary to better separate individual contributions, as toxicity and possible mitigation measures are diverse (Amato et al., 2014; Pietrodangelo et al., 2013). As an example, mitigation measures aiming at the minimization of the resuspension have been tested (Amato et al., 2010; Aldrin et al., 2008), as road cleaning and road dust binders (e.g. calcium magnesium acetate, $MgCl_2$, $CaCl_2$ and potassium formate), but no or low effectiveness was found in Southern Europe, compared to Scandinavian countries.

Effect of road type and other factors controlling resuspension and RD variability during space and time are still almost unknown, although some research has been done. In Scandinavian countries, for example, the use of studded tires and road salting/sanding are predictor variables (Denby et al., 2013a and 2013b), while in Central and Southern Europe time-variability of RD emissions potential is driven by meteorology (Schaap et al., 2009; Pay et al., 2011; Amato et al. 2012). Regarding the spatial variability several factors have been pointed out as responsible of RD resuspension potential: pavement characteristics (Raisanen et al., 2005; Gustafsson et al., 2009; China and James, 2012; Amato et al., 2013), traffic intensity and speed, fleet composition (Bukowiecki et al., 2010; Liu et al., 2016), proximity to traffic lights, but also the presence of external sources (e.g. construction dust, unpaved areas, African dust deposition, etc.). However, the comprehension of the impact of these predictors is yet unknown, hampering the description of these emissions, their parametrization in models and the knowledge of their impact on air quality and public health.

1.3 Bioavailability and bioaccessibility of PTEs

The second key feature that enhance and determine the health effect of HM is the bioavailability and the bioaccessibility of such elements. As not all the HM are easily released and could be adsorbed or interact with the body, toxicity and risk assessment studies pointed out the need to use bioavailable concentrations instead of total metal contents (Paustenbach, 2000; Guney and Zagury, 2016). In literature,

different terms have been used to define this process of dissolution, transport and absorption that lead to the HM fraction that is really available to the organism (Ng et al., 2015). In particular, in this thesis, *availability* and *bioavailability* will be generically used to define *the amount of contaminant that could be dissolved and absorbed by organisms*, while bioaccessibility will define *the fraction of a contaminant that is soluble in the gastrointestinal tract and, therefore, available for absorption*, and it will be used in case of *in vitro* methods (following Ruby et al., 1999).

A variety of leaching agents have been used to simulate the *in vivo* behavior of HM species. Regarding the plant availability, standardized solutions have been widely accepted, for example the use of single chelating agents (EDTA, DTPA) to simulate the plant available HM fraction in, respectively, acid and basic soils, is an official method used for several years already (Quevauviller et al., 1997; Colombo and Miano, 2015). Conversely, the bioaccessibility tests mimicking the human gastrointestinal or pulmonary tract have not been widely accepted until recent years due to the lack of extensive studies including different contaminants and soil types and for the lack of validation between *in vitro* and *in vivo* methodology (Mukhtar and Limbeck, 2013; Ng et al., 2015; Wiseman, 2015), also because of the difficulty and of the higher costs of such studies.

Currently, various synthetic body fluids have been proposed to simulate the occurring processes in human body that cause the dissolution of HM. Most of the methods deal with gastro-intestinal availability of HM in soil (the most important exposure pathway), and some of them have been correlated with *in vivo* bioavailability data for As, Cd, and Pb (Ruby et al., 1996; 1999; Oomen et al., 2002; Juhasz et al., 2007; Wragg et al., 2011). Gastric phases employ usually a pH of 1-2 together with enzymes, salts or chelating agents (pepsin, glycine), while for intestinal phases pH raises around neutrality and a wide range of chemicals have been used (Ng et al., 2015).

Because of the strong acidity, the main part of the metal dissolution take place during the gastric phase extraction, and several studies observed good relationships between the stomach dissolution and *in vivo* relative bioavailability of Pb for different methodologies (SBET, Drexler and Brattin, 2007; PBET, Ruby et al., 1996; UBM, Denys et al., 2012). Therefore, although only As, Cd and Pb bioavailability in contaminated soil have been studied extensively, simple methods using only the gastric phase started to be extensively used to assess a wide range of HM.

Following preliminary studies (Ruby et al., 1999; Drexler and Brattin, 2007), US EPA released in 2009 a standard and validated method to predict Pb bioaccessibility in soil and dusts (USEPA Method 1340, 2015), consisting in a single extraction

with a solution containing 0.4 M glycine as complexing agent buffered at pH 1.5 with the addition of HCl. Since it was a simple and cost-effective way to improve risk assessment practices this method was rapidly adopted and used for a wide range of heavy metals and matrices, such as urban, industrial, agricultural and playground soils (Ljung et al., 2007; Poggio et al., 2009; Juhasz et al., 2011) and, lately, also for road dust (Hu et al., 2011; Yu et al., 2014).

2. Objectives and structure of the work

The main objective of this thesis is the understanding of size fractionation and bioaccessibility effects on the risk posed by HM in urban soils and road dust.

More generally, this work aims to offer new insights in the research of actors and regulators, moving from total and bulk measures of concentrations to more specific metrics and procedures, such as the bioaccessible concentrations and the particle size fractionation, to have a deeper understanding of harmful particles and HM. Three different urban matrices were investigated, namely soils, road dust and playground sands and the results are presented here in form of three published articles and one book chapter.

As previously mentioned, there was a need to understand the impact of RD among all non-exhaust traffic sources and his contribution to air quality. Therefore, a review study was carried out in collaboration with the Institute of Environmental Assessment and Water Research (IDAEA-CSIC) of Barcelona (Spain) (reported in Chapter 3), with the aim to define and quantify the worldwide impact of road dust resuspension on the different air quality parameters.

The first experimental part of this thesis was focused on urban roadside soils, basing on previous studies performed by the research group, and the first article (Chapter 4) explores the correlation between roadside soils and road dust in a peri-urban transect in the city of Turin. The aim was to better define HM sources in the different size fractions of soils and RD and to evaluate the bioaccessibility of HM, as particles of different sizes could also have diverse bioaccessible fractions of HM.

The second experimental work of this thesis attempted to identify those parameters responsible of RD variability in urban environments. In the article reported in Chapter 5 we explored the seasonal variability and the relationship between particle loading of roads and site characteristics (pavement macrotecture, traffic intensity and proximity to the braking point).

Finally, Chapter 6 reports the investigation on urban sands in public playgrounds of the city of Barcelona with the aim of characterizing fine fractions of sand generated by human grinding and of tracing HM enrichments due to anthropic activities. Then, due to the high ingestion risk posed to children, the bioaccessible fraction of HM was measured and the sources contributing most to this fraction were investigated.

3. Road dust and non-exhaust emissions: impact on air quality

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Abstract

While the overall toxicity of bulk atmospheric particles is well-known, researchers and air quality managers still face difficulties in the understanding of the most harmful species and sources, which is based on the knowledge of their individual impact on PM_x levels. This chapter aims at reviewing the current knowledge of the impact on air quality of vehicle non-exhaust sources (as a whole and individually for road dust, brake wear, tire wear and road wear). Ninety-nine peer-reviewed articles were found providing contributions ranges, often in comparison with vehicle exhaust contributions. Variability of contributions was explored relatively to PM size fraction, type of location and climate.

3.1 Introduction

The evidence for adverse health effects of ambient air pollution has grown dramatically in the past 20 years. The Global Burden of Disease study ranked exposure to ambient fine particulate matter (PM_{2.5}) as the seventh most important risk factor, contributing to total mortality with 2.9 million premature deaths in 2013, globally, and as fifth largest contributor in East Asia (GBD 2013 Risk Factors Collaborators et al., 2015). Whereas the overall toxicity of bulk PM is known, researchers still face a long way towards the understanding of the most harmful species (or mixtures) and sources, which would help dramatically the prioritization of control actions at international and local level (West et al., 2016). Road traffic has been often pointed as one of the most harmful source category (Bell et al., 2010; Ostro et al., 2011) in multi-pollutants epidemiological studies. However, the road traffic sector comprises a number of different emission processes (combustion, wear, suspension), which need different control actions. Among these processes, it is necessary to identify those of higher impact, both on terms of air quality (contribution to the particle mass, or number) and health outcomes (relative toxicity, Amato et al., 2014a; Denier van der Gon et al., 2013).

In comparison to vehicle exhaust, there are few *in vivo* toxicity studies focused on non-exhaust sources, however the most recent data indicate that non-exhaust particles can be as hazardous as exhaust PM depending on the nature of the health effect studied. Particle mass, size and surface chemistry all affect PM toxicity. Oxidative stress is one of the main biological mechanisms causing toxicity and is often related to transition metals and/or redox active organics such as quinone (Borm et al., 2007; Kelly, 2003). Brake and tire wear particles have higher oxidative potential than other traffic-related sources and their effect is very local (50–100 m from the source) (Yanosky et al., 2012) yielding more oxidant PM (per $\mu\text{g}/\text{m}^3$) at road sites rather than at urban background sites. Tire wear particles have been shown to induce Reactive Oxygen Species (ROS) formation and inflammatory reaction in human alveolar cells (Gualtieri et al., 2005 and 2008) as well as inflammatory response in mouse lungs (Mantecca et al., 2009 and 2010). Other important factors to be investigated are PM size and size distribution, particle number, composition (including coating and surface modifications), shape, surface area/specific surface area, surface chemistry, and charge and solubility/dispersibility.

Happo et al. (2010) found significant inflammatory response in rats lungs exposed to coarse PM in Helsinki and correlated this with Fe and Cu content. A recent assessment using ascorbic acid depletion (marker for presence of redox active metals), electron spin resonance (marker for OH• radical) as well as DTT consumption (marker for redox active organics), showed a clearly higher oxidation potential of brake pad particles compared to diesel engine exhaust and tire or road

dust (Amato et al., 2014a). Gustafsson et al. (2008) showed at least as high inflammatory potential from road wear PM10 compared to diesel engine exhaust particles. Brake wear particles damage have been linked to oxidative stress and inflammatory responses in the lung using incubations of lung cells with brake wear particles.

An established terminology and hierarchy of non-exhaust emissions does not exist, hampering the comparison of literature studies. In this book, we therefore aim to promote the use of the following terminology.

Vehicle non-exhaust emissions include:

- Direct brake wear: the fraction of pad, disc and clutch wear particles which are directly airborne;
- Direct tire wear: the fraction of tire wear particles which are directly airborne;
- Direct road wear: the fraction of road wear particles which are directly airborne;
- Road dust suspension: any particle on (paved) road surface which is suspended to air by vehicles or wind, including deposited brake/tire/road wear particles and other deposited particles from various origin (salt, sand, exhaust, secondary, other mineral dust etc.).

Another part of traffic emissions arises from unpaved road dust suspension, but due to the different emission dynamics and possible remediation, unpaved roads remain out of the scopes of this book, even if their contribution can be important in cities of several developing countries.

The above-mentioned distinction is however only hypothetical, since separating the contribution of the single sources has been a difficult task for researchers over the past 20 years. In spite of the quite large number of studies on aerosol source apportionment, a clear separation has been rarely found. This chapter aims at reviewing the body of literature on non-exhaust emissions contribution to air pollution concentrations. In particular, we aim to shed light on:

- Impact on WHO standard parameters;
- Impact on different types of environment (Industrial, urban, traffic...);
- Impact of climate on road dust emissions.

Non-exhaust sources differ widely in terms of chemical composition and particle size distribution (Amato et al., 2011; Duong and Lee, 2011; Grigoratos and Martini, 2015; Pant and Harrison, 2013). For a comprehensive discussion on their physico-chemical characteristics please see other book chapters (in Amato, ed., 2017).

Briefly, brake pads and discs are composed of many ingredients, used as binders, fillers, lubricants, fibers and frictional additives (Grigoratos and Martini, 2015).

Thus, chemical profiles vary largely although Fe, Ba, Sb, Sn and Cu are commonly reported as reliable tracers in brake linings (Amato et al., 2009; Gietl et al., 2010; Hulskotte et al., 2014; Kukutschová et al., 2011; Thorpe and Harrison, 2008). As different materials crumble in different periods, wear debris composition can be significantly different from brake lining material (Thorpe and Harrison, 2008). Von Uexkull et al. (2005), for example, found that Ni and Cu were in much greater concentrations in the emitted dust than in the bulk brake material. Iijima et al. (2008) reported, for non-asbestos organic (NAO) pads, similar composition for bulk pad and dusts, with a slight increase for Fe and Ti.

Tire wear particles composition is mainly carbonaceous, but aluminum, silicon, zinc and sulfur have been found (Harrison et al., 2012; Rogge et al., 1993; Thorpe and Harrison, 2008). Zinc, in particular, is used in rubber as ZnS and considered as tracer for tire wear, along with organic compounds (e.g. styrene), as it is also emitted from other sources (Kreider et al., 2010; Pant and Harrison, 2013).

Road surface wear is the most difficult source to trace, as the composition is primarily mineral aggregates bound by bitumen. The higher variability of geologic materials used, as its usual similarity with soil dust (Wahlin et al., 2006), prevent the identification of unique elemental tracers, while organic tracers as asphaltenes and maltenes have been suggested by Fauser (1999).

Road dust particles can arise from all above-said wear sources, but also from exhaust emissions, road sanding and salting and from geogenic material carried onto the road. Chemical composition has found to be dominated from elements associated to crustal material, as soil and road wear (Gu et al., 2011; Kupiainen et al., 2005; Thorpe and Harrison, 2008) and therefore is likely to be site-dependent. Where road salting procedures and studded tire use is common a winter seasonality can be evident (Kupiainen et al., 2016).

3.2 Review method and limitations

In Scopus (www.scopus.com), we searched for publications on vehicle non-exhaust emission impact, using the following search terms: PM10, PM2.5, coarse PM, fine PM, particulate matter, air quality, wear, resuspension, suspension, non-exhaust, tyre, tire, brake, road dust, road wear, traffic, crustal, suspension, resuspension, airborne, particle number, particle volume, emission model, emission inventory, source apportionment, receptor model and binary and ternary combinations of these. The main tool used in the reviewed studies was a receptor modelling technique based on measured PM concentrations at some receptor site, coupled with chemical characterization. However, we also found studies based on emission inventories, emission models and chemical transport models. The contribution to particle number and volume concentrations was also reviewed, although the

number of studies is much smaller than those on PM mass. However, basing on this methodology some relevant information might be still missing. Our conclusions might still be affected by some limitations:

- As, previously mentioned, an established terminology does not exist, therefore source/factors labelling by individual authors may not coincide.
- An established hierarchy does not exist yet, therefore the non-exhaust label does not contain implicitly contributions from all brake, tire wear and road dust resuspension.
- Source identification: this chapter does not evaluate the goodness of the source apportionment study procedure in the published studies.

3.3 Results

3.3.1 Impact on ambient air particulate

In this review, a total of 146 articles worldwide were included, where at least one air pollution source/factor related to vehicle non-exhaust emissions was identified. Among them, 47 could not well disentangle a non-exhaust source (namely Road dust/Crustal, Road dust/Construction, Road dust/harbor, Road dust/Tram, Road dust and salt, Traffic/wear, Traffic/Road dust, Exhaust/wear, among others) and were, therefore, discarded. As one article often included more than one metric and/or monitoring station we collected a total number of 256 contributions estimates. The methods used for estimating non-exhaust contributions were grouped as follows.

Receptor modeling based on PM chemical characterization:

- Positive Matrix Factorization (PMF or ME-2, 55 articles)
- Chemical Mass Balance (19 articles)
- Principal Component Analysis (8 articles)
- COPREM (1 article)
- Unmix (1 article)
- Other PM observations:
- Metal size distribution (1 article)
- Scanning Electron Microscope (1 article)
- A-ToF AMS (1 article)
- Rubber Tracer concentration (1 article)

Dispersion modelling /Emission inventory:

- CAMx (1 article)
- URBIS (1 article)
- KCLurban (1 article)

- LOTOS-EUROS (1 article)
- CALIOPE (1 article)
- ATMOs (1 article)
- UCD/CiT (1 article)
- NORTRIP (1 article)
- VAPI (1 article)
- U.S. EPA ISCST3 (1 article)

The 256 estimates of non-exhaust contributions (Table 3.3, at the end of the section) span different climatic conditions (using the Köppen climate classification; Peel et al., 2007): Arid (3 estimates), Continental (51 estimates), Mediterranean (70 estimates), Oceanic (60 estimates), Tropical-monsoon (28 estimates) and Temperate-subtropical (43 estimates). The studies are mostly settled in Europe (150, Figure 1), Asia (51) and North America (48), while much fewer studies are available in Oceania (5) and Africa (1). The first studies were performed in the 80s in USA, followed by the first few European studies in the 90s (Figure 3.1). The number of studies increased sensibly in the new century including the rest of continents. Different types of environment were investigated: rural/regional (16), suburban (6), urban (undefined (113) commercial (3), residential (11), background (44) and roadside (41)), industrial (11), freeway (2) and tunnels (6).

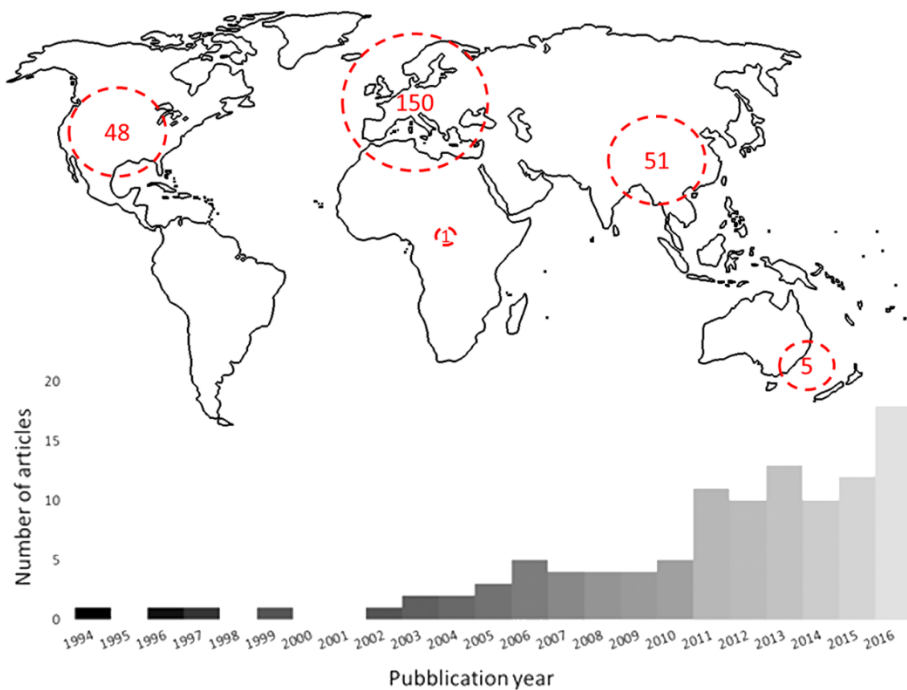


Figure 3.1 Number of study estimates for non-exhaust contributions per continent and number of articles per year.

Most of the estimates concerned the road dust emissions (71%), while only 9% and 8% refer to brake and tire wear, respectively. The rest of cases refer to a generic non-exhaust source (12%). Other studies, identifying miscellaneous factors (e.g. Road dust/traffic, Road dust/ Crustal), were discarded. The direct road wear has been rarely found, due to the high chemical similarity to road dust, was thus incorporated into the “road dust” category. We have grouped labels according to Table 3.1.

There are several variables influencing the impact of non-exhaust sources: activity (vehicle flow), climate (mostly for road dust and direct road wear), type of station (proximity to roadways), sampled PM size and time of the year. However, quantifying the influence of all these factors in terms of source contributions is hampered by the dearth of a sufficient number of studies covering such variability. As an example, we found only three studies estimating tire wear contribution to PM2.5, which does not allow investigating the variability with climate, season or type of site. At a first stage, we have grouped all studies, regardless of climate, type of station and period of the year in order to evaluate the overall impact of each source.

Table 3.1 Grouping of literature studies according to sources labelling

Source category	Non-exhaust and miscellaneous	Brake wear	Tire wear	Road dust
	Non-exhaust	Brake wear	Tire wear	Resuspension
	Non-exhaust (sum)			Road dust
	Non-exhaust (wear+resuspension)			Road wear
	Brake/Tire wear			Resuspended dust
	Tire and brake wear			
	Brake and tire wear			
	Road dust/brake wear			
% of the total number of estimates	12	9	8	71

The duration of the study is also crucial, mostly for road dust emissions, which can vary largely with meteorology. In the case of road dust, around ¾ of the studies were performed at least during one year.

The particles sizes under study were not always corresponding to the regulated metrics (i.e. PM10 and PM2.5) but includes also PM1 and PM coarse. Moreover, additional cut-off sizes were found and, for sake of simplicity, grouped as follows:

- PM1 (< 1 µm and 0.3-1 µm)
- PM2.5 (<2 µm; <2.1 µm; <2.5 µm; <3 µm and 1-2.5 µm)
- PM coarse (2.5-10 µm; 1.5-10 µm; 1.6-10.9 µm; 2.1-9 µm; 2-10 µm and 3-10 µm)
- PM10 (<10 µm; 1-10 µm and 0.9-11.5 µm)

Averaging all studies on PM10, road dust resulted to have a far higher impact than other reviewed sources. Mean contribution to PM10 (74 estimates in total) was 22%, ranging from 1 to 76% among the different studies, versus a range of 1-64% (21% as mean) from vehicle exhaust emissions (Figure 3.2).

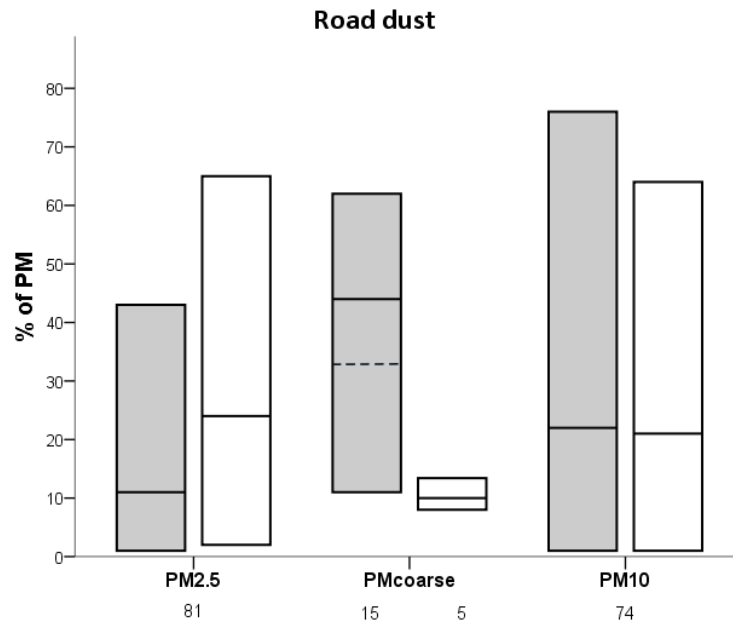


Figure 3.2 Range and mean road dust (in grey) and vehicle exhaust (in white) contribution (%) to different PM size fractions. Solid lines represent the average of the studies where both exhaust and non-exhaust sources were found, while dotted lines the mean of all studies (only for PMcoarse). The number of studies available are shown below each PM size fraction.

In absolute concentrations, the mean (among different studies) road dust contribution was $16.4 \mu\text{g}/\text{m}^3$ (ranging from 0.3 to $79.3 \mu\text{g}/\text{m}^3$), while $17.3 \mu\text{g}/\text{m}^3$ for exhaust (ranging from 1.2 to $103.6 \mu\text{g}/\text{m}^3$). For PM_{2.5} (81 estimates in total), road dust contributions were significantly lower, with a mean of 11%, ranging from 1 to 43% depending on the study, versus a mean of 24% (range of 2-65%) due to vehicle exhaust (Figure 3.2). In absolute terms the mean (among different studies) road dust contribution to PM_{2.5} was $3.8 \mu\text{g}/\text{m}^3$ ($8.8 \mu\text{g}/\text{m}^3$ for exhaust), ranging from 0.1 to $27.2 \mu\text{g}/\text{m}^3$ (0.3 - $59.8 \mu\text{g}/\text{m}^3$ for exhaust). For PM coarse (15 estimates in total), the relative contribution to PM mass was the highest, 34% (11-62%). In absolute concentrations, the average contribution was $5.8 \mu\text{g}/\text{m}^3$, ranging from 1.5 to $17.1 \mu\text{g}/\text{m}^3$. Only few studies allowed direct comparison with exhaust for PM coarse (Figure 3.2), revealing average contribution of 44% ($7.3 \mu\text{g}/\text{m}^3$) for road dust vs 10% ($1.9 \mu\text{g}/\text{m}^3$) for exhaust. For PM₁, we only found 2 studies with non-exhaust contributions of 2% and 5-21% although the latter is more uncertain as it was estimated by means of Scanning Electron Microscopy.

This comparison allows concluding that globally, regardless of the environment studied, non-exhaust emissions are already at least as important as exhaust ones for PM₁₀, considering also that the aforementioned contributions are derived mostly from receptor modelling, thus including the contribution of secondary PM for vehicle exhaust (while they are discarded in emission inventories). For PM_{2.5} they represent at least a third of total traffic contribution whilst they dominate the PM coarse ($>1.5 \mu\text{m}$) mode ($>80\%$).

Direct brake wear contributions to PM₁₀ (11 estimates, Figure 3.3) were found to vary from 0.1 to 20% (mean 7% of all studies) and, in absolute terms, from 0.1 to $8.0 \mu\text{g}/\text{m}^3$ (mean of $1.9 \mu\text{g}/\text{m}^3$). Only two studies allowed comparing with vehicle exhaust providing the same (5%) contribution (ranges of 1-11% for non-exhaust and 2-12% for exhaust).

For PM_{2.5} we only found 2 studies with brake wear contribution of 9% ($0.7 \mu\text{g}/\text{m}^3$) and 14% surprisingly with the latter at a rural site. In any case, only the former, performed at an urban site, allows comparing with exhaust emissions that contributed to 55% ($4.3 \mu\text{g}/\text{m}^3$, Figure 3.3).

For coarse particles, 4 estimates were found providing a contribution range of 7-23% (average 13%) and $0.7 \mu\text{g}/\text{m}^3$ varying from 0.3 to $1.3 \mu\text{g}/\text{m}^3$ (Figure 3.3). Only 1 study compared exhaust vs non-exhaust, providing a surprisingly ratio of 2 (1.6 vs $0.8 \mu\text{g}/\text{m}^3$, respectively), but as mentioned by authors, results were high uncertain due to the high correlation between the two factors contributions (Wahlin et al., 2006).

Several studies identified a contribution of disc wear to total brake wear emissions. Iijima et al. (2008) reported that approximately 30% of dust originated from disc in

their experiments, while Hulskotte et al. (2014) calculated that 70% of brake wear mass originate from disc wear. This wide variability is also reported for Fe, C and Cu from studies analyzing brake pads and discs composition. However, average Fe concentration is about 40% while is >90% in grey cast iron disc (Amato et al., 2009; Hulskotte et al., 2014; Kukutschová et al., 2011; Thorpe and Harrison, 2008).

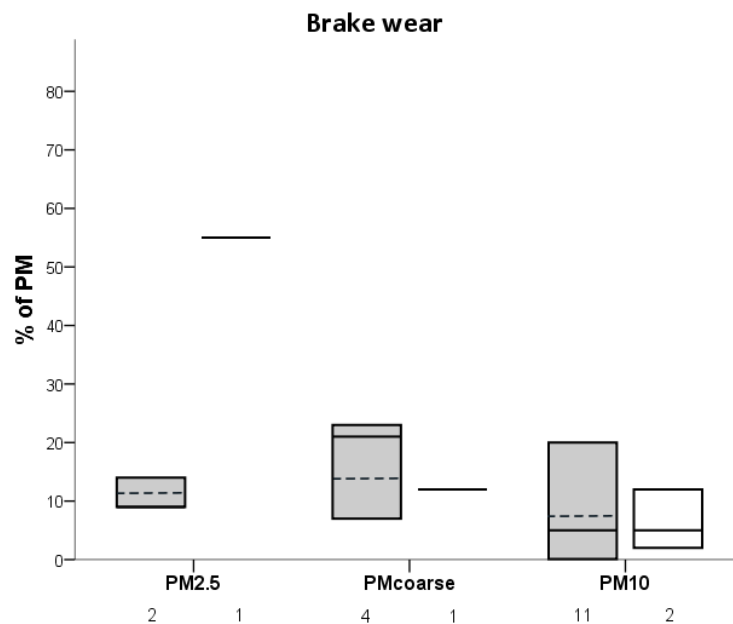


Figure 3.3 Range and mean brake wear (in grey) and vehicle exhaust (in white) contribution (%) to different PM size fractions. Solid lines represent the average of the studies where both exhaust and non-exhaust sources were found, while dotted lines the mean of all studies. The number of studies available are shown below each PM size fraction.

In Figure 3.4, we compare the average composition for brake pads (from Amato et al., 2009; Figi et al., 2010; Hjortenkrans et al., 2007; Hulskotte et al., 2014; Iijima et al., 2008; Kukutschová et al., 2011; von Uexkull et al., 2005) and brake discs (Hulskotte et al., 2014) with that of PMF brake wear factor profiles (Hedberg et al., 2012; Mooibroek et al., 2016; Sturtz et al., 2014; Visser et al., 2015; Wahlin et al., 2006).

Brake wear factor profiles are generally similar to those of brake pads, with Fe as main components in mass. The typical tracers Ba, Cu, Sb, and Sn have similar concentrations in brake pads and in PMF profiles. However, iron content in PMF profile results to be intermediate between disc and pads composition, confirming the importance of disc wear (Figure 3.4). On the contrary, sulphur content is slightly

higher in PMF profiles rather than in both pads and discs. This can be interpreted as poor representativeness of pads experimental profile or to a mix of PMF brake factors with other traffic-related sources (exhaust for example).

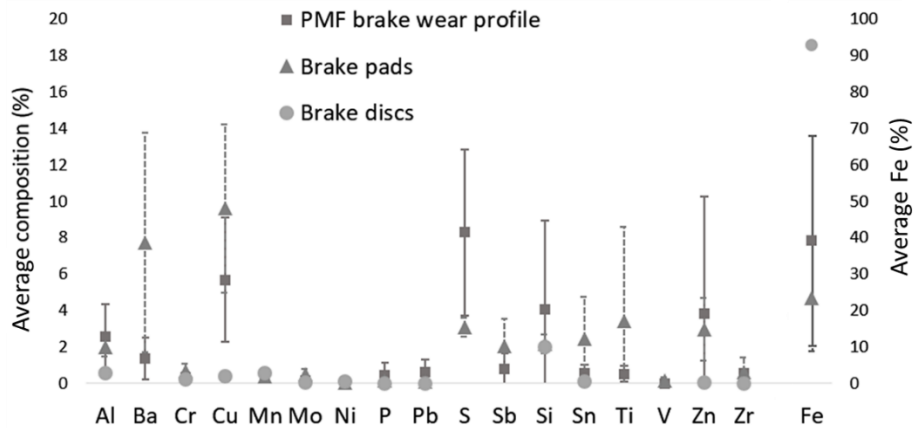


Figure 3.4 Average compositions of brake pads (Amato et al., 2009; Figi et al., 2010; Hjortenkrans et al., 2007; Hulskotte et al., 2014; Iijima et al., 2008; Kukutschová et al., 2011; von Uexkull et al., 2005), brake discs (Hulskotte et al., 2014) and PMF brake wear profile as found from source apportionment studies (Hedberg et al., 2012; Mooibroek et al., 2016; Sturtz et al., 2014; Visser et al., 2015; Wahlin et al., 2006).

Direct tire wear contribution (in %) was found to be lower than brake wear for all PM size fractions. In PM₁₀ (11 estimates) an average value of 4% (0.5-8%) and 1.8 $\mu\text{g}/\text{m}^3$ (0.6-3.4 $\mu\text{g}/\text{m}^3$) was found (Figure 3.5), except an outlier data with a mean contribution of 15.4 $\mu\text{g}/\text{m}^3$ in India. Only four studies allowed the inter-comparison with vehicle exhaust contribution, showing 22% (13-37%) from exhaust and 6% (2-8%) from tire wear. In PM_{2.5} we only found 3 studies; one in Spain that found, surprisingly, a 1:1 ratio with exhaust (18%), probably due to a co-linearity among the two PMF factors (Figure 3.5). The other two studies in USA found a contribution ranging from 0.9 to 3.3% (mean of 1.6%), with a mean contribution of 0.8 $\mu\text{g}/\text{m}^3$ (0.3-2.0 $\mu\text{g}/\text{m}^3$) (Figure 3.5). In the same studies, exhaust emissions contributed 32% (23-40%) and 20 $\mu\text{g}/\text{m}^3$ (12-26 $\mu\text{g}/\text{m}^3$). For coarse PM only 1 study was found (Figure 3.5), estimating contribution at 3 cities in the US: the mean contribution was 3.4%, varying from 1 to 7%, while in absolute concentrations 0.27 $\mu\text{g}/\text{m}^3$ (from 0.05 to 0.39 $\mu\text{g}/\text{m}^3$).

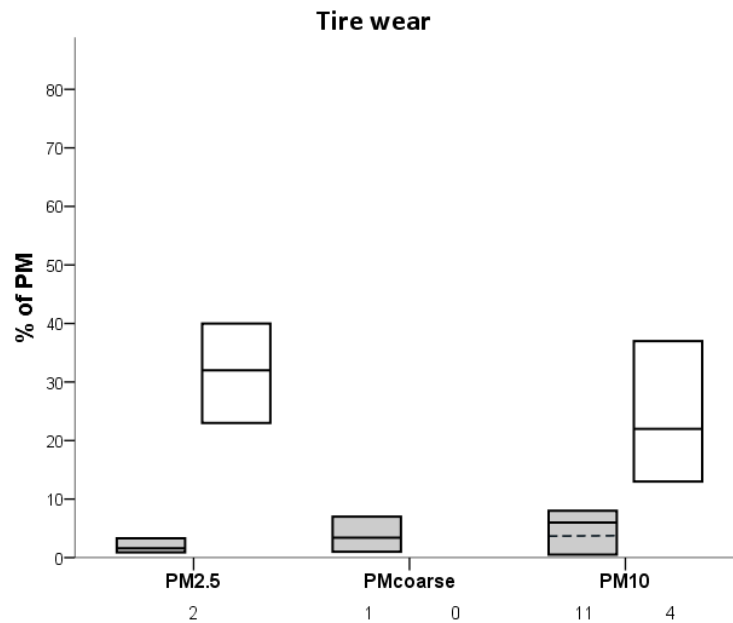


Figure 3.5 Range and mean tire wear (in grey) and vehicle exhaust (in white, not available for PM coarse) contribution (%) to different PM size fractions. Solid lines represent the average of the studies where both exhaust and non-exhaust sources were found, while dotted lines the mean of all studies. The number of studies available are shown below each PM size fraction.

Another category of studies included 12 articles identifying a generic “Non-exhaust” source or similar (Table 3.1, Figure 3.6).

The mean contribution of these studies to PM10 (18 estimates) was 8% (range: 1-14%, plus a 42% value found in a roadside station UK), being the absolute contribution estimated only by a part of them in $3 \mu\text{g}/\text{m}^3$ (range: $0.2\text{-}17 \mu\text{g}/\text{m}^3$). Selecting those studies that identified also the exhaust contribution, the comparison shows a mean 6% (1-15%) contribution of non-exhaust vs a mean 11% (1-23%) from exhaust (Figure 3.6). However we have to remind that, given the lack of definition on the term “non-exhaust”, this category cannot be intended a priori as the “total” non-exhaust contribution (i.e. road dust contribution might be hidden in “mineral” or “crustal” factors). In PM2.5, a mean contribution of 6% was found (range: 1-11%, Figure 3.6) except one study with 47% at a roadside site in UK being the absolute contribution estimated only by a part of them in $1.4 \mu\text{g}/\text{m}^3$ (range: $0.2\text{-}3.4 \mu\text{g}/\text{m}^3$), while the exhaust contribution was found to be in average 19% (6-37%) and to vary within $1.7\text{-}8.1 \mu\text{g}/\text{m}^3$ ($4.2 \mu\text{g}/\text{m}^3$ as average). In PM1 only a German study was found with a mean contribution of 3% versus 10% from exhaust (Figure 3.6).

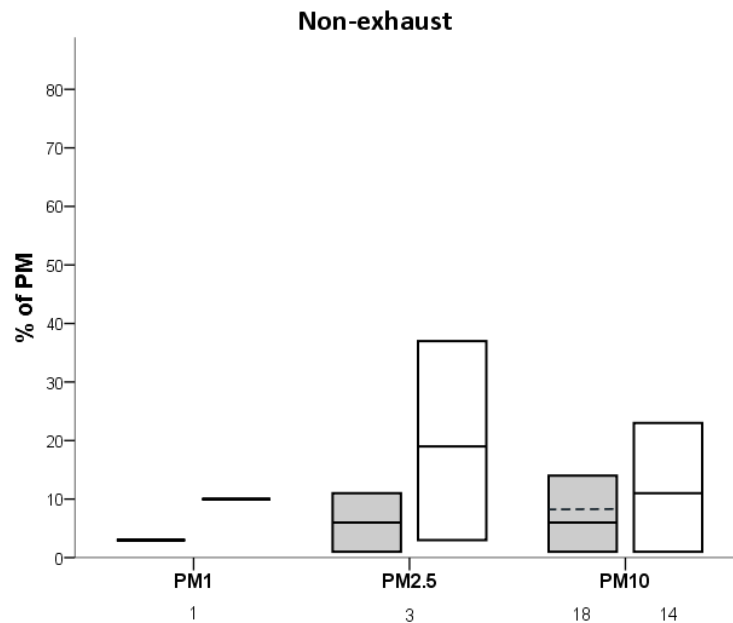


Figure 3.6 Range and mean non-exhaust (in grey) and vehicle exhaust (in white) contribution (%) to different PM size fractions. Solid lines represent the average of the studies where both exhaust and non-exhaust sources were found, while dotted lines the mean of all studies. The number of studies available are shown below each PM size fraction.

Non-exhaust emissions have been predicted to increase in relative importance to urban PM mass during the last two decades due to the reduction of exhaust emissions (Keuken et al., 2012; Kousoulidou et al., 2008; Rexeis and Hausberger, 2009). Recently, analysis of trends in atmospheric emissions reported first evidences of this increase of the share of coarse particles in PM10, as PM2.5 decrease more rapidly than PM10 (Masri et al., 2015). Similarly, at various European sites PM2.5 trends over last decade declined more rapidly than coarse PM (Barnpadimos et al., 2012). Font and Fuller (2016) also reported a general downward trend in PM2.5 in London, proving the usefulness of exhaust abatement policies, while for PM10 such trend was not noted. In Southern Spain for example, from 2004 to 2011 road dust contributions to PM10 levels measured at a number of sites did not decrease, while vehicle exhaust contributions decreased ($p < 0.001$) by 0.4 (0.57–0.24) $\mu\text{g}/\text{m}^3 \cdot \text{year}$ (Amato et al., 2014b). Further increase in Europe in the coming years may also be boosted by the economic crisis, the consequent poor maintenance of vehicles and roads and the possible increase of low-cost materials and technologies used, with worse quality and faster degradation/erosion.

The aforementioned figures on air quality (PM10 and PM2.5) impact are due to the coarser size distribution of non-exhaust particle volume/mass when compared to exhaust PM.

Size distribution of brake wear particles was recently reviewed by Grigoratos and Martini (2015), who classified 3 types of methodologies used to assessing it: i) emission studies in laboratory (e.g. brake dynamometer, or pin-on-disc; Garg et al. 2000; Gasser et al. 2009; Kukutschová et al. 2011; Iijima et al. 2007; Iijima et al. 2008; Mosleh et al. 2004; Sanders et al. 2003; Wahlström et al. 2010); ii) receptor modelling studies (Bukowiecki et al. 2009a and 2009b; Dongarra et al. 2009; Gietl et al. 2010; Harrison et al. 2012; Hjortenkrans et al. 2007; Fabretti et al. 2009; Wahlin et al. 2006) and iii) “real-world” emission studies (Mathissen et al. 2011). Most of the studies found unimodal brake wear mass distributions with maxima ranging between 1.0 and 6.0 μm , confirming the high impact of brake wear emissions also in PM2.5. For instance, Kukutschová et al. (2011) found unimodal distribution with maxima at 2–4 μm using low-metallic pads, while von Uexküll et al. (2005) conducted tests on front and rear truck brakes and found unimodal mass distributions with maxima at 2–3 μm . Similar conclusions were reached by Harrison et al. (2012), who collected size-fractionated samples of airborne PM and found that a unimodal PM10 mass distribution with a peak at 2–3 μm .

Regarding tire wear mass size distribution, only three studies were found: Kwak et al. (2013), investigated the mass size distributions of road (RWP) and tire wear (TWP) particles during constant speed conditions (50, 80, 110, and 140 km/h). The mode diameters of TWPs were between 2 and 3 μm . Harrison et al. (2012) estimated also a bimodal distribution with maxima at 2 and 8 μm , respectively, using Zinc as tracer of mass size distribution. Differently, Gustafsson et al. (2008) indicated tire wear as the source of particles <1 μm on a road simulator.

Concerning road wear, Kwak et al. (2013) found that peak values of RWPs generated at vehicle speeds of 50, 80, 110, and 140 km/h ranged between 2 and 3 μm , while for speeds greater than 80 km/h, RWPs showed a bimodal distribution with peaks at 2–3 μm and > 10 μm . Aatmeeyata et al. (2009), found about 32% of particle mass emitted from road-tire friction of PM10 was present below 1 μm . The number as well as mass size distribution for PM10 was observed to be bi-modal with peaks at 0.3 μm and 4–5 μm . Kupiainen et al., 2005 found however particle mass size distribution with maxima well above 2.5 μm , both with friction tires and studded tires.

Concerning strictly road dust, most of the studies identified only impact on PM2.5 or PM10 mass fraction, without further subtle fractionation. As it is generally identified as a mixture of the previously mentioned sources plus suspended soil, it is obviously enriched mostly in the 2.5-10 μm fraction. Most of the studies, based

on various methods, found a unimodal mass size distribution above, at least, 3-4 μm (Harrison et al. 2012; McKenzie et al. 2008; Tian et al. 2016; Zhu et al. 2015). For example, Harrison et al. (2012) collected size-fractionated samples of airborne PM and found a unimodal PM10 mass distribution of road dust particles peaking around 4 μm . Tian et al. (2016), using receptor modeling, report that road dust profile has the major relative contribution to PM (>10 %) above 3.3 μm . Roadway particles (which is assumable to be road dust) particle mass size distribution was also studied by Lee et al., (2013), who found a bimodal distribution at lower sizes, being the maxima at 0.7 and 2 μm .

3.3.2 Spatial variability

The micro-scale (rural to traffic locations) spatial variability of source contributions according to receptor sites shows the following:

Road dust suspension: at rural locations, PM10 mean contribution (4 estimates) was 8% (6-9%) vs a 15% (7-23%) from vehicle exhaust, 1.1 $\mu\text{g}/\text{m}^3$ vs 2.3 $\mu\text{g}/\text{m}^3$ in absolute contributions, respectively (Figure 3.7). This is likely due to the lower travelling distances of coarse particles. In PM2.5, the proportion of road dust particles is about 3 times lower than exhaust: 4% (1-9%) vs 12% (8-20%), 0.5 $\mu\text{g}/\text{m}^3$ vs 1.6 $\mu\text{g}/\text{m}^3$ since the coarse fraction of road dust is not captured. At suburban, although only a very limited number of studies was found (3 estimates,) PM10 contribution increased to 7% (except one study in Finland finding 43%, Kupiainen et al., 2016) vs 18% of exhaust emissions, corresponding to 1.8 $\mu\text{g}/\text{m}^3$ vs 4.9 $\mu\text{g}/\text{m}^3$. In PM2.5 the same pattern of rural background is observed: 3% vs 11% and 0.4 $\mu\text{g}/\text{m}^3$ vs 1.4 $\mu\text{g}/\text{m}^3$. The largest body of literature was found for urban locations (128 estimates): PM10 contributions averaged 23% (range of 1-59%) vs 22% of exhaust (range of 1-64%), 22.1 $\mu\text{g}/\text{m}^3$ vs 20.7 $\mu\text{g}/\text{m}^3$, respectively (Figure 3.7). In PM2.5 mean contributions of 11% (range of 1-32%) vs 24% (3-58%) and 3.8 $\mu\text{g}/\text{m}^3$ vs 8.2 $\mu\text{g}/\text{m}^3$ were found, while in PM coarse (1.5-10 μm approximately): 44% (17-47%) vs 10% (8-14%) from exhaust), 5.0 $\mu\text{g}/\text{m}^3$ (7.3 vs 1.8 $\mu\text{g}/\text{m}^3$).

A lower number of studies was found at roadside locations (19 estimates). PM10 contributions were on average 25% (12-53%), with 20% for exhaust (6-36%), but reaching 57-76% in Sweden and Denmark (Figure 3.7); in absolute concentrations mean values were 8.1 $\mu\text{g}/\text{m}^3$ for road dust vs 9.0 $\mu\text{g}/\text{m}^3$ for exhaust (higher due to the lack of absolute contribution in 1 study with SEM). Only 1 study quantified road dust contribution in freeway (11 vs 13%, 2.1 vs 2.4 $\mu\text{g}/\text{m}^3$) and other two in tunnels (19% vs 12%) (Figure 3.7). For PM2.5 mean contribution at roadside locations was 20% (10-31%) vs 30% for exhaust (12-62%), corresponding to 8.3 $\mu\text{g}/\text{m}^3$ vs 20.0 $\mu\text{g}/\text{m}^3$; while the only study in tunnel found 43% vs 21%. For coarse

PM only 1 study compared road dust contribution share with exhaust (31% vs 13% for exhaust).

Other 7 estimates were found in industrial settings: in PM10 16% (12-19%) was the average road dust contribution vs 22% (9-47%) of exhaust (Figure 3.7), corresponding to 10 $\mu\text{g}/\text{m}^3$ vs 15 $\mu\text{g}/\text{m}^3$, while in PM2.5 mean contribution of road dust was 12% (6-24%) vs 28% (2-65%) corresponding to 4.0 $\mu\text{g}/\text{m}^3$ vs 17.8 $\mu\text{g}/\text{m}^3$ respectively.

Brake wear: at rural locations, only 1 estimate was found (14% of PM2.5, 1 $\mu\text{g}/\text{m}^3$). The largest number of studies was found for urban locations (16 estimates). For PM10 only 2 studies were found (Figure 3.7): 1 study in northern Europe, where contributions averaged 4% (3-5%) vs 4% (2-5%) of exhaust, and 1 study in India (58% of PM10 from exhaust versus 0.1% from brake wear), who also found the same values for PM2.5. Another study in Denmark (Wahlin et al., 2006) found a mean contribution of brake wear of 9% vs 55% of exhaust. For urban PM coarse the average brake wear contribution was found to be 13% (6-23%) corresponding to 0.7 $\mu\text{g}/\text{m}^3$.

A lower number of studies was found at roadside locations (4 estimates). PM10 contributions were on average 11% (5-20%), 3.6 $\mu\text{g}/\text{m}^3$ for brake wear. The comparison with exhaust was made only in 1 tunnel study (11% vs 12%). Another study in an industrial setting found in PM10 0.7% as the brake wear contribution vs 1.8% of exhaust; while in PM0.3-3 a brake wear share of 0.4% was found.

Tire wear: very few studies were found for each location category; on average, it contribute 0.5% to rural PM10 and 1.9% to PM10 in urban sites, versus 13% of vehicle exhaust (Figure 3.7). In urban PM2.5, its share is 2% (1-3%) vs 30% (23-37%) from exhaust. In urban PM coarse, it increases slightly to 3% (2-7%), corresponding to 0.3 $\mu\text{g}/\text{m}^3$ on average. More studies are located roadside, providing a mean contribution of 5% of PM10, although it increase to 8% (7-8%) in those studies that also estimated contribution of exhaust, at 19% (18-20%), 2.1 ($\mu\text{g}/\text{m}^3$) as average. One roadside PM2.5 study showed a mean 1.1% contribution vs 39% contribution from exhaust, although another study found a 18% contribution, but likely due to a mix of sources. Only one estimate in industrial sites was found, displaying a value of 8% of PM10.

Non-exhaust: 29 estimates for the generic non-exhaust source were found (only 24 times together with exhaust). At rural sites, contribution to PM10 was found on average 3.75% (3.5-4%) vs 16% of exhaust (Figure 3.7). At suburban locations, only 2 studies revealed about 10% contributions for both PM10 and PM2.5 (approximately 1.8 $\mu\text{g}/\text{m}^3$). At urban sites 6% (1-14%) vs 10% (1-16%) in PM10 and 5% (1-8%) vs 17% (6-37%) in PM2.5. At roadside only two studies were found, calculating a contribution of 42% and 8% (vs 23% from exhaust) in PM10 and 45% and 5% (vs 32%) in PM2.5.

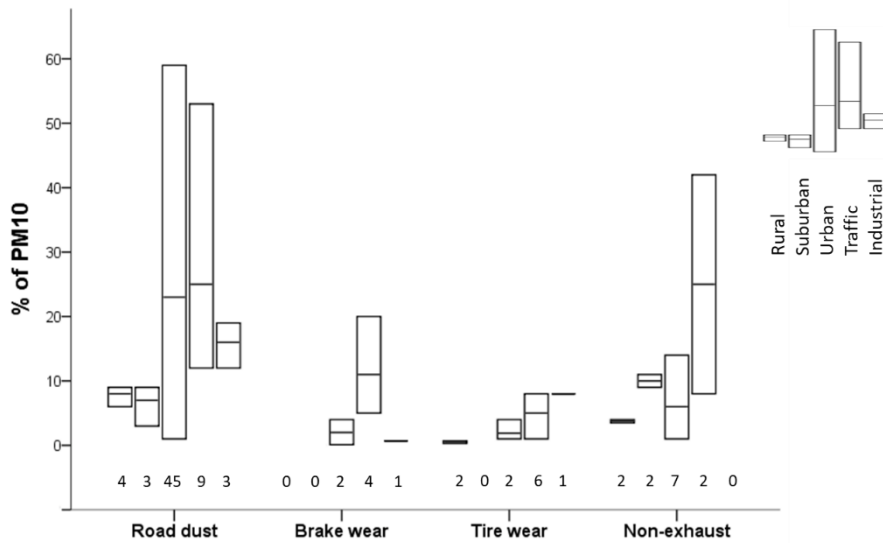


Figure 3.7 Range of contributions (%) to PM10 of different non-exhaust sources.

The macro-scale variability of non-exhaust emissions is mostly driven by climate. Road dust suspension was the only source which could be evaluated, being the number of studies was large enough to span well over different climatic conditions. In order to better visualize the climate dependence we only compared PM10 among urban and roadside sites (Table 3.2).

The lowest contribution of road dust relatively to exhaust emissions were found in Oceanic urban sites, where 5 studies found a mean road dust contribution of 13% vs 22% from exhaust (ratio 0.60). Slightly higher ratios (0.66) were found in urban continental sites with 16% vs 24% mean contributions. The importance of road dust increase considerably in Mediterranean and Tropical-Monsson climates where ratios increase to 0.85, and even above 1 at traffic sites. The worst scenario for road dust emissions was found in China where road dust contributions exceed exhaust ones with a ratio of 1.8.

Table 3.2 Average share of PM10 explained by road dust and exhaust factor in urban and roadside sites according to climate.

Climate (n° of studies)	Urban		Roadside	
	Road dust	Vehicle exhaust	Road dust	Vehicle exhaust
Continental (8)	16% (9-29%)	24% (11-62%)	14% (13-16%)	27% (18-36%)
Oceanic (7)	13% (6-21%)	22% (6-37%)	19% (9-28%)	only 1 study (13%)
Mediterranean (18)	19% (7-34%)	22% (9-64%)	23% (11-35%)	21% (19-27%)
Temperate (11, mostly in China)	29% (7-59%)	16% (7-40%)	no studies	no studies
Tropical-Monsoon (8, in India)	29% (1-51%)	34% (18-58%)	no studies	no studies

3.3.3 Other metrics

Although regulated air quality metrics only refer to particle mass, there is an increasing concern on particle number (PN) concentration, due the capability of finer particles to penetrate into the alveolar system and into the blood system. For brake wear particles, Garg et al. (2000) conducted dynamometer tests and found the highest number of emitted particles to lie into diameters smaller than 30 nm. This is in agreement with Mathissen et al. (2011), who exhibited a bimodal PN distribution with a nucleation mode at 10 nm and a second mode between 30 and 50 nm. Other studies found that, despite the negligible generation of small wear particles (<500 nm) at low rotor temperatures, the concentration of nanoparticles smaller than 100 nm significantly increase with the increase of the cast iron disc temperature (up to 340 °C) (Kukutschová et al., 2011; Nosko and Olofsson, 2017). They proposed that submicron particles are rather formed by the evaporation/condensation process, with subsequent aggregation of primary nanoparticles, than by an abrasive type of wear. Riediker et al. (2008) tested pad materials of six different passenger cars under controlled environmental conditions and found a bimodal PN distribution with peaks at 80 nm (depending on the tested car and braking behavior) and at 200–400 nm. They found that full stops result in higher nanoparticle production compared to normal deceleration.

Three studies were found investigating the size distribution of tire wear particle number. Dall'Osto et al. (2014), found a bimodal particle distribution below 100 nm with modes at about 35 nm and 85 nm. Unimodal (70–90 nm) and bimodal (<10 and 30–60 nm) number size distributions in the nano size range have been reported for tire particles under low and high-speed conditions, respectively (Mathissen et al., 2011). Dahl et al. (2006), found an enrichment of tire particles between 15 and 50 nm using a road simulator. They identified two types of particle: one comprising mineral oils from the softening filler, the other of soot-like agglomerates from the carbon-reinforcing filler material. Kreider et al. (2010) characterized the physical and chemical properties of particles generated from the interaction of tires and road surfaces. However, these particles were distributed (in number) in the very large coarse mode, spanning from 4–6 μm to 265–280 μm , with the mode centered at approximately 50–75 μm . Kreider et al. (2010) found, interestingly, that the mode of particle number size distribution of road wear particles was at 11-12 microns. Dahl et al., 2006 investigated particle number size distributions of the aerosol generated at different speeds with studded and non-studded tires on quartzite and granite pavements, finding in all cases maxima concentration below 50 nm.

Concerning the contribution of non-exhaust emissions to PN concentrations, four studies were found investigating non-exhaust contribution to particle number concentration (Gu et al., 2011; Harrison et al., 2011; Liu et al., 2016; Sowlat et al., 2016). All four sites were urban. The particle size range analyzed was, respectively, 3 nm-10 μm , 15 nm-20 μm , 15 nm-20 μm and 14 nm-10 μm . As expected, the non-exhaust contribution is negligible as compared to that from exhaust. Brake wear and road dust were found to contribute within 1-5% of PNC while exhaust contributed 54-67%.

Given the high metal content on brake and tire materials, and the strict IPPC regulation on industrial emissions, non-exhaust sources are becoming one of the largest source of some metals and metalloids in urban air. Using tunnel measurements could be useful to compare only traffic related emission, Fabretti et al. (2009), for example, calculated that resuspension and vehicular abrasion contributed 43% and 36% to the global emission of metals in PM_{2.5} in a tunnel, while combustion only a 21%. Also Lawrence et al. (2013) assessed source contribution through metal concentrations, and found resuspension to be the major contributor, followed by the sum of exhaust, brake and tire wear and from road wear. Visser et al. (2015) identified three factors, namely resuspended dust, brake wear and traffic-related (composed almost exclusively from Fe) that account for the majority of the total trace elements mass, together with sea/road salt.

Table 3.3 Results for exhaust and non-exhaust contributions to size-fractionated PM as reported in the literature.

Location	Climate	Year	Type of station	PM metric	Study Duration	Method	Source	Share (%)	Share ($\mu\text{g}/\text{m}^3$)	Exhaust (%)	Exhaust ($\mu\text{g}/\text{m}^3$)	Reference
Australia, Brisbane	Temperate	1993-1994	Urban	PM 2.5	Yearly	RM, CMB	Road dust	2	0.14			Chan et al., 1999
Australia, Brisbane	Temperate	1993-1994	Urban	PM 2.5-10	Yearly	RM, CMB	Road dust	15	1.5			Chan et al., 1999
Australia, Brisbane	Temperate	2003-2004	Urban	PM 10	Yearly	RM, PMF	Road dust	28	3.6	40	5.1	Chan et al., 2008
Australia, Melbourne	Oceanic	2003-2004	Urban	PM 10	Yearly	RM, PMF	Road dust	21	3.4	37	6	Chan et al., 2008
Bangladesh, Chittagong	Tropical-Monsoon	2007	Urban background	PM 2.5	Yearly	RM, PMF	Road dust	19	8.9	9.8	4.5	Begum et al., 2009
Belgium, Antwerp	Oceanic	2013-2014	Urban background	PM 10	Yearly	RM, PMF	Brake wear	4.9	1.5	3.9	1.2	Mooibroek et al. 2016
Belgium, Antwerpen	Oceanic	2011-2012	Urban background	PM 10	Yearly	RM, PMF	Non-exhaust	1	0.22	13	2.9	Maenhaut et al., 2016
Belgium, Brugge	Oceanic	2011-2012	Urban background	PM 10	Yearly	RM, PMF	Non-exhaust	1	0.23	9	2.1	Maenhaut et al., 2016
Belgium, Gent	Oceanic	2011-2012	Urban background	PM 10	Yearly	RM, PMF	Non-exhaust	1	0.25	11	2.8	Maenhaut et al., 2016

Location	Climate	Year	Type of station	PM metric	Study Duration	Method	Source	Share (%)	Share ($\mu\text{g}/\text{m}^3$)	Exhaust (%)	Exhaust ($\mu\text{g}/\text{m}^3$)	Reference
Belgium, Oostende	Oceanic	2011-2012	Urban background	PM 10	Yearly	RM, PMF	Non-exhaust	1	0.24	8	1.9	Maenhaut et al., 2016
Canada, Edmonton	Continental	2004-2008	Urban	PM 2.5	Yearly	RM, PMF	Road dust	7	0.6	12	1	Jeong et al., 2011
Canada, Montreal	Continental	2004-2008	Urban	PM 2.5	Yearly	RM, PMF	Road dust	4	0.4	14	1.4	Jeong et al., 2011
Canada, Toronto	Continental	2004-2008	Urban	PM 2.5	Yearly	RM, PMF	Road dust	3	0.4	10	1.3	Jeong et al., 2011
China, Beijing	Continental	2013	Urban	Particle Number	Short term	RM, PMF	Road dust	4		53.8		Liu et al., 2016
China, Beijing	Continental	2013	Urban	PM10 volume	Short term	RM, PMF	Road dust	11		13.4		Liu et al., 2016
China, Beijing	Continental	2000	Urban	PM 2.5	Short term	RM, UNMIX	Road dust	9	8.4	6	5.7	Song et al., 2006
China, Beijing	Continental	2013-2014	Urban	PM 2.1	Yearly	RM, PMF	Road dust	8	5.6	19.6	13.1	Tian et al., 2016
China, Beijing	Continental	2013-2014	Urban	PM 2.1-9	Yearly	RM, PMF	Road dust	11	6.8			Tian et al., 2016
China, Beijing	Temperate	2010	Urban	PM 2.5	Yearly	RM, PMF	Road dust	13	6.6	17.1	8.9	Yu et al., 2013
China, Handan	Temperate	2012-2013	Urban	PM 2.5	Yearly	RM, PMF	Road dust	11	17.45	7.7	11.5	Wei et al., 2014
China, Harbin	Continental	2006-2007	Urban	PM 10	Yearly	RM, CMB	Road dust	16	27.2	61.7	103.6	Huang et al., 2010
China, Jinan	Temperate	2002-2004	Urban	PM 10	Yearly	RM, CMB	Road dust	30	42.6	10	14.2	Zhao et al., 2006

Location	Climate	Year	Type of station	PM metric	Study Duration	Method	Source	Share (%)	Share ($\mu\text{g}/\text{m}^3$)	Exhaust (%)	Exhaust ($\mu\text{g}/\text{m}^3$)	Reference
China, Nanjing	Temperate	2013	Urban	PM 2.5	Yearly	RM, PMF	Road dust	9	10.9			Li et al., 2016
China, Panzhihua	Temperate	2007	Urban	PM 10	Short term	RM, CMB	Road dust	7	9.2	13.7	18.9	Xue et al., 2010
China, Shijiazhuang	Temperate	2002-2004	Urban	PM 10	Yearly	RM, CMB	Road dust	43	68.5	10	15.9	Zhao et al., 2006
China, Taiyuan	Temperate	2002-2004	Urban	PM 10	Yearly	RM, CMB	Road dust	32	54.6	15	25.6	Zhao et al., 2006
China, Taiyuan	Temperate	2001	Urban	PM 10	Yearly	PCA/MR-CMB	Road dust	26	79.3	13	39.7	Zheng et al., 2010
China, Tianjin	Temperate	2002-2004	Urban	PM 10	Yearly	RM, CMB	Road dust	34	43	13	16.4	Zhao et al., 2006
China, Urumqi	Temperate	2002-2004	Urban	PM 10	Yearly	RM, CMB	Road dust	30	40.4	9	12.1	Zhao et al., 2006
China, Yinchuan	Temperate	2002-2004	Urban	PM 10	Yearly	RM, CMB	Road dust	59	65.9	7	7.8	Zhao et al., 2006
Croatia, Rijeka	Oceanic	2013-2015	Urban	PM 2.5	Yearly	RM, PMF	Road dust	6	1.2	33	6.6	Ivošević et al., 2016
Cyprus, Larnaca	Mediterranean	2012	Urban	PM 2.5	Yearly	RM, PMF	Road dust	2	0.3	17	2.3	Achilleos et al., 2016
Cyprus, Larnaca	Mediterranean	2012	Urban	PM 2.5-10	Yearly	RM, PMF	Road dust	33	5.1			Achilleos et al., 2016
Cyprus, Limassol	Mediterranean	2012	Urban	PM 2.5	Yearly	RM, PMF	Road dust	4	0.5	32	4.1	Achilleos et al., 2016

Location	Climate	Year	Type of station	PM metric	Study Duration	Method	Source	Share (%)	Share (µg/m3)	Exhaust (%)	Exhaust (µg/m3)	Reference
Cyprus, Limassol	Mediterranean	2012	Urban	PM 2.5-10	Yearly	RM, PMF	Road dust	47	7.8			Achilleos et al., 2016
Cyprus, Nicosia	Mediterranean	2012	Urban	PM 2.5	Yearly	RM, PMF	Road dust	3	0.4	21	3.1	Achilleos et al., 2016
Cyprus, Nicosia	Mediterranean	2012	Urban	PM 2.5-10	Yearly	RM, PMF	Road dust	45	5.5			Achilleos et al., 2016
Cyprus, Paphos	Mediterranean	2012	Urban	PM 2.5	Yearly	RM, PMF	Road dust	2	0.3	14	1.7	Achilleos et al., 2016
Cyprus, Paphos	Mediterranean	2012	Urban	PM 2.5-10	Yearly	RM, PMF	Road dust	29	3.6			Achilleos et al., 2016
Czech Republic	Continental	2008-2010	Rural	PM 1-10	Short term	RM, PMF	Road dust / Brake wear	3.5	0.13			Pokorna et al., 2013
Czech Republic, Ostrava	Continental	2012	Urban Residential	PM 1.5-10	Short term	RM, PMF	Road dust	62	11.6			Pokorna et al., 2015
Denmark, Copenhagen	Oceanic	1999	Urban	PM10	Short term		Tire wear	5				Fausser, 1999
Denmark, Copenhagen	Continental	2003	Urban	PM 2.5	Short term	RM, COPRE M	Brake wear	9.3	0.72	55.2	4.3	Wahlin et al., 2006
Denmark, Copenhagen	Continental	2003	Urban	PM 2.5-10	Short term	RM, COPRE M	Brake wear	6.7	0.8	13.3	1.6	Wahlin et al., 2006

Location	Climate	Year	Type of station	PM metric	Study Duration	Method	Source	Share (%)	Share ($\mu\text{g}/\text{m}^3$)	Exhaust (%)	Exhaust ($\mu\text{g}/\text{m}^3$)	Reference
Denmark, Copenhagen	Continental	2003	Urban	PM 2.5	Short term	RM, COPRE M	Road dust	28	2.2	55.2	4.3	Wahlin et al., 2006
Denmark, Copenhagen	Continental	2003	Urban	PM 2.5-10	Short term	RM, COPRE M	Road dust	48	5.8	13.3	1.6	Wahlin et al., 2006
Denmark, Copenhagen	Oceanic	2006-2008	Urban roadside	PM 10		EM, NORTR IP	Tire wear	5.8	1.0			Denby et al., 2013
Denmark, Copenhagen	Continental	2006-2008	Urban roadside	PM 10		EM, NORTR IP	Brake wear	6.4	1.1			Denby et al., 2013
Denmark, Copenhagen	Continental	2006-2008	Urban roadside	PM 10		EM, NORTR IP	Road wear	57.2	9.6			Denby et al., 2013
Finland, Helsinki	Continental	2012	Suburban	PM10	Short term	RM,CM B	Road wear	43				Kupianinen et al., 2016
France, Lille	Oceanic	2013-2014	Urban background	PM 10	Yearly	RM, PMF	Brake wear	5	1.5	5.3	1.6	Mooibroek et al. 2016
France, Dunkirk	Oceanic	2012	Industrial	PM 2.5	Short term	RM, PCA-MLRA	Road dust	24	3.8	2	0.32	Mbengue et al., 2017
France, Nice	Mediterranean	2006	Tunnel	PM 2.5	Short term	RM, PMF	Road dust	43		21		Fabretti et al., 2009

Location	Climate	Year	Type of station	PM metric	Study Duration	Method	Source	Share (%)	Share ($\mu\text{g}/\text{m}^3$)	Exhaust (%)	Exhaust ($\mu\text{g}/\text{m}^3$)	Reference
France, Paris	Oceanic	2012-2013	Urban	PM 10	Yearly	RM, PMF	Road dust	13	6.3			Amato et al., 2016c
Germany, Augsburg	Continental	2006-2007	Urban background	Particle number	Short term	RM, PMF	Road dust	3		65.2		Gu et al., 2011
Germany, Augsburg	Continental	2006-2007	Urban background	PM10 volume	Short term	RM, PMF	Road dust	9		10.6		Gu et al., 2011
Germany, Augsburg	Continental	2006-2007	Urban	PM 10	Short term	RM, PMF	Road dust	20	6.4	16.6	5.3	Gu et al., 2011
Germany, Essen	Oceanic	2009	Urban background	PM 1	Yearly	SEM	Road dust	5		6		Weinbruch et al., 2014
Germany, Essen	Oceanic	2009	Urban roadside	PM 1	Yearly	SEM	Road dust	21		15		Weinbruch et al., 2014
Germany, Essen	Oceanic	2009	Urban background	PM 10	Yearly	SEM	Road dust	15		6		Weinbruch et al., 2014
Germany, Essen	Oceanic	2009	Urban roadside	PM 10	Yearly	SEM	Road dust	28		13		Weinbruch et al., 2014
Germany, Essen	Oceanic	2009	Urban background	PM 1-10	Yearly	SEM	Road dust	31		1		Weinbruch et al., 2014
Germany, Essen	Oceanic	2009	Urban roadside	PM 1-10	Yearly	SEM	Road dust	53		6		Weinbruch et al., 2014

Location	Climate	Year	Type of station	PM metric	Study Duration	Method	Source	Share (%)	Share ($\mu\text{g}/\text{m}^3$)	Exhaust (%)	Exhaust ($\mu\text{g}/\text{m}^3$)	Reference
Germany, Essen	Oceanic	2009	Urban background	PM 1	Yearly	SEM	Brake wear / Tire wear	4		6		Weinbruch et al., 2014
Germany, Essen	Oceanic	2009	Urban roadside	PM 1	Yearly	SEM	Brake wear / Tire wear	3		15		Weinbruch et al., 2014
Germany, Essen	Oceanic	2009	Urban background	PM 10	Yearly	SEM	Brake wear / Tire wear	6		6		Weinbruch et al., 2014
Germany, Essen	Oceanic	2009	Urban roadside	PM 10	Yearly	SEM	Brake wear / Tire wear	7		13		Weinbruch et al., 2014
Germany, Essen	Oceanic	2009	Urban background	PM 1-10	Yearly	SEM	Brake wear / Tire wear	4		1		Weinbruch et al., 2014
Germany, Essen	Oceanic	2009	Urban roadside	PM 1-10	Yearly	SEM	Brake wear / Tire wear	15		6		Weinbruch et al., 2014
Germany, North Rhine - Westphalia	Oceanic	2008-2009	Rural background	PM 10	Yearly	RM, PMF	Road dust	2	0.3			Beuck et al., 2011
Germany, North Rhine -	Oceanic	2008-2009	Urban background	PM 10	Yearly	RM, PMF	Road dust	8	2.4			Beuck et al., 2011

Location	Climate	Year	Type of station	PM metric	Study Duration	Method	Source	Share (%)	Share ($\mu\text{g}/\text{m}^3$)	Exhaust (%)	Exhaust ($\mu\text{g}/\text{m}^3$)	Reference
Westphalia												
Greece, Athens	Mediterranean	2002	Urban	PM 10	Yearly	RM, PMF	Road dust	34	3.62	19	1.84	Karanasiou et al., 2009
Greece, Athens	Mediterranean	2002	Urban	PM 2	Yearly	RM, PMF	Road dust	27	1.5	27	1.54	Karanasiou et al., 2009
Greece, Athens	Mediterranean	2002	Urban	PM 2-10	Yearly	RM, PMF	Road dust	53	2.09	8	0.3	Karanasiou et al., 2009
Greece, Athens	Mediterranean	2013	Urban background	PM 10	Yearly	RM, PMF	Non-exhaust	8	1.8	10	2.1	Amato et al., 2016a
Greece, Athens	Mediterranean	2013	Urban background	PM 2.5	Yearly	RM, PMF	Non-exhaust	5	0.6	15	1.7	Amato et al., 2016a
Greece, Attica	Mediterranean	2006		PM 10		DM, CAMx	Road dust	23	12.5			Athanasopoulou et al., 2010
Greece, Megalopolis	Mediterranean	2009-2011	Urban	PM 10	Yearly	RM, PMF	Road dust	15	3.6	12	2.9	Manousakas et al., 2015
Greece, Thessaloniki	Mediterranean	1994	Urban Commercial	PM 3	Yearly	RM, PCA-APCS	Road dust	28	27.2	38	36.9	Manoli et al., 2002

Location	Climate	Year	Type of station	PM metric	Study Duration	Method	Source	Share (%)	Share ($\mu\text{g}/\text{m}^3$)	Exhaust (%)	Exhaust ($\mu\text{g}/\text{m}^3$)	Reference
Greece, Thessaloniki	Mediterranean	1994	Urban Commercial	PM 3-10	Yearly	RM, PCA-APCS	Road dust	57	17.1	9	2.7	Manoli et al., 2002
Greece, Thessaloniki	Mediterranean	1997-1998	Industrial	PM 10	Yearly	RM, CMB	Road dust	19	13.7	46.7	34.6	Samara et al., 2003
Greece, Thessaloniki	Mediterranean	1997-1998	Urban	PM 10	Yearly	RM, CMB	Road dust	21	17.4	62.8	63.6	Samara et al., 2003
Greece, Thessaloniki	Mediterranean	1997-1998	Urban Residential	PM 10	Yearly	RM, CMB	Road dust	22	19.7	64.3	57.3	Samara et al., 2003
Hong Kong	Temperate	2005	Urban	PM 2.5	Yearly	RM, PMF	Road dust	1	0.55	29	16.1	Cheng et al., 2015
Hong Kong	Temperate	2005	Urban	PM 2.5-10	Yearly	RM, PMF	Road dust	17	4.4	11	2.8	Cheng et al., 2015
India, Bangalore	Tropical-Monsoon	2013	Urban	PM 10	Yearly	RM, CMB	Road dust	51	47	18	16.8	Sharma et al., 2013
India, Chennai City	Tropical-Monsoon	2009	Urban	PM 10	Yearly	RM, CMB	Road dust	1	0.7	58.5	31.9	Srimuruganandam and Shiva Nagendra, 2012b
India, Chennai City	Tropical-Monsoon	2009	Urban	PM 2.5	Yearly	RM, CMB	Road dust	1	0.59	57.7	23.5	Srimuruganandam and Shiva

Location	Climate	Year	Type of station	PM metric	Study Duration	Method	Source	Share (%)	Share ($\mu\text{g}/\text{m}^3$)	Exhaust (%)	Exhaust ($\mu\text{g}/\text{m}^3$)	Reference
India, Chennai City	Tropical-Monsoon	2009	Urban	PM 10	Yearly	RM, CMB	Brake wear	0.14	0.12	58.5	31.9	Nagendra, 2012b Srimuruganandam and Shiva Nagendra, 2012b
India, Chennai City	Tropical-Monsoon	2009	Urban	PM 2.5	Yearly	RM, CMB	Brake wear	0.14	0.09	57.7	23.5	Srimuruganandam and Shiva Nagendra, 2012b
India, Chennai City	Tropical-Monsoon	2009	Urban	PM 10	Short term	RM, PMF	Brake wear / Tire wear	4.1	3.4	15.8	13.1	Srimuruganandam and Shiva Nagendra, 2012a
India, Chennai City	Tropical-Monsoon	2009	Urban	PM 2.5	Short term	RM, PMF	Brake wear / Tire wear	5.4	3.4	6	3.8	Srimuruganandam and Shiva Nagendra, 2012a
India, Chennai City	Tropical-Monsoon	2009	Urban	PM 10	Short term	RM, PMF	Tire Wear / Brake wear	4.1	3.4	15.8	13.1	Srimuruganandam and Shiva Nagendra, 2012a

Location	Climate	Year	Type of station	PM metric	Study Duration	Method	Source	Share (%)	Share ($\mu\text{g}/\text{m}^3$)	Exhaust (%)	Exhaust ($\mu\text{g}/\text{m}^3$)	Reference
India, Chennai City	Tropical-Monsoon	2009	Urban	PM 2.5	Short term	RM, PMF	Tire Wear / Brake wear	5.4	3.4	6	3.8	Srimuruganandam and Shiva Nagendra, 2012a
India, Delhi	Tropical-Monsoon	2001	Urban	PM 1.6-10.9	Short term	RM, CMB	Road dust	26				Srivastava and Jain, 2007
India, Delhi	Tropical-Monsoon	2010		PM 2.5		EI + DM, ATMOS	Road dust	8	6.5			Guttikunda and Calori (2013)
India, Hyderabad	Tropical-Monsoon	2004-2005	Urban	PM 10	Yearly	RM, CMB	Road dust	40	48.5	22	26.7	Gummene ni et al., 2011
India, Hyderabad	Tropical-Monsoon	2004-2005	Urban	PM 2.5	Yearly	RM, CMB	Road dust	26	16.2	31	19.3	Gummene ni et al., 2011
India, Hyderabad	Tropical-Monsoon	2005-2006	Urban background	PM 10	Yearly	RM, CMB	Road dust	36	26.9	41.6	31.6	Guttikunda, Kopakka, Dasari, and Gertler (2013)

Location	Climate	Year	Type of station	PM metric	Study Duration	Method	Source	Share (%)	Share (µg/m3)	Exhaust (%)	Exhaust (µg/m3)	Reference
India, Hyderabad	Tropical-Monsoon	2005-2006	Urban Residential	PM 10	Yearly	RM, CMB	Road dust	31	39.6	38.4	48.6	Guttikunda, Kopakka, Dasari, and Gertler (2013)
India, Hyderabad	Tropical-Monsoon	2005-2006	Urban Residential	PM 10	Yearly	RM, CMB	Road dust	36	40.3	41.5	46.8	Guttikunda, Kopakka, Dasari, and Gertler (2013)
India, Hyderabad	Tropical-Monsoon	2005-2006	Urban background	PM 2.5	Yearly	RM, CMB	Road dust	20	7.5	38.1	14.3	Guttikunda, Kopakka, Dasari, and Gertler (2013)
India, Hyderabad	Tropical-Monsoon	2005-2006	Urban Residential	PM 2.5	Yearly	RM, CMB	Road dust	13	8.7	34	22.6	Guttikunda, Kopakka, Dasari, and

Location	Climate	Year	Type of station	PM metric	Study Duration	Method	Source	Share (%)	Share ($\mu\text{g}/\text{m}^3$)	Exhaust (%)	Exhaust ($\mu\text{g}/\text{m}^3$)	Reference
India, Hyderabad	Tropical-Monsoon	2005-2006	Urban Residential	PM 2.5	Yearly	RM, CMB	Road dust	17	8.9	38.1	20.2	Gertler (2013) Guttikunda, Kopakka, Dasari, and Gertler (2013)
India, Kanpur	Tropical-Monsoon	2007		PM 10		EI + DM, USEPA ISCST3	Road dust	14				Behera et al., 2011
India, Kolkata	Tropical-Monsoon	2003-2004	Urban Residential	PM 10	Yearly	RM, CMB	Road dust	21	36.6			Gupta et al., 2007
India, Kolkata	Tropical-Monsoon		Industrial	PM 10	Short term	RM, PCA-MLRA	Tire wear	8	15.8	37	73.1	Karar and Gupta, 2007
India, Mumbai	Tropical-Monsoon	2007-2008	Urban Residential	PM 10	Yearly	RM, PMF	Road dust	18	33.3	23	42.6	Gupta et al., 2012
India, Nagpur	Tropical-Monsoon	2009-2010	Urban Residential	PM 2.5	Short term	RM, CMB	Road dust	6	4	57	38.2	Pipalatkari et al., 2014
India, Nagpur	Tropical-Monsoon	2009-2010	Urban Roadside	PM 2.5	Short term	RM, CMB	Road dust	10	9.6	62	59.8	Pipalatkari et al., 2014

Location	Climate	Year	Type of station	PM metric	Study Duration	Method	Source	Share (%)	Share ($\mu\text{g}/\text{m}^3$)	Exhaust (%)	Exhaust ($\mu\text{g}/\text{m}^3$)	Reference
India, Nagpur	Tropical-Monsoon	2009-2010	Industrial	PM 2.5	Short term	RM, CMB	Road dust	9	7.7	65	55.4	Pipalatkari et al., 2014
Indonesia, Serpong	Tropical-Monsoon		Urban	PM 2.5		RM, PMF	Road dust	17	3.5	30	6.2	Santoso et al., 2011
Iran, Ahvaz	Arid	2010-2011	Urban	PM 10	Yearly	RM, PMF	Road dust	6	17.6	11.5	36.8	Sowlat et al., 2013
Italy, Bologna	Temperate	2006	Urban background	PM 10	Yearly	RM, PMF	Road dust	11	4.9	35	15.6	Tositti et al., 2014
Italy, Civitavecchia	Mediterranean	2010-2014	Rural	PM 10	Yearly	RM, PMF	Road dust	6	1	7.2	1.2	Cesari et al., 2016
Italy, Civitavecchia	Mediterranean	2010-2014	Urban	PM 10	Yearly	RM, PMF	Road dust	13	2.8	16.9	3.7	Cesari et al., 2016
Italy, Civitavecchia	Mediterranean	2010-2014	Urban background	PM 10	Yearly	RM, PMF	Road dust	7	1.1	9	1.5	Cesari et al., 2016
Italy, Florence	Mediterranean	2009	Urban	PM 2.5	Yearly	RM, ME-2	Non-exhaust	7	1.4	37	8	Crespi et al., 2016
Italy, Florence	Mediterranean	2013	Urban background	PM 10	Yearly	RM, PMF	Non-exhaust	9	1.8	13	2.5	Amato et al., 2016a
Italy, Florence	Mediterranean	2013	Urban background	PM 2.5	Yearly	RM, PMF	Non-exhaust	2	0.3	18	2.5	Amato et al., 2016a

Location	Climate	Year	Type of station	PM metric	Study Duration	Method	Source	Share (%)	Share ($\mu\text{g}/\text{m}^3$)	Exhaust (%)	Exhaust ($\mu\text{g}/\text{m}^3$)	Reference
Italy, Milan	Oceanic	2006-2009	Urban	PM 10	Yearly	RM, CMB + Calculations	Road dust	6	2.6	22	11.1	Perrone et al., 2012
Italy, Milan	Oceanic	2006-2009	Urban	PM 2.5	Yearly	RM, CMB + Calculations	Road dust	3	0.65	20.5	4.5	Perrone et al., 2012
Italy, Milan	Oceanic	2006-2009	Rural	PM 2.5	Yearly	RM, CMB + Calculations	Road dust	1	0.15	7.7	1.7	Perrone et al., 2012
Italy, Milan	Oceanic	2013	Urban background	PM 10	Yearly	RM, PMF	Non-exhaust	14	5.8	7	2.8	Amato et al., 2016a
Italy, Milan	Oceanic	2013	Urban background	PM 2.5	Yearly	RM, PMF	Non-exhaust	8	2.5	6	1.8	Amato et al., 2016a
Italy, Po valley	Temperate		Regional background	PM10	ToF-AMS		Tire wear	0.5				Dall'Osto et al., 2014
Korea, Daejeon	Temperate	2000-2002	Industrial	PM 10	Yearly	RM, PMF	Road dust	12	10.3	9	7.7	Lim et al., 2010
Korea, Seoul	Temperate	2006-2007	Urban	PM 10	Yearly	RM, PMF	Road dust	18	10.2	16.6	9.5	Yi and Hwang, 2014

Location	Climate	Year	Type of station	PM metric	Study Duration	Method	Source	Share (%)	Share ($\mu\text{g}/\text{m}^3$)	Exhaust (%)	Exhaust ($\mu\text{g}/\text{m}^3$)	Reference
New Zealand, Auckland	Oceanic	2003	Urban background	PM 2.5-10	Yearly	RM, PMF	Road dust	19	1.67			Wang and Shooter, 2005
Pakistan, Karachi	Arid	2006-2007	Urban	PM 2.5	Yearly	RM, PMF	Road dust	16	12.8	18.5	14.7	Mansha et al., 2012
Poland, Krakow	Continental	2014-2015	Urban	PM 2.5	Yearly	RM, PMF	Road dust	3	0.96	43	14.2	Samek et al., 2017
Portugal, Lisbona	Mediterranean	2001	Urban	PM 2.5	Yearly	RM, PCA-MLRA	Road dust	14	3.4	22	5.3	Almeida et al., 2005
Portugal, Lisbona	Mediterranean	2001	Urban	PM 2.5-10	Yearly	RM, PCA-MLRA	Road dust	13	2.1			Almeida et al., 2005
Portugal, Oporto	Mediterranean	2013	Urban roadside	PM 10	Yearly	RM, PMF	Non-exhaust	8	2.9	23	7.9	Amato et al., 2016a
Portugal, Oporto	Mediterranean	2013	Urban roadside	PM 2.5	Yearly	RM, PMF	Non-exhaust	5	1.3	32	8.1	Amato et al., 2016a
Spain	Mediterranean	2004		PM 10		EI + DM, CALIOPE, HERMES	Road dust	27	3.5			Pay et al., 2011
Spain, Barcelona	Mediterranean	2003-2007	Urban background	PM 1	Yearly	RM, ME-2	Road dust	2	0.3	36	6.2	Amato et al., 2009

Location	Climate	Year	Type of station	PM metric	Study Duration	Method	Source	Share (%)	Share ($\mu\text{g}/\text{m}^3$)	Exhaust (%)	Exhaust ($\mu\text{g}/\text{m}^3$)	Reference
Spain, Barcelona	Mediterranean	2003-2007	Urban background	PM 10	Yearly	RM, ME-2	Road dust	17	6.9	21	8.5	Amato et al., 2009
Spain, Barcelona	Mediterranean	2003-2007	Urban background	PM 2.5	Yearly	RM, ME-2	Road dust	8	2.2	32	8.8	Amato et al., 2009
Spain, Barcelona	Mediterranean	2010	Urban background	PM 10	Short term	RM, PMF	Road dust	12	3.3	18	5	Brines et al., 2016
Spain, Barcelona	Mediterranean	2010	Urban roadside	PM 10	Short term	RM, PMF	Road dust	12	3.8	27	8.7	Brines et al., 2016
Spain, Barcelona	Mediterranean	2010	Urban	PM 10	Short term	RM, PMF	Road dust	9	2.3	11	2.9	Brines et al., 2016
Spain, Barcelona	Mediterranean	2010	Urban background	PM 10	Short term	RM, PMF	Road dust	8	1.6	10	1.9	Brines et al., 2016
Spain, Barcelona	Mediterranean	2009	Urban background	PM 10		DM, URBIS	Road dust	12	10			Amato et al., 2016b
Spain, Barcelona	Mediterranean	2009	Urban traffic	PM 10		DM, URBIS	Road dust	33.5	10			Amato et al., 2016b
Spain, Barcelona	Mediterranean	2013	Urban background	PM 10	Yearly	RM, PMF	Non-exhaust	12	2.6	14	3.2	Amato et al., 2016a
Spain, Barcelona	Mediterranean	2013	Urban background	PM 2.5	Yearly	RM, PMF	Non-exhaust	1	0.2	19	2.9	Amato et al., 2016a

Location	Climate	Year	Type of station	PM metric	Study Duration	Method	Source	Share (%)	Share ($\mu\text{g}/\text{m}^3$)	Exhaust (%)	Exhaust ($\mu\text{g}/\text{m}^3$)	Reference
Spain, Barcelona	Mediterranean		Urban roadside	PM10	ToF-AMS		Tire wear	2				Dall'Osto et al., 2014
Spain, Cádiz	Mediterranean	2003-2010	Industrial	PM 10	Yearly	RM, PMF	Road dust	19	6.7	12.2	4.4	Amato et al., 2014
Spain, Cádiz	Mediterranean	2003-2010	Industrial	PM 2.5	Yearly	RM, PMF	Road dust	10	2.3	15.7	3.6	Amato et al., 2014
Spain, Cordoba	Mediterranean	2003-2010	Urban	PM 10	Yearly	RM, PMF	Road dust	29	10.4	16	5.6	Amato et al., 2014
Spain, Cordoba	Mediterranean	2003-2010	Urban	PM 2.5	Yearly	RM, PMF	Road dust	11	1.9	22	3.8	Amato et al., 2014
Spain, Granada	Mediterranean	2003-2010	Urban roadside	PM 10	Yearly	RM, PMF	Road dust	24	10.4	20	8.8	Amato et al., 2014
Spain, Granada	Mediterranean	2003-2010	Urban roadside	PM 2.5	Yearly	RM, PMF	Road dust	22	8.2	18	6.5	Amato et al., 2014
Spain, Granada	Mediterranean	2003-2010	Urban roadside	PM 10	Yearly	RM, PMF	Tire wear	8	3.4	20	8.8	Amato et al., 2014
Spain, Granada	Mediterranean	2003-2010	Urban roadside	PM 2.5	Yearly	RM, PMF	Tire wear	18	6.6	18	6.5	Amato et al., 2014
Spain, Madrid	Continental	2009	Urban	PM 10	Short term	RM, PMF	Road dust	29	14.6	31	15.6	Karanasiou et al., 2011
Spain, Málaga	Mediterranean	2003-2010	Rural	PM 10	Yearly	RM, PMF	Road dust	9	1.3	23	3.5	Amato et al., 2014
Spain, Málaga	Mediterranean	2003-2010	Urban roadside	PM 10	Yearly	RM, PMF	Road dust	21	9	19	8	Amato et al., 2014
Spain, Málaga	Mediterranean	2003-2010	Rural	PM 2.5	Yearly	RM, PMF	Road dust	7	1.4	20	3.9	Amato et al., 2014

Location	Climate	Year	Type of station	PM metric	Study Duration	Method	Source	Share (%)	Share ($\mu\text{g}/\text{m}^3$)	Exhaust (%)	Exhaust ($\mu\text{g}/\text{m}^3$)	Reference
Spain, Málaga	Mediterranean	2003-2010	Urban roadside	PM 2.5	Yearly	RM, PMF	Road dust	21	4.8	12	2.8	Amato et al., 2014
Spain, Seville	Mediterranean	2003-2010	Urban	PM 10	Yearly	RM, PMF	Road dust	34	13.9	12	4.7	Amato et al., 2014
Spain, Seville	Mediterranean	2003-2010	Urban roadside	PM 10	Yearly	RM, PMF	Road dust	35	14.4	20	8.1	Amato et al., 2014
Spain, Seville	Mediterranean	2003-2010	Urban	PM 2.5	Yearly	RM, PMF	Road dust	31	9.5	10	3.2	Amato et al., 2014
Spain, Seville	Mediterranean	2003-2010	Urban roadside	PM 2.5	Yearly	RM, PMF	Road dust	31	9.5	19	5.8	Amato et al., 2014
Sri Lanka, Colombo	Tropical-Monsoon	2000-2005	Urban	PM 2.5	Yearly	RM, PMF	Road dust	27	7.8	48	13.9	Seneviratne et al., 2011
Sri Lanka, Colombo	Tropical-Monsoon	2003-2008	Urban Residential	PM 2.5	Yearly	RM, PMF	Road dust	9	2.1	17	4	Seneviratne et al., 2011
Sweden, Lycksele	Continental	2002	Rural	PM 2.5	Short term	RM, PMF	Brake wear	13.9	1			Hedberg et al., 2012
Sweden, Stockholm	Continental	2003-2004	Freeway	PM 10	Short term	RM, PMF	Road dust	11	2.1	13	2.4	Furusjö et al., 2007
Sweden, Stockholm	Continental	2003-2004	Urban roadside	PM 10	Short term	RM, PMF	Road dust	13	4.6	36	13	Furusjö et al., 2007
Sweden, Stockholm	Continental	2006-2007	Urban roadside	PM 10		EM, NORTRIP	Brake wear	5.5	1.7			Denby et al., 2013

Location	Climate	Year	Type of station	PM metric	Study Duration	Method	Source	Share (%)	Share ($\mu\text{g}/\text{m}^3$)	Exhaust (%)	Exhaust ($\mu\text{g}/\text{m}^3$)	Reference
Sweden, Stockholm	Continental	2006-2007	Urban roadside	PM 10		EM, NORTRIP	Road wear	76	23.3			Denby et al., 2013
Switzerland, Basel	Continental	1999	Suburban	PM10	Yearly	RM	Road dust	7	1.8	18.2	4.9	Gehrig et al., 2001
Switzerland, Bern	Continental	1999	Urban roadside	PM10	Yearly	RM	Road dust	16	6.4	18.4	7.6	Gehrig et al., 2001
Switzerland, Bern	Continental	1999	Urban roadside	PM10	Yearly	RM	Tire wear	7.5		18.4	7.6	Gehrig et al., 2001
Switzerland, Erstfeld	Continental	2008	Rural	PM 10	Yearly	RM, PMF	Brake wear / Tire wear	4	0.56	16	2.2	Ducret-Stich et al., 2013
Switzerland, Erstfeld	Continental	2007-2009	Rural	PM 10	Yearly	RM, PMF	Road dust	8	1.1	16	2.2	Ducret-Stich et al., 2013
Switzerland, Zurich	Continental	1999	Urban background	PM10	Yearly	RM	Road dust	10	2.5	13.2	3.4	Gehrig et al., 2001
Switzerland, Zurich	Continental	1999	Urban background	PM10	Yearly	RM	Tire wear	1.9		13.2	3.4	Gehrig et al., 2001
The Netherlands, Amsterdam	Oceanic	2013-2014	Urban background	PM 10	Yearly	RM, PMF	Brake wear	2.8	0.7	2	0.5	Mooibroek et al. 2016

Location	Climate	Year	Type of station	PM metric	Study Duration	Method	Source	Share (%)	Share ($\mu\text{g}/\text{m}^3$)	Exhaust (%)	Exhaust ($\mu\text{g}/\text{m}^3$)	Reference
The Netherlands, Wijk aan Zee	Oceanic	2013-2014	Industrial	PM 10	Yearly	RM, PMF	Brake wear	0.67	0.2	1.8	0.5	Mooibroek et al. 2016
Turkey, Aliaga	Mediterranean	2009	Urban	PM 10	Yearly	RM, PMF	Road dust	23	11.8			Kara et al., 2015
UK, Birmingham	Oceanic	1992	Urban	PM 2.1	Yearly	RM, PCA-MLRA	Road dust	32		25		Harrison et al., 1997
UK, Hatfield	Oceanic	2006	Tunnel	PM 10	Short term	RM, PCA-MLRA	Brake wear	11		12		Lawrence et al., 2013
UK, Hatfield	Oceanic	2006	Tunnel	PM 10	Short term	RM, PCA-MLRA	Road dust	27		12		Lawrence et al., 2013
UK, Leicester	Oceanic	2013-2014	Urban background	PM 10	Yearly	RM, PMF	Brake wear	3.8	0.8	4.3	0.9	Mooibroek et al. 2016
UK, London	Oceanic	2007	Urban	Particle Number	Short term	RM, PMF	Brake wear	1.7		65.4		Harrison et al., 2011
UK, London	Oceanic	2007	Urban	PM20 volume	Short term	RM, PMF	Brake wear	13.7		22.4		Harrison et al., 2011
UK, London	Oceanic	2007	Urban	Particle Number	Short term	RM, PMF	Road dust	5		65.4		Harrison et al., 2011
UK, London	Oceanic	2007-2011	Urban roadside	PM 0.9-11.5	Short term	Extrapolation	Brake wear	13.5	3.3			Harrison et al., 2012

Location	Climate	Year	Type of station	PM metric	Study Duration	Method	Source	Share (%)	Share (µg/m3)	Exhaust (%)	Exhaust (µg/m3)	Reference
UK, London	Oceanic	2007-2011	Urban roadside	PM 0.9-11.5	Short term	Extrapolations	Tire wear	2.7	0.65			Harrison et al., 2012
UK, London	Oceanic	2007-2011	Urban roadside	PM 0.9-11.5	Short term	Extrapolations	Road dust	9	2.3			Harrison et al., 2012
UK, London	Oceanic	2008	Urban roadside	PM 10		EI, LAEI + DM, KCLurb an EI,	Tire wear	5	2			Beevers et al., 2013
UK, London	Oceanic	2008	Urban roadside	PM 10		EI, LAEI + DM, KCLurb an EI,	Brake wear	20	8			Beevers et al., 2013
UK, London	Oceanic	2008	Urban roadside	PM 10		EI, LAEI + DM, KCLurb an EI,	Non-exhaust	42.5	17			Beevers et al., 2013
UK, London	Oceanic	2008	Suburban	PM 10		EI, LAEI + DM, KCLurb an EI,	Non-exhaust	9.8	2			Beevers et al., 2013
UK, London	Oceanic	2008	Urban roadside	PM 2.5		EI, LAEI + DM,	Non-exhaust	44.6	9			Beevers et al., 2013

Location	Climate	Year	Type of station	PM metric	Study Duration	Method	Source	Share (%)	Share (µg/m3)	Exhaust (%)	Exhaust (µg/m3)	Reference
UK, London	Oceanic	2008	Suburban	PM 2.5		KCLurb an EI, LAEI + DM, KCLurb an	Non-exhaust	11.4	1.5			Beevers et al., 2013
UK, London	Oceanic	2012	Urban roadside	PM 2.5-10	Short term	RM, PMF	Road dust	31		13.4		Crilley et al., 2017
USA, Albuquerque	Arid	2007-2008	Urban	PM 2.5	Yearly	RM, PMF	Road dust	11	0.59	5.9	0.33	Kavouras et al., 2015
USA, Atlanta	Temperate	2001-2005	Urban	PM 2.5	Yearly	RM, CMB	Road dust	2	0.34	15.9	2.7	Chen et al., 2012
USA, Atlanta	Temperate	2001	Urban	PM 2.5	Short term	RM, PMF	Road dust	7	1.1	17	2.84	Ke et al., 2008
USA, Atlanta	Temperate	2008-2010	Urban	PM 2.5	Yearly	RM, PMF- CMB	Road dust	4	0.5	9	0.92	Watson et al., 2015
USA, Atlanta	Temperate	2001-2005	Rural	PM 2.5	Yearly	RM, CMB	Road dust	2	0.35	12.7	1.85	Chen et al., 2012
USA, Birmingham	Temperate	2001-2005	Urban	PM 2.5	Yearly	RM, CMB	Road dust	3	0.57	15.7	2.88	Chen et al., 2012
USA, Birmingham	Temperate	2002-2004	Urban	PM 2.5	Yearly	RM, PMF	Road dust	6	1.2	25	5.1	Baumann et al., 2008

Location	Climate	Year	Type of station	PM metric	Study Duration	Method	Source	Share (%)	Share (µg/m3)	Exhaust (%)	Exhaust (µg/m3)	Reference
USA, Birmingham	Temperate	2008-2010	Urban	PM 2.5	Yearly	RM, PMF-CMB	Road dust	6	0.8	18.7	2	Watson et al., 2015
USA, California	Temperate	1993	Industrial	PM 2.5	Short term	RM, CMB	Road dust	6	2.5	30.1	11.9	Schauer et al., 2002
USA, California	Temperate	1993	Urban roadside	PM 2.5	Short term	RM, CMB	Road dust	14	9.26	39.5	25.9	Schauer et al., 2002
USA, California	Temperate	1993	Urban background	PM 2.5	Short term	RM, CMB	Road dust	7	4.1	37.4	22.2	Schauer et al., 2002
USA, California	Temperate	1993	Urban background	PM 2.5	Short term	RM, CMB	Road dust	20	8.7	26.5	13.7	Schauer et al., 2002
USA, California	Temperate	1993	Industrial	PM 2.5	Short term	RM, CMB	Tire wear	1	0.4	30.1	11.9	Schauer et al., 2002
USA, California	Temperate	1993	Urban roadside	PM 2.5	Short term	RM, CMB	Tire wear	1.1	0.73	39.5	25.9	Schauer et al., 2002
USA, California	Temperate	1993	Urban background	PM 2.5	Short term	RM, CMB	Tire wear	3.3	2	37.4	22.2	Schauer et al., 2002
USA, California	Mediterranean	1987	Urban	PM 10	Yearly	RM, CMB	Road dust	24	15.6			Watson et al., 1994
USA, California	Mediterranean	2000-2004	Rural background	PM 2.5	Yearly	RM, PMF	Road dust	9	0.27	10.7	0.34	Green et al., 2012

Location	Climate	Year	Type of station	PM metric	Study Duration	Method	Source	Share (%)	Share ($\mu\text{g}/\text{m}^3$)	Exhaust (%)	Exhaust ($\mu\text{g}/\text{m}^3$)	Reference
USA, California	Mediterranean	2005-009	Rural background	PM 2.5	Yearly	RM, PMF	Road dust	5	0.14	8.5	0.26	Green et al., 2012
USA, California	Mediterranean	2002-2012	Urban Commercial	PM 2.5	Yearly, 10	RM, PMF	Road dust	5	0.58	24.2	2.74	Wang and Hopke, 2013
USA, Centreville	Temperate	2001-2005	Rural	PM 2.5	Yearly	RM, CMB	Road dust	2	0.31	9.6	1.3	Chen et al., 2012
USA, Chicago	Continental	2009	Urban	PM 2.5-10	Short term	RM, PMF	Brake wear	23.2	1.29			Sturtz et al., 2014
USA, Chicago	Continental	2009	Urban	PM 2.5-10	Short term	RM, PMF	Tire wear	7	0.39			Sturtz et al., 2014
USA, Connecticut	Continental	2000-2004	Urban	PM 2.5	Yearly	RM, PMF	Road dust	9	1.2	31.3	4.2	Lee et al., 2011
USA, Connecticut	Continental	2000-2004	Urban	PM 2.5	Yearly	RM, PMF	Road dust	15	2	25	3.3	Lee et al., 2011
USA, Connecticut	Continental	2000-2004	Urban	PM 2.5	Yearly	RM, PMF	Road dust	7	0.8	26	3.1	Lee et al., 2011
USA, Connecticut	Continental	2000-2004	Urban	PM 2.5	Yearly	RM, PMF	Road dust	17	2.9	29.4	5	Lee et al., 2011
USA, Detroit	Continental	2005	Urban	PM 2.5	Yearly	RM, CMB	Road dust	4	0.7	30	5.3	Duvall et al., 2012

Location	Climate	Year	Type of station	PM metric	Study Duration	Method	Source	Share (%)	Share ($\mu\text{g}/\text{m}^3$)	Exhaust (%)	Exhaust ($\mu\text{g}/\text{m}^3$)	Reference
USA, Detroit	Continental	2005	Urban background	PM 2.5	Yearly	RM, CMB	Road dust	2	0.34	40	6.1	Duvall et al., 2012
USA, Gulfport	Temperate	2001-2005	Urban	PM 2.5	Yearly	RM, CMB	Road dust	4	0.48	7.5	0.9	Chen et al., 2012
UK, Hatfield	Oceanic	2006	Tunnel	PM 10	Short term	RM, PCA-MLRA	Road wear	11		12		Lawrence et al., 2013
USA, Houston	Temperate	2000	Urban	PM 2.5	Yearly	RM, PMF	Road dust	17	0.8			Buzcu et al., 2003
USA, Little Rock	Temperate	2002-2010	Urban	PM 2.5	Yearly	RM, PMF	Road dust	8	1	11.7	1.5	Chalbot et al., 2013
USA, Los Angeles	Mediterranean	1982	Urban	PM 2	Yearly	RM, CMB	Road dust	12	3.9	22.7	20.2	Schauer et al., 1996
USA, Los Angeles	Mediterranean	1982	Urban	PM 2	Yearly	RM, CMB	Tire wear	0.9	0.25	22.7	20.2	Schauer et al., 1996
USA, Los Angeles	Mediterranean	1993		PM 2.5		EI + DM, UCD/CIT	Road dust	13	7.7			Held et al., 2005
USA, Massachusetts	Continental	2000-2004	Urban	PM 2.5	Yearly	RM, PMF	Road dust	11	1.4	27.7	3.6	Lee et al., 2011
USA, New York	Continental	2011	Urban	PM 2.5	Short term	RM, PMF	Road dust	25	4.13	3.2	0.52	Li et al., 2004

Location	Climate	Year	Type of station	PM metric	Study Duration	Method	Source	Share (%)	Share ($\mu\text{g}/\text{m}^3$)	Exhaust (%)	Exhaust ($\mu\text{g}/\text{m}^3$)	Reference
USA, Oak Grove	Temperate	2001-2005	Rural	PM 2.5	Yearly	RM, CMB	Road dust	5	0.6	13.2	1.65	Chen et al., 2012
USA, Pensacola	Temperate	2001-2005	Suburban	PM 2.5	Yearly	RM, CMB	Road dust	3	0.41	11.3	1.36	Chen et al., 2012
USA, Pensacola	Temperate	2001-2005	Urban	PM 2.5	Yearly	RM, CMB	Road dust	4	0.53	13.4	1.82	Chen et al., 2012
USA, Sacramento	Mediterranean	2010	Urban	PM 0.1	Yearly	RM, PMF	Brake wear	4	0.007	2	0.003	Kuwayama et al., 2013
USA, San Joaquin Valley	Mediterranean	1996		PM 2.5		EI + DM, UCD/CIT	Road dust	1	1.05			Held et al., 2005
USA, St. Paul	Continental	2009	Urban	PM 2.5-10	Short term	RM, PMF	Brake wear	5.6	0.27			Sturtz et al., 2014
USA, St. Paul	Continental	2009	Urban	PM 2.5-10	Short term	RM, PMF	Tire wear	1.9	0.09			Sturtz et al., 2014
USA, Winston-Salem	Temperate	2009	Urban	PM 2.5-10	Short term	RM, PMF	Brake wear	18.4	0.61			Sturtz et al., 2014
USA, Winston-Salem	Temperate	2009	Urban	PM 2.5-10	Short term	RM, PMF	Tire wear	1.6	0.05			Sturtz et al., 2014

3.4 Conclusions

Our literature review on the impact of non-exhaust emissions on air quality resulted in 99 peer-reviewed articles who estimated contributions of at least one of the non-exhaust sources, providing a total of 256 estimates due to the fact that several studies analyzed >1 PM fraction or >1 location. Most of studies were carried out with receptor modelling, and more than half by means of Positive Matrix Factorization and performed in the last 15 years, with a significant increasing trend. Geographically, most of studies are carried out in Europe, Eastern Asia and US. There is a dearth of studies in central and South America, Africa, Middle East and Oceania.

We observed the lack of a common terminology and hierarchy for non-exhaust sources. Therefore, based on the majority of available studies, we proposed the following :vehicle non-exhaust emissions include: “Direct brake wear”, “Direct tire wear”, “Direct road wear” and “Road dust suspension”. However “direct road wear” falls often within the “road dust” category due to their similar chemical composition. The road dust category was the most identified source (Figure 3.8), with slightly higher contributions range (22% as mean) than vehicle exhaust (21%) in PM₁₀, and sensibly higher than brake wear (7%) and tire wear (4%). In PM_{2.5} the road dust contribution is still the highest (mean of 11% of PM_{2.5}) among non-exhaust ones (9% from brake wear and 2% from tire wear), but sensibly lower than vehicle exhaust (24%). This comparison allows concluding that globally, regardless of the environment studied, non-exhaust emissions are already at least as important as exhaust ones for PM₁₀, considering also that the aforementioned contributions are derived mostly from receptor modelling, thus including the contribution of secondary PM for vehicle exhaust (while they are discarded in emission inventories). For PM_{2.5} they represent at least a third of total traffic contribution whilst they dominate the PM coarse (>1.5 μm) mode (>80%).

However, there is still limited information on brake (17 estimates) and tire wear (15 estimates) contributions. Based on these few studies, there is evidence that brake wear particles include an important portion (about half of the mass) of disc wear. Backward trend analysis of source contributions and PM concentrations indicate a relative increment of the share of non-exhaust particles versus the exhaust ones.

In spite of the limited number of observations for each location category, it was possible to observe an increasing gradient of contributions (% of PM₁₀) from rural to traffic locations for all non-exhaust sources. For road dust the largest increase was found from sub-urban to urban location (due to the relatively coarser size distribution) indicating the need of local measures at municipal level.

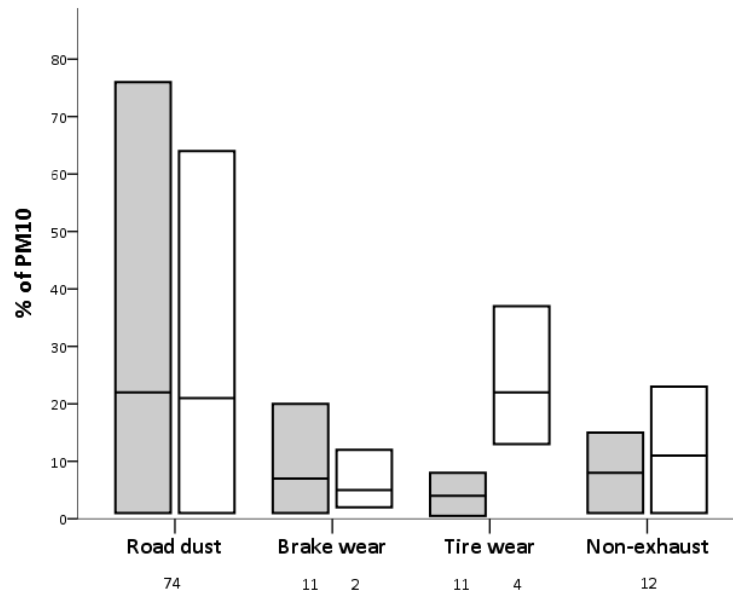


Figure 3.8 Range of non-exhaust (in grey) and vehicle exhaust (in white) contributions (%) to PM10 of different non-exhaust sources.

A climate-dependence was also found for road dust contribution: the lowest contribution of road dust relatively to exhaust emissions were found in Oceanic urban sites, where a mean road dust contribution of 13% vs 22% from exhaust was found (ratio 0.60). Slightly higher ratios (0.66) were found in urban Continental sites with 16% vs 24% mean contributions. The importance of road dust increase considerably in Mediterranean and Tropical-Monsoon climates where ratios increase to 0.85, and even above 1 at traffic sites. The worst scenario for road dust emissions was found in China where road dust contributions exceed exhaust ones with a ratio of 1.8.

Further research is necessary to better separate individual contributions from road dust resuspension, brake, tire and road wear given that the relative toxicity and mitigation measures are different. In this sense, valuable information can be offered by size and time-resolved PM chemical characterization and particle size distribution measurement, as well as improved source apportionment tools.

4. Bioaccessibility and size distribution of metals in road dust and roadside soils along a peri-urban transect

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Abstract

Road dust (RD), together with surface soils, is recognized as one of the main sinks of pollutants in urban environments. Over the last years, many studies have focused on total and bioaccessible concentrations while few have assessed the bioaccessibility of size-fractionated elements in RD. Therefore, the distribution and bioaccessibility of Fe, Mn, Cd, Cr, Cu, Ni, Pb, Sb and Zn in size fractions of RD and roadside soils (<2.5 µm, 2.5-10 µm and 10-200 µm) have been studied in Turin (Italy) using aqua regia extraction and the Simple Bioaccessibility Extraction Test.

Concentrations of metals in soils are higher than legislative limits for Cu, Cr, Ni, Pb and Zn. Fine fractions (<2.5 and 2.5-10 µm) appear enriched in Fe, Mn, Cu, Pb, Sb and Zn, and 2.5-10 µm particles are the most enriched. In RD, Cu, Pb, Sb and Zn derive primarily from non-exhaust sources, while Zn is found in greater concentrations in the <2.5 µm fraction, where it most likely has an industrial origin.

Elemental distribution across soils is dependent on land use, with Zn, Ni, Cu and Pb being present in higher concentrations at traffic sites. In addition, Fe, Ni and Cr feature greater bioaccessibility in the two finer fractions, while anthropic metals (Cu, Pb, Sb and Zn) do not.

In RD, only Zn has significantly higher bioaccessibility at traffic sites compared to background, and the finest particles are always the most bioaccessible; more than 90% of Pb, Zn and Cu is bioaccessible in the <2.5 µm fraction, while for Mn, Ni, Sb, Fe and Cr, values vary from 76% to 5%. In the 2.5-10 µm fraction, the values were 89% for Pb, 67% for Zn and 60% for Cu.

These results make the evaluation of the bioaccessibility of size-fractionated particles being a necessity for correct estimation of risk in urban areas.

4.1 Introduction

In Europe, urban areas host three-quarters of the population. However, urbanization is still ongoing and, nowadays, peri-urban spaces are increasing at a much faster rate than traditional core cities (European Commission, 2011). One of the consequences of the expansion of urban areas on the environment is soil and air pollution. This is currently one of the primary causes of concern for human health (Lim et al., 2012).

Road dust (RD) is at the interface between the soil and atmosphere, being a complex environmental medium originating from both natural and anthropogenic processes. Major sources include particles from soil materials, vehicle exhaust and non-exhaust emissions, atmospheric deposition and industrial activities (Pant and Harrison, 2013; Thorpe and Harrison, 2008). Together with surface soils, RD is a source and a sink of various pollutants in urban environments (Biasioli et al., 2006; Christoforidis and Stamatis, 2009). Metals are one of the most problematic as they are potentially toxic, persistent in the environment and often present at high concentrations.

RD and soil particles can be easily re-suspended by vehicles or wind, resulting in an important source of atmospheric particulate matter (PM) (Amato et al., 2009; Pant and Harrison, 2013). In recent years, research has focused on RD characterization and source apportionment of mineral PM (Aimar et al., 2012; Fujiwara et al., 2011; Kumar et al., 2013; Putaud et al., 2010). Concerns over RD contributions are growing based on the lack of legislation pertaining to all non-exhaust sources (Amato et al., 2014a; Kousoulidou et al., 2008; Querol et al., 2004). In fact, with the continuous reduction of exhaust emissions, non-exhaust particles will increase their contribution to the total vehicle-generated particulate matter and may become dominant over the coming years in terms of both emissions and contributions to air quality (Denier van der Gon et al., 2013).

In city environments, metals in soil and RD can exert their toxicity through entering the human body via inhalation, dermal contact and ingestion, with ingestion being the most likely pathway for RD and soil fine particles (for example, <50 µm) (Ruby

and Lowney, 2012; Siciliano et al., 2009). Shi et al. (2011) calculated that, for children, ingestion contributed 97.5% and 81.7% to total exposure doses of non-carcinogenic and carcinogenic elements, and that the contribution rates for adult were 91.7% and 52.9%, respectively. Kong et al. (2012) computed that for <2.5 µm and <10 µm particles of RD, non-carcinogenic risks based on exposure to metals were two orders of magnitude higher for ingestion than for inhalation.

While a number of studies on RD have concentrated on the elemental composition of samples (Amato et al., 2011; Gunawardana et al., 2012; McKenzie et al., 2008; Varrica et al., 2003), few have considered that the total or pseudo-total content does not necessarily represent the most dangerous chemical fraction of the metal. Analogously, whole soil content would not serve as a reliable assessment of the transfer potential of particles, as the coarser fractions are rarely removed (Bi et al., 2015; Paustenbach, 2000; Turner and Ip, 2007). Therefore, an evaluation of metal bioaccessibility is necessary to better evaluate human health risks to metals in order to obtain a more realistic ingestion exposure (Hu et al., 2011; Yu et al., 2014).

As there is a general need to better define the hazards and the health relevance of RD and non-exhaust PM sources (Denier van der Gon et al., 2013; Guney and Zagury, 2016), the aim of this study was to assess the total and bioaccessible concentrations of metals in size-resolved fractions of RD and roadside soils in Turin (Italy).

4.2 Material and methods

4.2.1 Study area

The metropolitan area of Turin (Italy) (45°04' N; 7°41' E) has a population of 1.7 million inhabitants and is the fourth most populated metropolitan area in Italy. It is characterized by a very high volume of vehicular traffic and has a long industrial history, mainly because of the automotive and metallurgical industries. The city was built and extended at the bottom of an alluvial plain in the Po valley, and is shielded by hills to the east and by the Alps to the north and west. This setting causes PM levels to often exceed EU limits not only in Turin, but also in many other urban areas within the Po valley (Eeftens et al., 2012; Padoan et al., 2016), and these atmospheric emissions can result in a major source of diffuse metal soil contamination (Biasioli and Ajmone Marsan, 2007).

Ten sampling sites were selected along a peri-urban transect (7.5 km), starting near the ring road and reaching the city center along an approximately straight line (Figure 4.1). Six sites were on a main road (Corso Allamano) and could be separated into three groups: samples influenced by industrial activities (A1, A2),

sites located in a residential area (S1, S2) and sites surrounded by agricultural fields (A3, A4). Each group included a sampling site just before a traffic light or a roundabout (braking sites: A1, A4, S1) and one at least 200 m after (acceleration sites: A2, A3, S2). All sites have a similar traffic intensity, varying between 13000 (S1, S2) and 9500 (A3, A4) vehicles day⁻¹ (data provided by 5T s.r.l.). The industrial area and the residential area counted with one additional sampling site each, located on a secondary road, with a mean traffic of 1000 and 3000 vehicles day⁻¹, respectively, to appreciate the impact of low traffic volumes. Two urban background sites were additionally sampled - a paved road within the largest park of the city (PE) and within the university campus (AG), as remotely as possible from direct traffic sources but still in the urban area. Soil samples were collected as close as possible to the RD sampling point.

At each site, samples were gathered during three different seasons: April 2015, August 2015 and February 2016, after, at least, seven dry days. In order to minimize time variability between sampling sites, during each season, all samples were collected on the same day.



Figure 4.1 Sampling sites. In red (A1 to S2) samples on the main road, in blue (RI and BO) secondary road sites and in green (AG and PE) urban background sites (background image from Google Maps (online), Digital Globe, 2016).

4.2.2 Sampling methodology

At each site, three subsamples of RD were collected, 1 m² each, centered within the right-most active lane using a polyethylene brush (Acosta et al., 2011; Li et al., 2013; Sutherland et al., 2012; Varrica et al., 2003). This method could result in a loss of fine particles, so special care was taken to avoid re-suspension during the sampling by sweeping directly into a plastic bag. The collected sample quantities varied from 20 to 200 g.

Soil samples were taken from a 0–5 cm depth at all locations and within 2 m from the edge of the road. At each site, three sub-samples were collected at a distance of 1 m between each other, and the sub-samples were homogenized into one composite sample for further analysis. The brush and shovel were been washed with a mild acidic solution and deionized water before and between samplings. All samples were air dried in the laboratory at room temperature and passed through a plastic 2-mm sieve prior to laboratory analyses.

4.2.3 Analytical procedures

All samples were analyzed for pH (1:2.5, soil:water), total carbon (TC) and nitrogen (TN) (CE Instruments, NA2100 Elemental Analyzer, ISO 10694) and carbonates (volumetric method, ISO 10693). The particle-size distribution (PSD) was measured via the hydrometer method (Colombo and Miano, 2015; Gee and Bauder, 1986).

In order to partition RD and soil samples into four size fractions (<2.5, 2.5-10, 10-200 and 200-2000 µm), samples were dispersed with Na-hexametaphosphate and resuspended, with the <2.5 µm fraction separated by centrifugation (ALC-4227R) while the remaining fractions were separated by repeated sedimentation and decanting (Ajmone Marsan et al., 2008); the process was repeated until the supernatant was clear. Following separation, the fractions were dried prior to analysis.

An *aqua regia* (HCl/HNO₃, 3:1 v/v) extraction was performed with microwave digestion of 0.5 g of sample (Milestone Ethos D, ISO 11466). Extractable (pseudo-total) content of Fe, Mn, Cd, Cr, Cu, Ni, Pb and Zn were determined in bulk samples (ground to pass through a 150-µm sieve prior to analysis) and in the <2.5-, 2.5-10-, 10-200-µm fractions by flame atomic absorption spectrometry (FAAS) (Perkin-Elmer AA-400), while Sb was detected by HG-AAS (Perkin-Elmer 4100 equipped with a FIAS 400 hydride generator). The coarse sand fraction (200-2000 µm) was not analyzed because it was determined to be outside the scope of this research, which focused on inhalable or ingested particles. Accuracy was verified using certified reference materials for *aqua regia*-soluble contents (CRM 141R,

Community Bureau of Reference, Geel, Belgium) and recovery is reported in Table 4.1. All reagents were of an ultrapure or analytical grade.

Metal bioaccessibility was assessed using a widely employed and validated *in vitro* extraction method, the Simple Bioaccessibility Extraction (SBET) method (Oomen et al., 2002; Ruby et al., 1999). It was developed for soils and was recently utilized for the first studies on RD, albeit being performed without size fractionation (Bi et al., 2015; Li et al., 2014; Patinha et al., 2015; Turner and Ip, 2007). Half a gram of sample was mixed with 50 ml of a 0.4 M glycine solution with pH adjusted to 1.5 with concentrated HCl. Extraction was performed for 1 h at 37°C (U.S. EPA Method 1340, 2013). The mixture was then centrifuged and the supernatant filtered through cellulose filter (Whatman N°4). The SBET extract metal concentrations were determined by FAAS and HG-AAS.

Detection (LOD) and quantification limits (LOQ) for the methods were calculated with the calibration curves. According to the ICH Harmonized Tripartite Guideline (ICH, 2005), the following equations were used:

$$\text{LOD} = 3.3 \sigma_a/S \quad \text{LOQ} = 10 \sigma_a/S$$

where σ_a represents the standard deviation of the intercept of regression line and S is the slope of the calibration curve. Recovery tests were carried out using blank solutions spiked with metals at three concentration levels (0.1 – 20 mg/kg) and using a previously well-characterized soil. Results for LOD, LOQ and recoveries are reported in Table 4.1. As no certified reference material was available for this method, results were considered satisfactory when the variation coefficient between duplicates was lower than 10%. Enrichment factors (EF) of elements were calculated according to:

$$EF = \left(\frac{C_{Me}}{C_{Re}}\right)_{\text{sample}} / \left(\frac{C_{Me}}{C_{Re}}\right)_{\text{crust}}$$

where (C_{Me}/C_{Re}) is the concentration ratio between the metal and the reference element in the sample and in the earth's upper crust as reported by Wedepohl (1995). We also computed the EF_L , relative to the local background values in Turin soils, for Cr, Ni, Cu, Pb, Sb and Zn based on the ISO 19258/2005 norms from the Regional Agency for Environmental Protection (ARPA Piemonte, 2015). The natural background value was provided for Cr and Ni, while the natural-anthropogenic background for Pb, Cu, Zn and Sb. This last value originates from the sum of the concentrations based on natural and diffuse anthropic sources, such as atmospheric deposition and agronomic operations, and was calculated for the topsoil (0-10 cm). Statistical analysis, including analysis of variance (ANOVA), Student's t-test, Pearson correlations and hierarchical cluster analysis (HCA), was conducted by means of SPSS v.22 software (IBM Corporation, Armonk, NY).

Table 4.1 Detection and quantification limits and recovery test results (average of the three concentrations and three repetitions) for all analyzed elements.

Element	LOD (mg/l)	LOQ (mg/l)	<i>Aqua regia</i> recovery (CRM 141R)	SBET recovery (in blank matrix)
Cd	0.011	0.033	96 ± 9%	90 ± 6%
Cr	0.01	0.03	101 ± 8%	95 ± 3%
Cu	0.011	0.035	90 ± 4%	96 ± 9%
Fe	0.06	0.18	96 ± 5%	102 ± 11%
Mn	0.01	0.03	104 ± 6%	96 ± 4%
Ni	0.015	0.045	104 ± 8%	101 ± 5%
Pb	0.01	0.03	102 ± 6 %	98 ± 5%
Sb	0.0005	0.0015	94 ± 10%	90 ± 6%
Zn	0.01	0.03	92 ± 1 4%	93 ± 5%

4.3 Results and discussion

4.3.1 Physicochemical properties of soils

Table 4.2 lists the mean values of the measured soil and RD properties. The soils' average pH was slightly alkaline, which is in agreement with previous studies reporting that city soils have higher pH than the adjacent agricultural soils, probably for the historical inclusion of extraneous material, such as construction debris (Biasioli et al., 2006). For the same reason, soils have a high sand content (50 µm – 2 mm), with a mean of 70% (Biasioli et al., 2006). Particles <2.5 and 2.5-10 µm had mean concentrations of 8% and 6%, respectively.

TC content in roadside soils was high on the average, potentially reflecting the accumulation of plant residues, as these areas are rarely disturbed. However, part of this content may also be ascribable to anthropic organic contaminants derived from oils, gasoline, brake pads and organic compounds within asphalt.

Average metal content (*aqua regia* extraction) in the bulk samples is reported in Table 4.3, and is compared to a previous extensive study of city soils (Biasioli et al., 2006). In bulk soils, concentrations were high for all metals considering that, according to the Italian legislation (MATTM, 2006), average values of Cu, Cr, Ni, Pb and Zn were above the limits for residential and green areas (120 mg/kg, 150 mg/kg, 120 mg/kg, 100 mg/kg and 150 mg/kg, respectively). The values observed in this study were also higher than reported in previous studies in Turin (Biasioli

and Ajmone Marsan, 2007), which included ornamental garden and park sites, highlighting the impact of traffic emissions. Comparing these findings with other industrial cities worldwide (Ajmone Marsan and Biasioli, 2010), our results place Turin in the higher range for all metals. These metals can be released from different sources: Pb could mainly derive from historical leaded fuel and paints, Sb and Cu from brakes and Zn from tires (Grigoratos and Martini, 2015; Thorpe and Harrison, 2008 and references therein). Ni and Cr, conversely, naturally contribute in high proportions as they may derive from the alteration of serpentinite rocks present in the alluvial deposits upon which the soils developed, as described in previous studies (Ajmone Marsan et al., 2008; ARPA Piemonte, 2015; Biasioli et al., 2006). Other sources can be heavy oil combustion, metallurgical industries, vehicle factories and traffic.

Table 4.2 Descriptive statistics for some soil and road dust properties (n=29 for RD and N=18 for soils).

	pH	TC	TN	Carbonates	Particle size distribution (mass %)				
		%	%	%	< 2.5 µm	2.5-10 µm	10-50 µm	50-200 µm	0.2-2 mm
Soil									
Mean	7.6	4.27	0.30	3.1	8	6	16	37	33
Median	7.7	4.20	0.27	2.4	5	6	14	34	35
Min	7.1	1.98	0.10	0.0	2	0.5	9	18	8
Max	8.1	7.94	0.63	9.5	16	17	30	71	60
Std. Dev.	0.3	1.53	0.13	2.6	5	4	6	13	16
Road Dust									
Mean	7.6	4.10	0.10	5.4	4	2	5	27	62
Median	7.6	3.65	0.10	3.8	2	2	3	27	60
Min	6.6	2.19	0.02	2.1	0.6	0.2	0	0	20
Max	9.8	8.77	0.32	16	24	8	17	62	98
Std. Dev.	0.7	1.69	0.07	3.8	5	2	4	17	19

4.3.2 Physicochemical properties of RD

The average pH of RD samples was very close to that of soils, but with a higher variability probably related to a higher amount of carbonates. The separation of RD samples into particle-sized fractions uncovered that RD was coarser than soils. Sand was still the dominant fraction, however, while fractions <2.5 µm and 2.5-10 µm ranged from 0.6 to 24 % and from 0.2 to 8 % sand. The C/N ratios were much higher than in roadside soils, indicating an addition of C from non-natural sources, such as organic contaminants and bitumen.

Table 4.3 Descriptive statistics of metal pseudo-total content in soils (n=18) and road dust (n=29). All values are in mg/kg.

	Fe	Mn	Cd	Cu	Cr	Ni	Sb	Pb	Zn
Soil									
Mean	27513	857	0.6	128	405	254	5.4	319	286
Median	26039	817	0.5	100	332	229	4.9	133	242
Min	14523	589	0.2	26	147	145	1.5	38	96
Max	54955	1195	1.9	433	1048	465	13	1213	618
Std. Dev.	11742	173	0.4	97	269	93	3.2	331	141
Previous study^a	na	na	na	90	191	209	na	149	183
Legislative Limit	--	--	2.0	120	150	120	10	100	150
Road Dust									
Mean	24060	527	0.8	181	519	294	7.7	74	200
Median	23118	517	1.0	158	463	246	4.0	55	170
Min	9778	380	0.2	17	299	161	0.4	16	51
Max	43141	681	1.7	717	1248	678	33	189	827
Std. Dev.	9102	87	0.4	161	213	136	8.2	49	161

^a Biasioli et al., 2006; na= not analyzed

In RD samples, average elemental concentrations were comparable with previous studies in other cities of the world (Acosta et al., 2011; Christoforidis and Stamatis, 2009; Hu et al., 2011) except for Ni and Cr, having higher values in Turin, which is in line with their local geogenic origin. Most of the metals have average concentrations close to those of the soil samples, while only Mn and Pb had significantly lower means in RD (t-test, $p < 0.05$). However, comparing

concentrations across the six sites ($n = 18$), where both soil and RD were sampled, only Fe was well correlated between the soil and RD samples ($r = 0.80$, $p < 0.01$), while other metals did not exhibit a significant correlation. This behavior was probably based on the different strengths of the anthropogenic sources of metals between sites, while RD Fe could have a main geogenic (soil) contribution.

4.3.3 Seasonal and spatial variability

Seasonality in soil and RD metal concentrations was evaluated by comparing mean values from different seasons at both traffic ($n=8$) and background sites ($n=2$). No seasonal variability was observed in soil samples at either site. With RD samples from traffic sites, Fe was significantly higher in concentration (t-test, $p < 0.05$) in the summer and spring than in the winter, potentially because of the lower soil resuspension in the latter season. At background sites (PE and AG), similar results were also found, with the highest values for Fe and Mn being in the summer, although they were not significant. Average bulk concentrations of Fe, Mn, Cr, Ni, Cu, Pb, Sb and Zn at each site were reported in Figure 4.2.

In the soil samples, Fe, Mn, Ni and Cr had low spatial variability, and the average of the traffic sites was not statistically different from the background sites. On the contrary, Cu, Pb, Sb and Zn had significantly ($p < 0.05$) higher concentrations at traffic sites, with the highest being at the A2 and S1 sites, and the lowest at the two background sites (AG and PE). This indicated road traffic as the main source of these metals. Pb was found at the highest concentration among metals (and the highest EF), consistent with its remarkable use in various human activities, such as a gasoline fuel additive, that have contaminated roadside soils (Ajmone Marsan and Biasioli, 2010).

In RD samples, the spatial variability of Fe, Mn, Ni and Cr is more pronounced, with higher concentrations at the A2 and RI sites located in an industrial area. As in the soils, average Fe content at traffic sites was not significantly different from background sites (although higher, 24.9 versus 20.2 g/kg). This, considering also the significant correlation between Fe in RD and soil samples, could indicate that a substantial proportion of Fe was soil-derived. If so, the higher variability between the sites could be because of the different contribution of soil to RD.

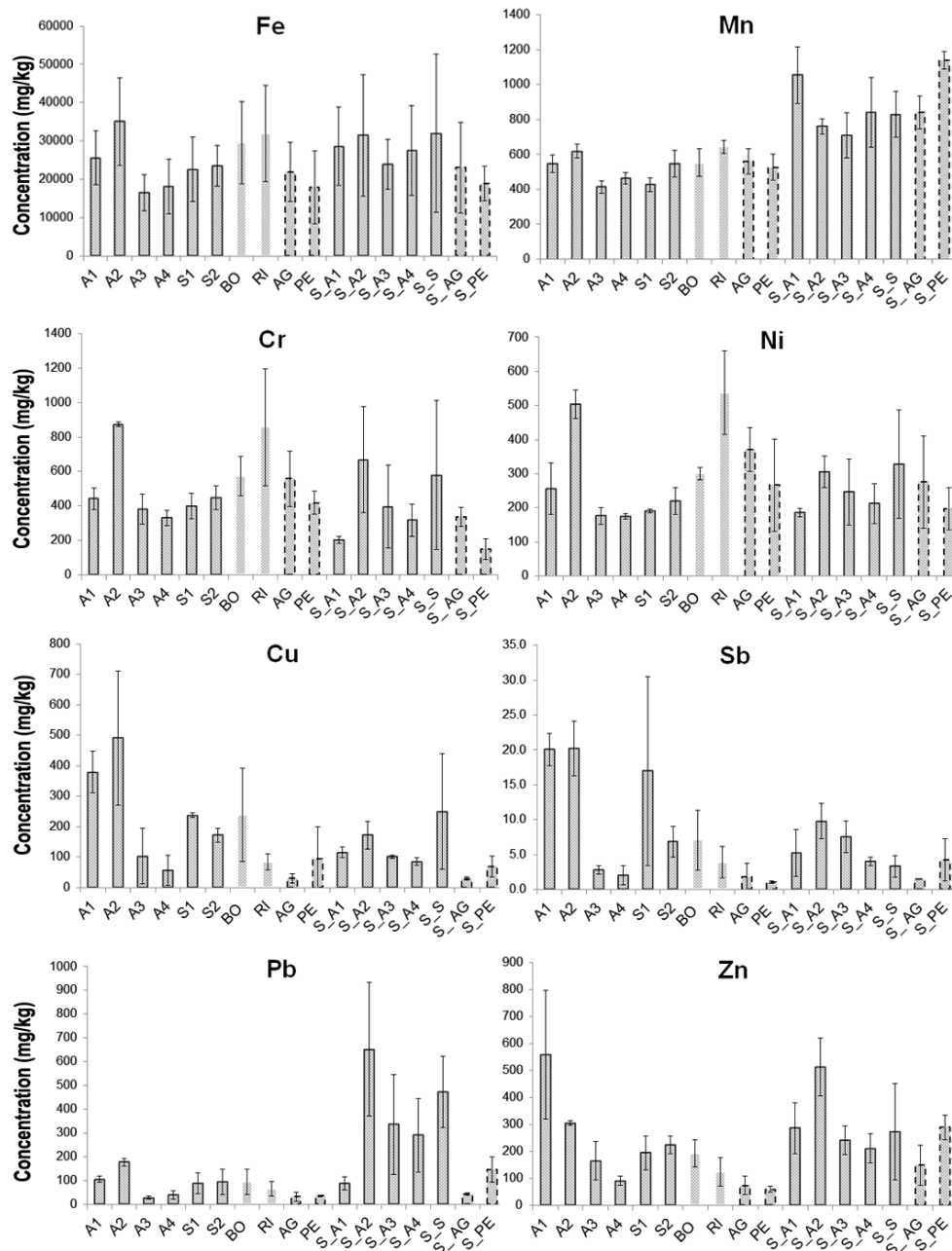


Figure 4.2 Concentrations (mg/kg) and standard deviations of Fe, Mn, Cr, Ni, Cu, Sb, Pb and Zn in RD and soil samples (reported with site name preceded by S). Sites from A1 to S2 are on the main road (from S_A1 to S_S for soils), BO, RI sites are in secondary streets (no soil was present), AG and PE sites are urban background sites.

Cu, Pb, Sb and Zn had similar spatial patterns, with higher concentrations at the A1 and A2 sites (the most trafficked) near the industrial zone, and at sites in the city center (S1, S2, BO). Conversely, the A3, A4 and RI sites, with lower traffic or located near agricultural areas, featured lower concentrations that were not statistically different from the background sites (AG, PE). Therefore, correlations between soil and RD concentrations at these last five sites were calculated (n=15, A2 soil for RI site in view of their proximity), obtaining a significant correlation not only for Fe, but also for Cu and Pb ($p < 0.05$, $r = 0.84$, 0.90 and 0.72 , respectively). This suggests that at sites with low vehicular traffic, urban soils could be one of the major origins for these metals in RD.

In order to confirm these associations, Pearson correlations for RD samples were calculated (n=28, $p = 0.05$), as reported in Table 4.4. TC and TN appeared strongly related, as are Fe and Mn along with Cr and Ni, suggesting a common origin from soil material. Cu, Sb, Pb and Zn were significantly correlated with each other, as well, confirming the hypothesis of a single source. In fact, Sb and Cu could have emanated from brake wear (Grigoratos and Martini, 2015), Cu and Pb from the resuspension of contaminated roadside soils and Zn could derive from tire wear (Harrison et al., 2012), validated by the significant, albeit low, correlation with TC. Cd is the only metal without any significant association with other metals, probably having a different anthropic (industrial) origin.

Table 4.4 Pearson correlations for bulk samples of road dust, n=28. Bioaccessible concentrations are listed as “B”. In bold correlations significant at the 0.01 level.

	TC	TN	Fe	Mn	Cd	Cr	Cu	Ni	Pb	Sb	Zn	Fe B	Mn B	Cu B	Ni B	Pb B	Sb B	Zn B
TC	1																	
TN	0.83	1																
Fe	-0.24	-0.06	1															
Mn	-0.30	-0.13	0.69	1														
Cd	0.24	0.12	-0.09	0.18	1													
Cr	-0.33	-0.15	0.56	0.69	0.28	1												
Cu	0.08	0.08	0.26	0.15	0.19	0.25	1											
Ni	-0.42	-0.24	0.47	0.70	0.17	0.89	0.05	1										
Pb	0.04	0.08	0.51	0.40	0.32	0.34	0.73	0.20	1									
Sb	0.09	0.15	0.37	0.14	0.11	0.13	0.70	0.00	0.72	1								
Zn	0.42	0.23	0.05	0.06	0.15	-0.03	0.68	-0.09	0.46	0.59	1							
Fe B	0.04	-0.02	0.50	0.35	0.21	0.17	0.32	0.14	0.45	0.41	0.42	1						
Mn B	0.08	0.19	0.22	0.46	-0.01	0.09	-0.12	0.04	-0.05	-0.10	0.08	0.26	1					
Cu B	0.35	0.28	0.30	0.11	0.08	0.00	0.67	-0.09	0.59	0.73	0.83	0.59	0.04	1				
Ni B	-0.14	0.04	0.69	0.72	0.01	0.71	-0.06	0.75	0.12	0.01	-0.07	0.28	0.28	0.01	1			
Pb B	0.04	-0.07	0.40	0.33	0.20	0.22	0.61	0.22	0.82	0.53	0.64	0.57	-0.02	0.66	0.10	1		
Sb B	0.26	0.17	0.25	0.20	0.36	0.12	0.83	-0.02	0.68	0.75	0.77	0.65	0.04	0.82	-0.02	0.61	1	
Zn B	0.38	0.23	0.16	0.10	0.03	-0.11	0.62	-0.17	0.47	0.62	0.93	0.51	0.16	0.89	-0.05	0.60	0.77	1

4.3.4 EFs

EFs of the elements in soils and RD relative to upper crustal composition (Wedepohl, 1995) and to the local soil composition are reported in Tables 4.5 and 4.6). Fe was used as a reference metal, although this may have led to an underestimation of EF because of anthropic input of Fe, especially in RD. Alternatively, Cr was also utilized, given its main lithogenic origin in Turin (Ajmone Marsan et al., 2008, Bonifacio et al., 2010; Padoan et al., 2016).

Table 4.5 Enrichment Factors against Fe of the elements in soil and road dust relative to upper crustal composition (U) (Hans Wedepohl, 1995) and relative to the local soil composition (L). For Mn and Cd the natural background value was not provided from ARPA Piemonte.

Site	Mn		Cr		Ni		Cd		Cu		Pb		Sb		Zn	
	U	U	L	U	L	U	U	L	U	L	U	L	U	L	U	L
Road dust																
A 1	1	6	2	8	1	13	26	6	12	2	113	26	15	4		
A 2	1	9	3	11	2	13	24	5	15	3	83	19	6	2		
A 3	2	8	2	8	2	16	11	2	5	1	25	6	7	2		
A 4	2	6	2	8	1	12	5	1	7	1	16	4	3	1		
S 1	1	6	2	7	1	13	18	4	11	2	109	25	6	2		
S 2	1	7	2	7	1	18	13	3	12	2	42	10	6	2		
BO	1	7	2	8	1	12	14	3	9	2	34	8	4	1		
RI	1	9	3	13	2	12	5	1	6	1	18	4	3	1		
AG	2	9	3	13	2	22	2	1	4	1	12	3	2	1		
PE	2	8	2	11	2	8	9	2	6	1	8	2	2	1		
Soil																
A 1	2	2	1	5	1	9	7	2	9	2	2	6	2	2		
A 2	1	7	2	8	1	11	9	2	60	11	1	10	7	3		
A 3	2	6	2	8	1	7	7	2	41	7	2	11	6	2		
A 4	2	4	1	6	1	9	5	1	31	5	2	5	4	1		
S 1	2	6	2	8	2	14	13	3	43	8	2	3	6	2		
AG	2	5	2	9	2	6	2	1	5	1	2	2	5	1		
PE	4	3	1	8	2	20	6	1	23	4	4	7	3	3		

The results using the crustal composition as reference values always exhibited values higher than local soil composition, but with a strongly similar pattern. In addition, using Cr or Fe as reference metals yielded similar results, identifying Sb and Pb as the most enriched metals in soils. Sb and Pb were averagely enriched (EFs = 6 and 5, respectively) against Fe and local soil, while Cu and Zn appeared only slightly enriched (EF = 2). Conversely, Mn, Cr and Ni had mean EF values of 1. Taken together, these findings imply that Cr could also be a suitable reference element in soils in areas of diffuse natural background.

In the RD samples, Sb was still the most enriched element, followed by Cd, Cu and Pb. Average Sb EF values at traffic sites were 55 and 13 against crust and local soil, respectively. Additionally, Cr, Ni, and Zn were slightly enriched in RD with respect to the crustal composition, while Mn was not (EFs of 7, 9, 6 and 1, respectively).

From the EF results, an increasing gradient trend towards the city center was apparent (from A1 to A4), with higher values for almost all metals at the most trafficked sites (A1, A2 and S1).

Table 4.6 Enrichment Factors against Cr of the elements in soil and road dust relative to the local soil composition.

Site	Fe	Ni	Cu	Pb	Sb	Zn
Road dust						
A 1	0.6	0.8	3.1	1.2	14	2.2
A 2	0.4	0.8	2.0	1.0	7	0.6
A 3	0.4	0.6	1.0	0.4	2	0.8
A 4	0.5	0.7	0.6	0.6	2	0.5
S 1	0.5	0.7	2.2	1.1	14	0.8
S 2	0.5	0.7	1.4	1.0	5	0.9
BO	0.5	0.7	1.5	0.8	4	0.6
RI	0.4	0.9	0.4	0.4	1	0.3
AG	0.4	0.9	0.2	0.3	1	0.2
Soil						
A 1	1.4	1.3	2.1	2.2	8	2.5
A 2	0.5	0.6	0.9	4.8	5	1.3
A 3	0.6	0.8	0.9	4.2	6	1.1
A 4	0.8	0.9	1.0	4.5	4	1.2
S 1	0.5	0.8	1.6	4.0	2	0.8
AG	0.7	1.1	0.3	0.6	1	0.8
PE	1.2	1.8	1.7	4.8	9	3.4

4.3.5 Metal concentrations in size fractions

PSD of metals in soils and RD is a key parameter when performing an assessment of health risks from ingestion and inhalation. For inhaled particles, the most hazardous thresholds are at 10 and 2.5 μm . For accidental ingestion, based on adhesion to the hands, the threshold was approximately 50-63 μm , although certain studies have reported values up to 200 μm (Ruby and Lowney, 2012; Siciliano et al., 2009; U.S. EPA, 2011). This size was therefore selected for this study to be the maximum size for analysis. Average *aqua regia* extractable contents of metals for each size fraction are available in Table 4.7.

Table 4.7 Average concentration of metals in size fractions, at traffic (TR) and background (UB) sites.

Fraction	Site type	Fe	Mn	Cu	Cd	Cr	Ni	Pb	Sb	Zn
Road Dust (mg/kg)										
< 2.5 μm	TR	15411	343	196	1.7	161	148	169	17	942
	UB	16166	400	129	1.2	149	148	113	10	414
2.5 - 10 μm	TR	32323	649	333	2.1	373	296	233	29	819
	UB	27242	883	101	1.6	353	348	99	9.5	337
10 - 200 μm	TR	31327	487	180	0.8	312	225	131	8.0	309
	UB	24935	385	40	0.5	259	112	45	1.0	139
Bulk	TR	24594	520	204	0.6	517	283	81	8.5	240
	UB	20236	546	29	0.6	502	329	33	1.5	68
Soil (mg/kg)										
< 2.5 μm	TR	42934	1049	287	2.0	168	299	952	16	805
	UB	29356	1176	120	0.6	136	227	168	2.0	443
2.5 - 10 μm	TR	46001	1179	240	1.5	228	303	757	17	681
	UB	57497	1277	91	0.9	109	238	146	1.0	540
10 - 200 μm	TR	30715	579	88	0.4	202	158	289	6.7	346
	UB	31267	648	41	0.7	156	126	75	1.0	131
Bulk	TR	28684	840	145	0.4	432	256	368	6.0	305
	UB	21656	941	42	0.5	273	249	76	2.4	195

In soils, all metals (except Cr and Ni) showed highest concentrations in the finest fractions. In particular, Fe and Mn had the highest concentrations in the 2.5-10 μm fraction, while Cu, Pb and Zn had the highest concentrations with <2.5 μm . To

better interpret the data, as for bulk concentrations, Pearson correlations between metals for each size fraction were calculated. In the $<2.5 \mu\text{m}$ fraction, Pb and Zn were highly related ($r = 0.90$) and could have originated from the same sources, like combustion or industrial processes. Zn could also derive from the same wear process as Cu (wheels and tires) - they are highly correlated in roadside soils ($r = 0.78$). Ni and Cr did not demonstrate any significant differences between different size fractions, with the latter being slightly enriched in the coarser fraction. This confirmed their mostly geogenic origin, as previously observed by Ajmone Marsan et al. (2008).

In RD samples, Zn was of the highest concentration in the $<2.5 \mu\text{m}$ fraction, almost four times the concentration in bulk samples, while the $2.5\text{-}10 \mu\text{m}$ fraction was slightly less enriched. Industrial processes, such as smelting activities, emit Zn in the fine-size range, while Zn-containing tire wear particles have a peak between 2.5 and $10 \mu\text{m}$ (Harrison et al., 2012). Cu, Sb and Pb had the highest values in $2.5\text{-}10 \mu\text{m}$ particles, just as in the soil samples. This is congruent with the suggested source process (abrasion and wear of brakes and wheel clips) - brake emission tests show particle emission modes between 1.0 and $6.0 \mu\text{m}$ (Grigoratos and Martini, 2015). Mn and Fe revealed little enrichment in the $2.5\text{-}10 \mu\text{m}$ and coarser fractions, while Cr was greatest with respect to concentration in the bulk sample, as in the soils.

These results overall validate the importance, for RD samples, of discriminating between $<2.5 \mu\text{m}$ and $2.5\text{-}10 \mu\text{m}$ particles, as combustion processes mostly consist of particles $<2.5 \mu\text{m}$, while wear processes produce coarser ($2.5\text{-}10 \mu\text{m}$ and larger) particles.

In Table 4.8a, Pearson correlations in the $2.5\text{-}10 \mu\text{m}$ size fraction of RD are reported. Confirming our hypothesis, Zn seemed to be correlated with Cu, Pb and Fe in particles of $2.5\text{-}10 \mu\text{m}$, while they were not correlated to any other metal in particles $<2.5 \mu\text{m}$, suggesting different sources in various size ranges. In the $2.5\text{-}10 \mu\text{m}$ fraction, a significant correlation between C, Fe, Cu and Sb suggested, for C and Fe, an emission from brake wear, which is in agreement with their abundant presence in brake materials (Grigoratos and Martini, 2015). In the coarser fraction ($10\text{-}200 \mu\text{m}$), no such relationship was observed. Cr and Ni are correlated between them and Ni with carbon and nitrogen, which was in line with a dominant natural origin.

No significant seasonal variability was found in soil samples nor RD samples, while the spatial variability of size-fractionated metals followed the same patterns observed in bulk samples. When calculating average concentrations in traffic and background sites, in soil samples, only Pb and Zn in the $<2.5 \mu\text{m}$ fraction showed statistically significant variations between traffic and background samples. Instead,

in RD, Cu, Pb, Zn and Sb were present in significantly higher concentrations at traffic sites for all size fractions.

Eventually, a comparison of elemental concentrations in braking and in acceleration sites (9+9 samples) was conducted. Within braking zones, Zn and Cu concentrations were higher than at acceleration sites in the 2.5-10 µm fraction, although not significantly. This could possibly indicate that particles emanating from braking did not fall immediately on the road but were released also during the acceleration event, as recently found by Hagino et al. (2016).

Table 4.8 Pearson correlations between metals in the 2.5-10 µm fraction. in all sites (a) and in only braking sites (b). In bold significant correlations (p<0.05), n=28 for Table 4a and n=9 for Table 4b.

a	C	N	Fe	Mn	Cd	Cr	Cu	Ni	Pb	Sb	Zn
C	1										
N	0.90	1									
Fe	0.64	0.35	1								
Mn	0.70	0.65	0.55	1							
Cd	-0.46	-0.39	0.03	0.32	1						
Cr	0.26	0.06	0.38	0.25	-0.15	1					
Cu	0.54	0.21	0.76	0.21	-0.22	0.46	1				
Ni	0.63	0.58	0.45	0.66	-0.07	0.76	0.27	1			
Pb	0.49	0.14	0.61	0.25	-0.24	0.24	0.67	0.25	1		
Sb	0.64	0.41	0.73	0.32	0.03	0.14	0.75	0.16	0.64	1	
Zn	0.25	-0.13	0.51	0.18	-0.09	0.08	0.50	0.12	0.80	0.72	1
b	C	N	Fe	Mn	Cd	Cr	Cu	Ni	Pb	Sb	Zn
C	1										
N	0.86	1									
Fe	0.85	0.47	1								
Mn	0.69	0.24	0.58	1							
Cd	-0.87	-0.65	0.05	0.72	1						
Cr	-0.12	-0.61	0.57	0.15	-0.17	1					
Cu	0.90	0.56	0.85	0.25	-0.34	0.79	1				
Ni	0.40	-0.12	0.83	0.52	0.10	0.91	0.84	1			
Pb	0.74	0.36	0.63	0.35	-0.27	0.30	0.63	0.46	1		
Sb	0.50	0.15	0.79	0.56	0.03	0.43	0.67	0.65	0.62	1	
Zn	0.68	0.33	0.71	0.48	-0.19	0.28	0.64	0.49	0.89	0.90	1

In Table 4.8b, correlations considering only braking sites are reported. Here, contrary to the results, when all sites were pooled, Cr was significantly related to Cu, and Ni to Sb. Despite the limited number of samples, this could mean that a

limited emission from brakes or road wear was also relevant for these metals, this process hindered by natural contributions when considering all sites.

The Cu:Sb ratio has been suggested in the literature to be a useful chemical tracer for brake wear particles. In our results, a shift between fine and coarse particles of RD was evident, being 12, 13, 26 and 36 being the ratios for <2.5 µm, 2.5-10 µm, 10-200 µm fractions and bulk RD, respectively. These values fall within the range found for RD particles <10 µm, specifically from 7 to 17 (Amato et al., 2011; Grigoratos and Martini, 2015), while coarser particles are less enriched with Sb. The soil particles showed a larger and more constant ratio, between 16 and 24 for all fractions, indicative of a much lower enrichment of Sb in roadside soils. The homogeneity of values could be based on the natural processes occurring in soils that change the size of the metal-bearing particles (Ajmone Marsan et al., 2007) or on anthropic historical disturbances.

4.3.6 Bioaccessibility of metals

The bioaccessibility results showed the amount of a contaminant soluble in the gastrointestinal environment and, consequently, that would be available for absorption (Paustenbach, 2000). Average concentrations and percentages of the *aqua regia* extractable content for Fe, Mn, Cu, Ni, Pb, Sb and Zn at every site are listed in Table 4.9. Values for Cr and Cd were below the detection limit (DL) in all samples, and, thus, not described herein.

In bulk soil samples, Pb was the most accessible metal, followed by Zn, Cu, Mn, Ni, Sb, Fe and Cr. Pb, Zn, and Cu were found in greater than 40% of the *aqua regia* extractable content, implying a significant risk in the case of ingestion. Cr and Fe were the least bioaccessible metals, in line with their inferred origin, with the first being <DL in most of the samples and Fe having an average bioaccessible fraction of 1% in soils.

In RD samples, Zn was the only element more bioaccessible than in the soils, followed by Pb > Cu > Mn > Sb > Fe > Ni > Cr. As in soils, metals enriched in the fine-size range were more bioaccessible, while Fe, Ni and Cr were the least bioaccessible metals. Sb had similarly low values in both matrices, aligned with its unique origin. These values are similar to the few studies that used the same methodology on RD samples, evidencing, probably, similar sources and chemical forms (Hu et al., 2011; Luo et al., 2011; Patinha et al., 2015).

Table 4.9 Average metal bioaccessible concentrations (mg/kg) and percentage of the *aqua regia* extraction in each site.

Site	Fe		Mn		Cu		Ni		Pb		Sb		Zn	
	mg/k g	%	mg/k g	%	mg/k g	%	mg/k g	%	mg/k g	%	mg/k g	%	mg/k g	%
Road dust														
A 1	2633	10	130	24	110	29	6.6	3	55	52	1.1	5	415	74
A 2	2419	7	86	14	61	12	14	3	78	44	0.1	5	128	42
A 3	361	2	103	25	17	17	2.2	1	2.3	8	0.1	4	76	46
A 4	338	2	92	20	8.3	15	0.0	0	11	27	0.1	5	30	33
S 1	469	2	78	18	67	28	1.1	1	16	19	0.5	3	121	63
S 2	555	2	125	23	57	33	4.9	2	34	36	0.4	6	156	70
BO	615	2	77	14	43	18	3.6	1	34	36	0.3	5	116	61
RI	540	2	138	21	27	33	24	4	16	24	0.1	3	54	44
AG	230	1	132	24	4.9	16	11	3	3.4	11	0.02	1	32	43
PE	274	1	134	25	10	11	3.2	1	7.4	21	0.1	9	23	39
Soil														
A 1	257	1	359	34	40	35	14	7	33	38	0.3	6	140	49
A 2	320	1	214	28	122	71	20	7	382	59	0.6	6	270	53
A 3	383	2	214	30	45	44	11	5	181	54	0.3	4	108	45
A 4	164	1	208	25	34	40	11	5	131	45	0.3	6	70	33
S 1	205	1	300	36	44	18	39	12	351	74	0.2	5	111	41
AG	353	2	326	39	6.3	22	20	7	8.6	21	0.1	4	32	21
PE	243	1	402	35	29	43	20	10	82	56	0.5	11	32	11

As not all chemical forms were equally extracted, correlations between total and bioaccessible content could help in distinguish sources. For Pb, in particular, the two amounts were perfectly correlated in soils (Pearson $r = 0.98$) and well correlated in RD samples ($r = 0.82$). As at the less trafficked sites, Pb could be considered arising primarily from soil (Paragraph 4.3.1), and so we calculated correlations for RD samples in the highly trafficked sites ($n = 15$), trying to determine whether traffic was still a source of Pb. Here, total and bioaccessible Pb were less related in bulk samples ($r = 0.63$) than in size fractions, as they were perfectly correlated in all three fractions ($r > 0.95$). This could indicate that, at highly trafficked sites, different sources of bioaccessible Pb coexist; coarse Pb, probably deriving from soils, and fine Pb, most likely from traffic sources (e.g., brake pads, wheel clips, yellow paint).

No significant variations in bioaccessibility content with seasons were found with either matrix, probably also based on the limited number of samples.

Spatial distribution of bioaccessible metals in soils followed the trend seen for the total content, with Cu, Pb and Zn showing significantly higher concentrations at traffic rather than background sites. Traffic sites had also a higher proportion of bioaccessibility, implying that, for these metals, traffic sources were more bioaccessible than those that were natural.

In RD samples, Fe, Cu, Pb, Sb and Zn were found at significantly higher concentrations (mg/kg) at traffic sites, but only Fe and Cu were observed in significantly greater proportions. This is probably because, contrary to Pb, Sb and Zn, at background sites, they mainly derive from geogenic, and less bioaccessible, sources (as suggested earlier). Fe, in particular, was considerably higher in concentration and proportion at trafficked industrial sites (A1 and A2) (10% and 7%, while the average was 2%) than all others. Ni and Mn did not exhibit any differences between traffic and background sites.

4.3.7 Bioaccessibility in size fractions

The average proportions for all metals and size fractions are outlined in Figure 4.3.

In soil samples Fe, Mn, Cr and Ni adhered to the same trend, with concentrations and proportion decreasing with the increase in size. Fine particles were significantly more bioaccessible at traffic than at background sites, consistent with the idea of a lithogenic origin of larger particles and a more anthropic, and bioaccessible, input for fine particles for all metals.

Cu, Pb and Zn had were most bioaccessible content and found in the greatest proportions, with Pb being the most extractable metal. Along with Sb, they did not feature significant differences between size fractions, but they did significantly higher values at traffic sites. This is probably based on the long-term build-up of contamination, as in the case of Pb, and because in soils, metal-bearing particles can be aggregated by iron oxides, organic matter and carbonates or perturbed by the addition of fine particles and the mixing of roadside soils (Ajmone Marsan et al., 2008).

In RD samples, the bioaccessible percentage of the finer fractions was higher than in soils for all metals, and a clear difference in bioaccessibility between fine and coarse fractions could be observed. This confirmed the probable different sources of metals in fine and coarse RD and, for a number of them, can probably pose a serious health risk. In particular, Pb, Zn and Cu were almost totally bioaccessible in the <2.5 μm fraction (98%, 96%, 89%, respectively) and in the 2.5-10 μm fraction (89%, 67% and 59%, respectively), while only 30% of Ni and Sb was extractable. As a result, bioaccessible Zn and Pb concentrations reached, in several samples, 1981 mg/kg and 612 mg/kg, respectively, in the 2.5-10 μm fraction and

1252 and 210 mg/kg in the <2.5 µm fraction. With the bioaccessible concentrations, average values were still higher than the legislative limit for the total concentration in soils (666 mg/kg for Zn and 245 mg/kg for Pb in the 2.5-10 µm fraction and 530 mg/kg and 139 mg/kg in the <2.5 µm fraction).

On the contrary, Fe, Mn, Ni and Cr followed the same trend observed in soils - the finer the fraction, the more bioaccessible the metals, though concentrations were twice that found in soils. No seasonal variability was observed in either matrix.

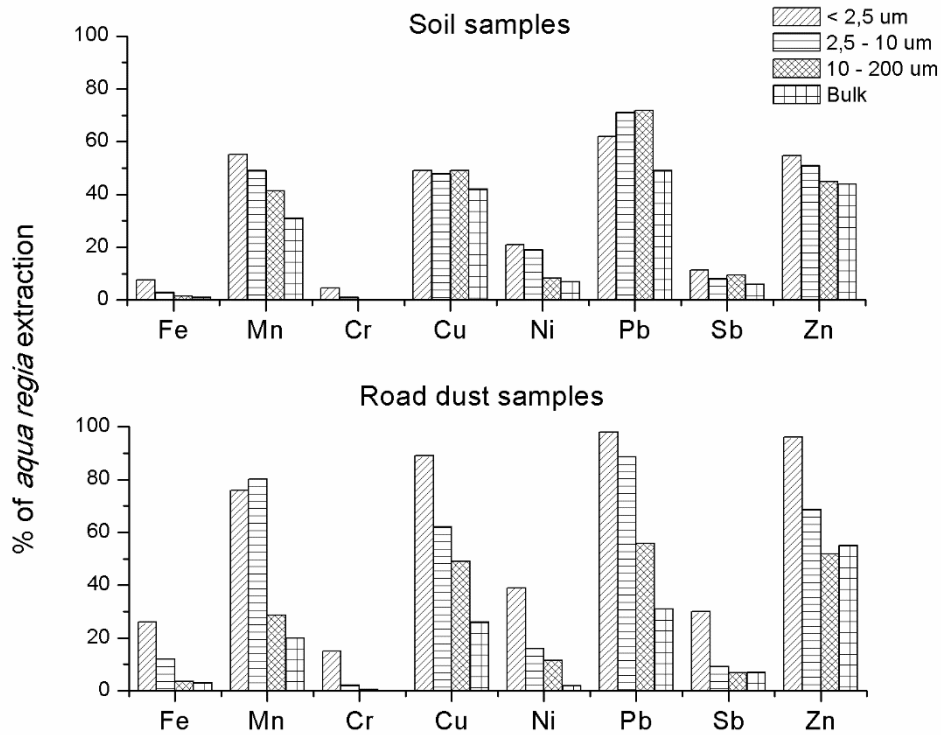


Figure 4.3 Bioaccessibility of metals in size fractions, percentage of bioaccessible to pseudo-total content.

4.3.8 Statistical analysis

Chemometric data treatment was applied to the two data sets (RD and soil samples) separately and as a whole. Missing values were interpolated using the two values obtained in the other seasons, while for below the DL, a value of DL/2 was applied. Cd and bioaccessible Cr were discarded because of the high number of values <DL and data sets were normalized and autoscaled utilizing z-scores.

Q-mode HCA was performed on the data sets to highlight similarities between variables, which could indicate common sources. The results were very similar for both media (RD and soils), thus only RD results were reported in Figure 4.4.

Metals appeared separated into four clusters. The first links together Cr, Ni, Mn and Fe, having the same main source in the parent material of soil and asphalt. The second cluster links C and N, as the organic fraction of RD could derive from either soil or anthropic activities, while the third was formed only by Pb and the extractable portion of Ni. These probably have a similar industrial source or mixed source as they can arise from traffic sources and soil. The last group is made up of all the metals with their primary origins in vehicular traffic, confirming the probable anthropic source of the extractable parts of Fe and Mn, while non-extractable Fe and Mn are soil-related, enclosed in a crystalline (or more stable) matrix.

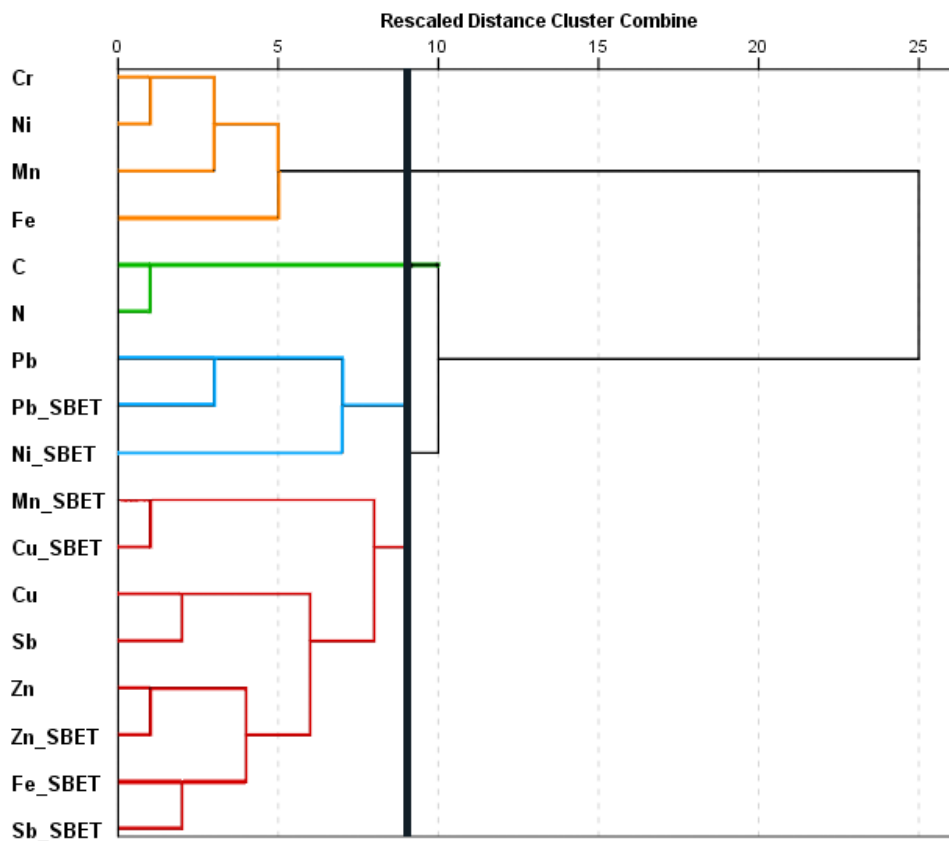


Figure 4.4 Dendrogram obtained by Q-mode HCA considering the data set of road dust samples.

4.4 Conclusions

Pseudototal and bioaccessible fractions of Fe, Mn, Cd, Cr, Cu, Ni, Pb, Sb and Zn were determined in RD and roadside soils of Turin. In the soils, the observed values were higher than reported in previous studies and above the legislative limits. Fine particles (<2.5 and 2.5-10 µm in size) were enriched for all metal (loids) except Cr and Ni, compared to the bulk samples, and spatial variation along the transect was more pronounced for elements mostly emitted by traffic sources (Cu, Sb, Pb and Zn).

In RD samples, the analysis of fractions identified two different sources for Zn (likely industrial in <2.5 µm fraction and tire wear in the 2.5-10 µm). The fraction between 2.5 and 10 µm was the most enriched for all metals but Zn, and almost all analyzed metals (except Mn) seemed to be highly correlated in this fraction. This is probably because the particle emissions from brake, road and tire wear fall mostly within this dimensional range.

In the soil samples, the bioaccessibility of Fe, Mn, Cr and Ni increased in fine particles, likely based on the higher anthropic contribution and greater reactivity, while Cu, Pb, Sb and Zn had almost constant bioaccessibility for all sizes.

In the RD samples, the bioaccessibility of fine particles was clearly greater than in soils for all metals in the order Pb > Zn > Cu > Ni >> Cr. For Pb, Cu and Zn, the bioaccessible fraction reached 90% in the <2.5 µm fraction, which also had the most enrichment when compared to the earth's crust, so these results appear to be critical for the estimation of risk to human health in urban areas.

In general terms, the contents of the bulk samples should not be considered as reliable indicators of the concentration and bioaccessibility of metals in fine fractions of RD and soils, thus size fractionation appears to be a necessity to obtain more useful information for risk assessment in the urban environment.

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5. An empirical model to predict road dust emissions based on pavement and traffic characteristics

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Abstract

The relative impact of non-exhaust sources (i.e. road dust, tire wear, road wear and brake wear particles) on urban air quality is increasing. Among them, road dust resuspension has generally the highest impact on PM concentrations but its spatio-temporal variability has been rarely studied and modeled. Some recent studies attempted to observe and describe the time-variability but, as it is driven by traffic and meteorology, uncertainty remains on the seasonality of emissions. The knowledge gap on spatial variability is much wider, as several factors have been pointed out as responsible for road dust build-up: pavement characteristics, traffic intensity and speed, fleet composition, proximity to traffic lights, but also the presence of external sources. However, no parameterization is available as a function of these variables.

We investigated the mobile fraction of road dust smaller than 10 μm (MF10) in two cities with different climatic and traffic conditions (Barcelona and Turin), to explore MF10 seasonal variability and the relationship between MF10 and site

characteristics (pavement macrotexture, traffic intensity and proximity to braking zone). Moreover, we provide the first estimates of emission factors in the Po Valley both in summer and winter conditions. Our results showed a good inverse relationship between MF10 and macro-texture, traffic intensity and distance from the nearest braking zone. We also found a clear seasonal effect of road dust emissions, with higher emission in summer, likely due to the lower pavement moisture. These results allowed building a simple empirical model, predicting maximal dust loadings and, consequently, emission potential, based on the aforementioned data. This model will need to be scaled for meteorological effect, using methods accounting for weather and pavement moisture. This can significantly improve bottom-up emission inventory for spatial allocation of emissions and air quality management, to select those roads with higher emissions for mitigation measures.

5.1 Introduction

Particulate matter (PM) emissions from road dust resuspension are an increasing concern for air quality and public health (Denier van der Gon et al., 2013; Amato et al., 2014a). The stricter PM emission standards adopted in Europe, with the EURO Directive, have brought now more attention to the non-exhaust particles from road traffic (i.e. road dust, tire wear, road wear and brake wear particles), for which emissions are not controlled, and their relative impact on urban air quality is increasing (Amato et al., 2014b; Barmadipos et al., 2012). In Southern Spain, for example, Amato et al. (2014b) found decreasing contributions for motor exhaust ($p < 0.001$) of 0.4 (0.57–0.24) $\mu\text{g m}^{-3}\text{year}^{-1}$ from 2004 to 2011. Conversely, in the same period, road dust contributions to PM10 levels remained stable. Current estimates suggest that, in the European domain, non-exhaust vehicle emissions represent 70% of urban primary PM10 emissions since 2015 (Keunen et al., 2014).

Among non-exhaust sources, road dust resuspension has generally the highest impact in PM concentrations, however, a comprehensive assessment of road dust impact both in terms of pollutants (dust, carbonaceous particles and metals) concentrations and health outcomes has been rare (Ostro et al., 2011). This is due to the lack of reliable emission factors (for source oriented models, Schaap et al., 2009), and the similarity of the chemical composition of road dust with other mineral sources (Amato et al., 2009). Moreover, experimental studies on road dust characterization generally found high variability of road dust loadings in space and time, suggesting the need of bottom-up inventories and improvement in the description of spatial and temporal variability. Spatial inequalities of air pollution levels have been in fact observed at the urban scale, mostly for PM10 and its coarser fraction, which is dominated by road dust resuspension.

Time variability is crucial for epidemiological studies but information is lacking on the day-to-day and seasonal variability of emission factors. Some recent studies attempted to observe and possibly describe the spatio-temporal variability. In Scandinavian countries, the use of studded tires and road salting/sanding are predictor variables to estimate road dust loadings and the NORTRIP model has been successfully applied in order to predict both spatial and temporal variability of road dust loadings (Denby et al., 2013a and 2013b); while in Central and Southern Europe, where time-variability is driven by meteorology, in addition to traffic flow, several authors used the ON/OFF approaches to account for road moisture due to precipitation (Pay et al., 2011; Schaap et al., 2009). Amato et al. (2012) studied the day-to day variability of road dust suspendible fraction in one Spanish and one Dutch streets, observing relatively short recovery rates within 24 h and 72 h respectively, which is in agreement with the recovery of ambient air PM coarse curbside increment (Amato et al., 2011; Keuken et al., 2010). However, uncertainty remains on the seasonal variability of road dust emissions, which can be also affected by meteorological pattern (higher relative humidity in winter, higher drought in summer, intense Saharan dust intrusions in spring, for example).

Concerning the spatial variability, the gap of knowledge is much wider. Several factors have been pointed out as responsible of road dust build-up (i.e. emission potential): pavement characteristics (texture, mineralogy, age (Amato et al., 2013; Berger and Denby, 2011; China and James, 2012; Denby et al., 2013b; Gehrig et al., 2010; Gustafsson et al., 2009; Raisanen et al., 2005), traffic intensity and speed, fleet composition (Bukowiecki et al., 2010; Liu et al., 2016), proximity to traffic lights, but also the presence of external sources (e.g. construction dust, unpaved areas, African dust deposition, etc.). However, no parameterization is available as a function of these variables. Moreover, to understand the impact of these predictors is also important for air quality management since remediation measures can be designed.

In this study, we present a simple empirical model able to predict road dust suspendible fraction and, consequently, emission potential, based on pavement macrotexture, traffic intensity and proximity to braking zone. This model is based on field measurement in the cities of Turin (Italy) and Barcelona (Spain), thus considering quite contrasting environments (Mediterranean and Continental) and aims to estimate the maximum emission factor for single roads (without considering the effect of meteorology); it could be, therefore, suitable for spatial allocation of emissions. Moreover, the article offers the first estimates of emission factors in the Po Valley (Italy), one of the most polluted regions in Europe, both in summer and winter conditions.

5.2 Material and methods

5.2.1 Study area

Four sampling campaigns were performed in the cities of Turin (Italy) and Barcelona (Spain), three in the summer period (June and September 2016 in Turin, August 2016 in Barcelona) and one in winter (January 2017, in Turin). The two cities under study have a common high density of vehicle emissions (among the highest in Europe) but different climatic conditions.

The Turin metropolitan area has a population of around 1.5 million inhabitants, and is the fourth most populous metropolitan area in Italy. The high car density (5300 veh km⁻²) provokes (as sum of exhaust and non-exhaust) almost 40% of the total primary emitted PM₁₀, the second most important source (after biomass burning) according to the regional inventory (IREA, 2010). Climate is classified as humid subtropical, with moderately cold but dry winters and hot summers, when rains are infrequent but heavy. Average rainfall is around 1000 mm per year (mostly concentrated in spring and autumn) and daily temperatures vary within 2-22 °C (monthly averaged; ARPA Piemonte, 2014). The city is located at the western end of the Po valley, surrounded by hills to the East and by the Alps to the North and West. Thus, the dispersion of pollutants is very low, as in all cities of the Po valley (Belis et al., 2011; Eeftens et al., 2012), due to the very low wind speed and the thermal inversion occurring in wintertime. Consequently, EC air quality standards are not met. In 2016, for example, PM₁₀ concentrations in the city center exceeded the EU daily limit value for 70 days (ARPA Piemonte, 2016).

The Barcelona greater metropolitan area has around 4 million inhabitants and, with ~1 million vehicles, has also one of the highest car densities in Europe (5900 veh km⁻²). The city is located in the western coast of the Mediterranean basin, with a Mediterranean climate (mild winter and hot summers), and the scarce and infrequent precipitation (614 mm as mean from 2010 to 2015) facilitate the mobilization and resuspension of road-deposited particles. In Barcelona, traffic emissions are the most important pollution source of PM₁₀, although other significant sources are mineral dust, shipping and industry (Amato et al., 2016). At urban background sites, annual PM₁₀ concentrations due to the regional contribution are less than 30% of the total, while non-exhaust vehicle emissions contribute 17% (7 mg m⁻³), with the total road traffic contribution calculated at 46% (Amato et al., 2009). Thus, controlling local sources is very important for attaining PM₁₀ limit values. The exposure scenario is even more problematic considering that 56% of urban population live less than 70 m away from major roads (>10,000 vehicles day⁻¹).

5.2.2 Road dust sampling

The mobile fraction (able to be suspended under the applied airflow, 30 l min^{-1}) of road dust below $10 \mu\text{m}$ in aerodynamic diameter (MF10) was sampled by means of a field dry resuspension chamber consisting in a sampling tube, a methacrylate deposition chamber, an elutriation filter, where MF10 was separated, and a filter holder, where particles were collected (Figure 5.1). More details on the sampler and on the sampling method can be found in Amato et al. (2009 and 2011).

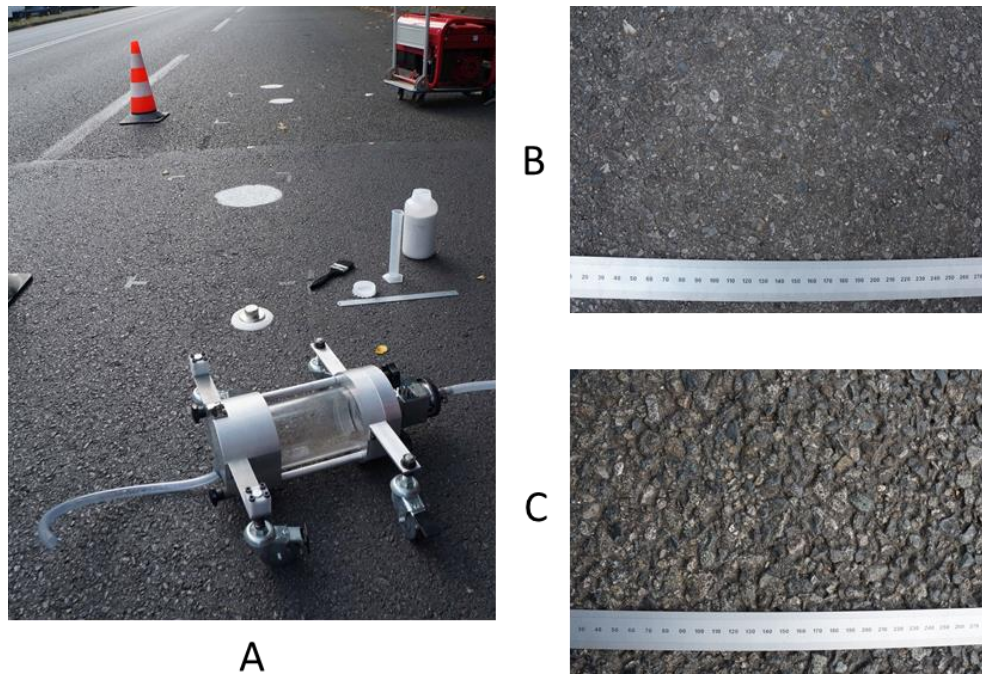


Figure 5.1 Photo of the experimental setup during measurements (A) and sampled pavements with different MTD (B = 1.23 mm; C = 0.57 mm)

In Turin, sampling sites were selected in order to characterize different fleet conditions, pavements and traffic characteristics. To this aim, sites were chosen in residential, commercial and industrial neighborhoods and, at some sites, sampling was performed in both traffic directions. In Barcelona, sampling sites were chosen in a limited area, but on streets with different pavements and traffic conditions. In total, 72 filters were collected, characterizing 30 sites in Turin and 6 sites in Barcelona (Figure 5.3). In order to ensure a complete re-establishment of the stationary conditions of dust loadings, all the samplings were performed after, at least, one week without precipitation.

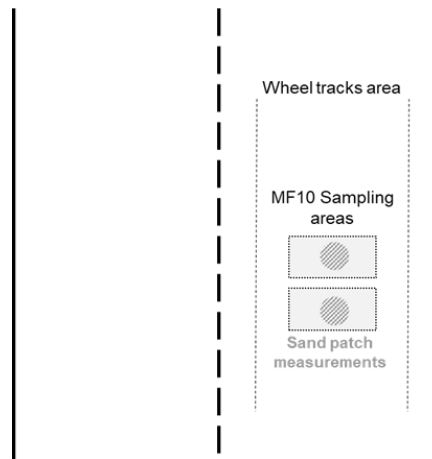


Figure 5.2 Placement of the sampling area within the road.

Each MF10 sample was collected as in previous studies, from a 50 x 100 cm area with the wider side centered within the most-right active lane (excluding parking area), thus representing the area covered by wheel tracks (Figure 5.2). For each site 2 filters were collected in adjacent areas to improve the representativeness of the final road dust loading estimate. Before sampling, quartz fiber filters (Pall, Ø47 mm) were dried at 205°C for 5 h and conditioned for 48 h at 20°C and 50% relative humidity and weighed two times (every 24 h) and kept in PETRI holders. After sampling, filters were brought back to the laboratory and weighed after 24 and 48 h of conditioning at the same T and HR condition (Amato et al., 2009).

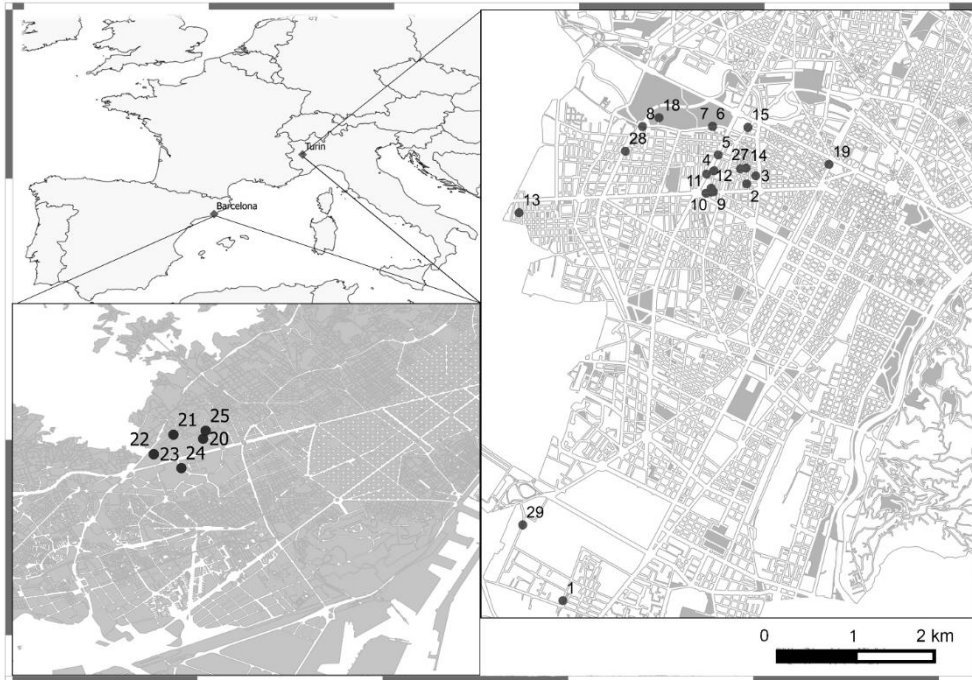


Figure 5.3 Map of the sampling sites.

5.2.3 Pavement macro-texture measurements

The macro-texture of road pavement corresponds to the size of the aggregate particles and the gaps between them in the asphalt mixture (Henry, 2000). In our study, pavement macro-texture was characterized through the combination of photographic analysis and the Mean Texture Depth (MTD) analysis (China and James, 2012). Pictures of the pavement surfaces were taken at a fixed distance (50 cm) using a 16.1 MP camera, with a millimeter scale ruler in the field of view, and used to estimate average size of aggregates. In each site, two photos were taken and the size distribution and mean horizontal size of aggregates was estimated by counting the total number and the size of each aggregate along the ruler (Amato et al., 2013).

Since aggregates are embedded in the asphalt binder, the texture was estimated also by means of a MTD analysis. This analysis, called sand patch method (China and James, 2012; Praticò and Vaiana, 2015), is a standard evaluation of the surface macrostructure by careful application of a known volume of standard material on the surface, and subsequent measurement of the total area covered (ASTM E 965, 2015). At each site, two MTD measurements were made using 30 ml of glass spheres (clean silica sand passing a 300 μm and retained on a 150 μm BS sieve, Mastrad ltd) and the average circular area was calculated using the average of 3

diameter measurements. This area was then divided by the applied volume of the spheres to calculate the MTD. The area used for photographic and MTD measurements was within the area of the MF10 measurement (Figure 5.2), and performed after the MF10 sampling and after sweeping the surface with a brush. Using these analyses, we calculated the corrected aggregate mode (CAM) according to the formula proposed by China and James (2012):

$$(CAM)_i = MTD_i * (\text{aggregate mode})_i / (\text{aggregate mean})_i \quad (1)$$

where the CAM of the *i*-th sample is calculated starting from the MTD, the mode of the aggregates observed through photographic analysis and the mean value of the horizontal size of the aggregates.

5.2.4 Data analysis

Multiple linear regression analysis was run to assess the feasibility of using pavement and site features to predict MF10. As predictor variables, we used the corrected aggregate mode (CAM), the traffic intensity (TR) and the distance (DIST) from the closest braking zone. The method was cross-validated using the leave-one-out method (Todeschini, 1998). The indices used to interpret the validity of the model were the Relative Prediction Error (RPE) the Standard Error of Cross-Validation (SECV) and the Cross-Validated Coefficient of Determination (Q2) (Gunawardena et al., 2014).

Regression curves have been calculated by means of a least squares fit, minimizing the sum of residuals scaled by the standard deviation among duplicated measurements. All calculations were performed using Windows Excel 2013 and IBM SPSS 23. Data on traffic intensity was provided by the city council for Barcelona and, for Torino, by the in-house company of the city (5T s.r.l.), refers to the monthly averaged daily fluxes in the sampled month. DIST was calculated from the sampling site to the stop sign (or the traffic light line on the pavement).

5.3 Results and discussion

5.3.1 MF10 loadings and emission factors

Descriptions of the sampling sites, macro-texture, traffic data, MF10 and emission factors for each site are reported in Table 5.1. The MF10 loadings (the suspendible fraction of road dust) in Turin streets ranged between 0.8 – 42.7 mg m⁻², being the highest three registered at sites next to unpaved parks (12.3 mg m⁻²) and construction works (11.5 and 42.7 mg m⁻²). Excluding these sites, the urban range was found to be 0.8-8.8 mg m⁻² (mean of 2.0 mg m⁻²) which is in the central range of European cities characterized with the same methodology (Amato et al., 2011;

2012; 2014b and 2016; AIRUSE, 2016) but higher than other Central European cities such as Paris (0.7-2.2), and Zurich (0.7-1.3). However, Turin measurements include summer and winter data, while in Zurich and Paris measurements were only performed in winter. In fact, we observed a clear difference between summer and winter samples (Figure 5.2), with a mean winter value of 1.0 mg m^{-2} , significantly lower than in summer (2.7 mg m^{-2}). In Barcelona, summer MF10 loadings were found in the range of $1.1 - 3.4 \text{ mg m}^{-2}$, confirming the values found in previous studies (Amato et al., 2012).

Road dust emission factors (EFs) were estimated based on MF10 using the power relationship proposed by Amato et al. (2011), which has a similar theoretical basis of the U.S. EPA AP-42 model but uses the MF10 instead of the silt ($<75 \mu\text{m}$) loading:

$$EF_i [\text{mg VKT}] = a \cdot MF10_i^b \quad (2)$$

where $MF10_i$ is the road dust suspendible fraction at the i th location, and a and b are empirically determined coefficients (VKT: Vehicle Kilometer Traveled). In the case of Barcelona sites, we used the coefficients ($a=52.9$; $b=0.82$) obtained in the same city by Amato et al. (2012), while for Turin we used the average ($a=45.9$; $b=0.81$) between Barcelona and Zurich due to the climatic conditions of Turin. Emission factors for each site are reported in Table 5.1 and must be intended as fleet-averaged.

Typical urban roads in Turin showed annual-averaged values within $10 - 85 \text{ mg VKT}^{-1}$ (Table 5.1), with a mean value of $27 \pm 19 \text{ mg VKT}^{-1}$ (excluding the sites influenced by construction works or unpaved areas nearby), which is the first estimate in the Po Valley and, to our knowledge, the first annual-averaged value in Europe (accounting also for seasonal differences).

Table 5.1 Site description, pavement MTDs, MF10 loadings and calculated emission factors for each sample (average of 2 filters).
* indicates traffic values estimated with mobility models.

Season	Site number (city)	Distance from closest braking zone [m]	N° vehicles per lane [veh day ⁻¹]*	Average speed (km/h)	MTD ± S.D (mm)	MF10 ± S.D. (mg m ⁻²)	EF ± S.D. (mg VKT ⁻¹)	Notes
Summer	1 S (Turin)	68	1454	38.6	0.77±0.04	1.6±0.4	18±5	
	2 S (Turin)	340	1500	25.5	0.68±0.05	3.5±0.5	34±6	
	3 (Turin)	103	500*	-	0.57±0.01	8.8±0.2	72±2	
	4 (Turin)	95	15367	36.9	-	2.9±1.0	36±13	
	5 (Turin)	52	2993	30.1	0.65±0.03	2.3±0.2	25±2	
	6 (Turin)	278	2651	-	1.23±0.12	1.5±0.3	17±4	
	7 (Turin)	280	2651	-	0.62±0.04	1.8±0.2	20±2	
	8 S (Turin)	70	3255	-	1.17±0.1	1.9±0.1	21±1	
	9 S (Turin)	210	1519	29.6	-	3.6±0.6	44±7	
	10 (Turin)	210	1519	-	0.63±0.02	2.2±0.2	24±2	
	11 (Turin)	123	3542	32.2	0.97±0.03	1.0±0.2	13±2	
	12 (Turin)	54	500*	-	1.27±0.04	5.6±0.5	50±6	
	13 (Turin)	23	500*	-	0.85±0.02	5.2±0.4	47±5	
	14 S (Turin)	25	700*	-	0.64±0.03	4.0±0.1	38±1	
	15 S (Turin)	155	1367	-	1.28±0.27	2.7±0.2	27±2	
	16 S (Turin)	150	1000	-	-	2.2±0.2	27±3	
	17 (Turin)	-	-	-	-	5.5±0.8	68±10	Campus road

	18 (Turin)	-	-	-	-	12.3±1.6	152±20	Park road
	19 (Turin)	70	4700	-	-	42.7±5	528±62	Construction works nearby
	20 (Barcelona)	5	1200	-	0.73±0.08	3.4±0.4	34±5	
	21 (Barcelona)	80	2350	-	1.0±0.04	1.5±0.1	17±1	
	22 (Barcelona)	65	800	-	0.89±0.07	2.0±0.01	23±1	
	23 (Barcelona)	65	800	-	1.27±0.04	2.1±0.7	21±10	
	24 (Barcelona)	200	4733	-	1.52±0.08	1.1±0.2	14±3	
	25 (Barcelona)	95	-	-	0.40±0.05	1.1±0.2	13±3	
Winter	1 W (Turin)	72	1454	38.6	0.91±0.07	1.3±0.1	16±2	
	2 W (Turin)	340	1500	25.5	0.78±0.04	0.85±0	11±0	
	8 W (Turin)	455	3255	-	0.88±0.07	1.1±0.6	14±9	
	9 W (Turin)	260	1519	29.6	0.86±0.13	0.9±0.3	11±3	
	14 W (Turin)	45	500*	-	0.71±0.07	1.6±0.4	19±4	
	15 W (Turin)	155	1367	-	1.25±0.05	0.8±0.2	10±3	
	16 W (Turin)	150	1000	-	1.02±0.10	0.9±0.3	11±3	
	26 (Turin)	130	500*	-	-	11.5±4.5	142±55	Construction works nearby
	27 (Turin)	93	500*	-	1.03±0.16	6.9±2.2	85±27	
	28 (Turin)	170	2464	14.7	0.83±0.03	1.2±0.3	15±4	
	29 (Turin)	1000	2311	23.1	0.61±0.04	0.9±0.1	12±1	

Separating winter and summer EFs the averages would be 20 ± 8 and 31 ± 16 mg VKT⁻¹, respectively, although not all sites were sampled at the same spot both in summer and in winter (Figure 5.2). An explanation for this higher emission factor in summer could be the lower pavement moisture, as all winter measurements were performed under morning haze and high air humidity. In addition, road hygroscopicity could have been increased by road salting, although only some roads were salted the week before the sampling campaign. Unfortunately, we do not have any precise information on this operation (it was made at least two days before the sampling). Moreover, other unknown dust sources, such as a higher soil contribution due to the drier climate, or construction dust could have influenced the results.

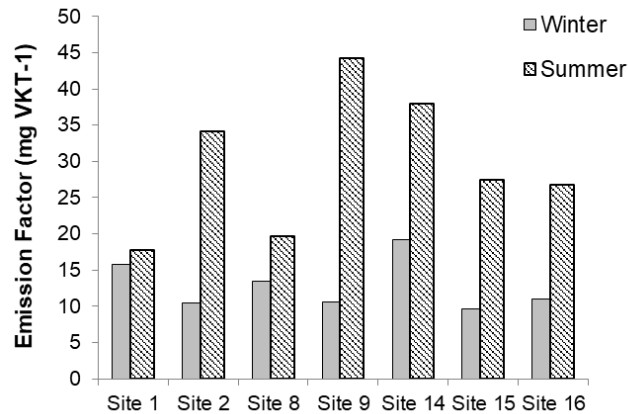


Figure 5.2 Comparison of summer and winter emission factors at selected Turin sites (where sampling was made at the same spot in both seasons).

In Barcelona, emission factors were estimated within 13 – 34 mg VKT⁻¹, with an average value of 20 ± 8 mg VKT⁻¹ (Table 5.1). If we compare our results with the emission factors estimated in European studies using the same experimental set-up, these values are in the central (for Turin) or lower observed range. For example, studies reported 5.4-17 mg VKT⁻¹ in Paris (Amato et al., 2016), 12-51 mg VKT⁻¹ in Switzerland (Amato et al., 2012) and 77-480 mg VKT⁻¹ in southern Spain (Amato et al., 2013).

5.3.2 Effect of traffic intensity and distance from braking zones

The impact of traffic intensity on the road dust EF is poorly known although important for improving the emission parameterization for modelling. Recent studies found or hypothesized lower EFs for high capacity roads, as high traffic

intensity and speed are both expected to lead to a lower road dust reservoir (Amato et al. 2013; Abu-Allaban et al., 2003; Etyemezian et al., 2003; Schaap et al., 2009). Conversely, Bukowiecki et al., (2010) found the opposite, comparing the city center with a major freeway, revealing the need of more empirical studies. In the present study, we have explored the relationship between MF10 and street characteristics, such as traffic intensity and the distance from nearest braking zone (crossing, traffic light or roundabout), using combined data of both cities to enhance the representativeness of the models. We used traffic intensity data provided by city councils, based either on measurements or on mobility models. We observed a rather good inverse correlation between MF10 and the number of vehicles circulating on the lane (Figure 5.3), obtained by dividing the total traffic volume by the number of lanes. MF10 decreases with increasing traffic intensity following a power law fit, reaching a background loading probably related to pavement characteristics and meteorological conditions. In Figure 5.3, we have separated summer and winter samples in order to avoid the meteorological disturbance on the goodness of the fitting. Below 1000 vehicles day⁻¹, MF10 increased due to lower traffic volumes, which led to higher steady state MF10 than at high traffic sites. However, also unknown sources could have contributed to the additional load, such as construction dust, due to the poor state of the pavement (at some sites).

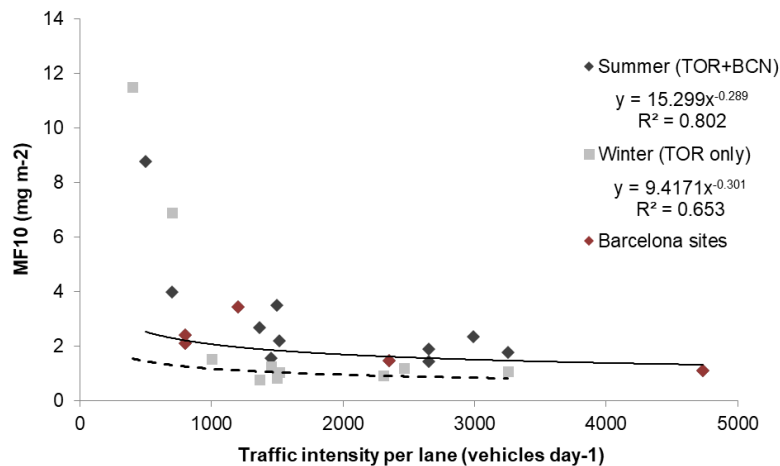


Figure 5.3 Relationship between MF10 and traffic intensity per lane. All sites with available traffic intensity data were used.

Emission factors for secondary roads were therefore higher than for high capacity roads. This finding is relevant for emission inventories, since using a single or constant emission factor for the calculation of non-exhaust contribution to PM in a whole region (top-down approach), may result in a mistake in emission estimates (Figure 5.4), e.g emissions from road with higher intensity would be overestimated.

The use of real or modeled EFs (as the site-specific relation in Figure 5.4) for each road or area (bottom-up approach) for road dust emissions is therefore needed to improve modeling results.

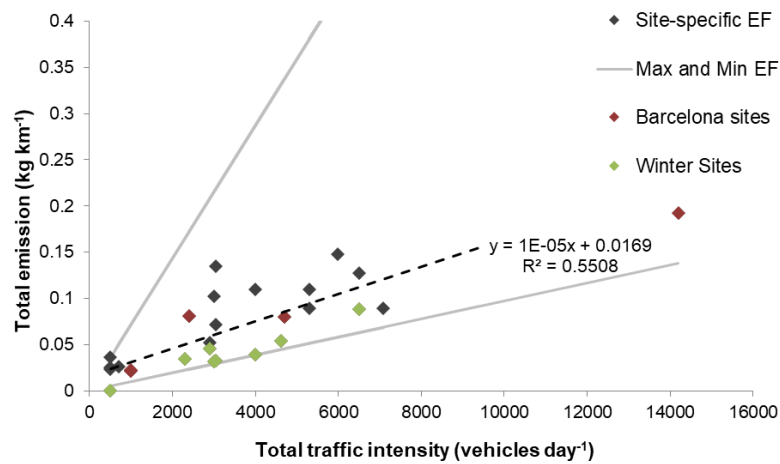


Figure 5.4 Site-specific relationship between total emission per km and traffic intensity (using data of both cities). Grey line represents the interval generated using the maximum and the minimum value of EFs. The site with the higher traffic intensity (in red) was excluded from the fit, although in line with other samples.

Brake wear particles are a major source of road dust (Grigoratos and Martini, 2015; Thorpe and Harrison, 2008). In Barcelona, Amato et al. (2013) estimated that 27% of MF10 was made of brake wear, as traced by Cu, Sb, Ba among other elements. Therefore, we explored the relationship between MF10 and proximity to braking zone (Figure 5.5) as a possible predictor of MF10 loading. We explored the relationship with the distance both to the following braking zone and to the previous, or the smaller of the two. Results reported in Figure 5.5 show a rather poor correlation in the case of using the minimum distance but a negative trend is apparent, suggesting that 70-100 m away from braking zone no significant increase in MF10 is observed due to brake particles. These results are in agreement with Hagino et al. (2015), who found two peaks of brake PM emission in dynamometer tests: the first peak during the application of a braking force and the second one afterwards, during wheel rotation. In one case, the peak was even after 30 s of acceleration, thus after a considerable space in the real world, and the emission during the acceleration phase represented almost 50% of the emitted PM.

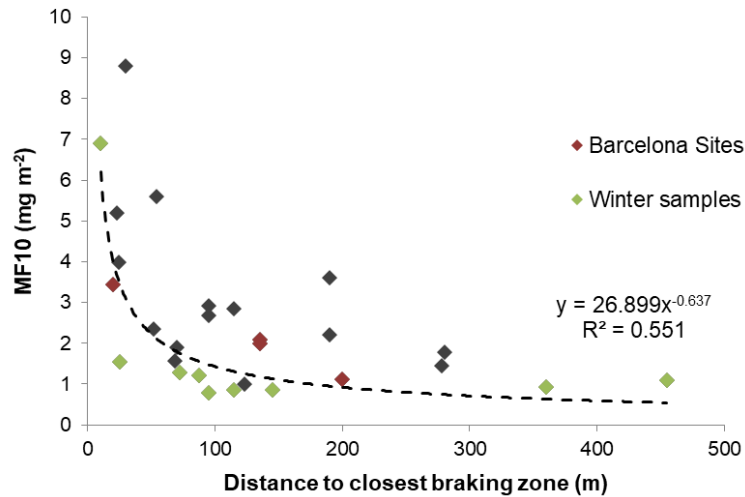


Figure 5.5 Relationship between MF10 and the distance from the closest braking point: stop, traffic light or roundabout (using data of both cities).

5.3.3 Effect of macro-texture

In this study macro-texture was investigated through MTD and photographic measurements in order to calculate CAM values. The classic MTD measurement typically resulted in a value indicating the mean size of the gaps between aggregate particles, thus higher MTDs indicated deeper or larger pores (coarser texture), while the CAM value also incorporated an estimation of the horizontal size of the particles.

MTD values ranged from 0.56 to 1.30 mm in Turin, and from 0.36 to 1.54 mm in Barcelona (Table 5.1), showing quite a large variability in pavement macro-texture. Figure 5.6 shows the relationship between MF10 and both the MTD and the CAM, using data of both cities but excluding roads with less than 1000 vehicles day⁻¹, where, as described above, unknown sources could have contributed to the high loadings. In addition, in these streets the traffic data was only modeled and not measured as in all other sites, thus introducing an additional error. Results show a significant inverse correlation with both parameters ($r^2 = 0.48$ and 0.54 for MTD and CAM, respectively). The correlation is higher with the corrected aggregate mode (Figure 5.6), revealing that the higher the porosity of asphalt, the higher the capability to inhibit resuspension. A similar result was found by China and James (2012), who analyzed the relationship of mean corrected mode with the resuspension potential using standard soil freshly applied to asphalt, and by Gehrig et al. (2010), using mobile load simulators. Moreover, Jacobson and Wågberg (2007) found that, with studded tires, the aggregate diameter of the pavements influences the total wear in as much as coarser material results in lower wear.

However, those studies were both dealing with controlled experiments, which might not be fully applicable to the real world, while our study offers the first evidence, to our knowledge, in real-world conditions (regarding road dust loading and physico-chemical properties). The resuspension inhibition could be influenced by the physical shielding of pores and by the size distribution of particles in the bitumen matrix, as evidenced by the improvement of the fit using the CAM. This improvement could be attributed to the use of the ratio of mode to mean (in equation 1). A value lower than 1 means that some large particles are enclosed in the matrix, so dust could be occluded between these particles and the pavement or sheltered from them, causing a higher build-up or road dust. On the other hand, if we have a number of particles finer than the average, they can smooth or occlude the pores between larger particles, thus lowering the dust accumulation potential. Still, it must bear in mind that this relationship is only valid in summer, being completely masked in winter by the stronger effect of road moisture (Figure 5.6).

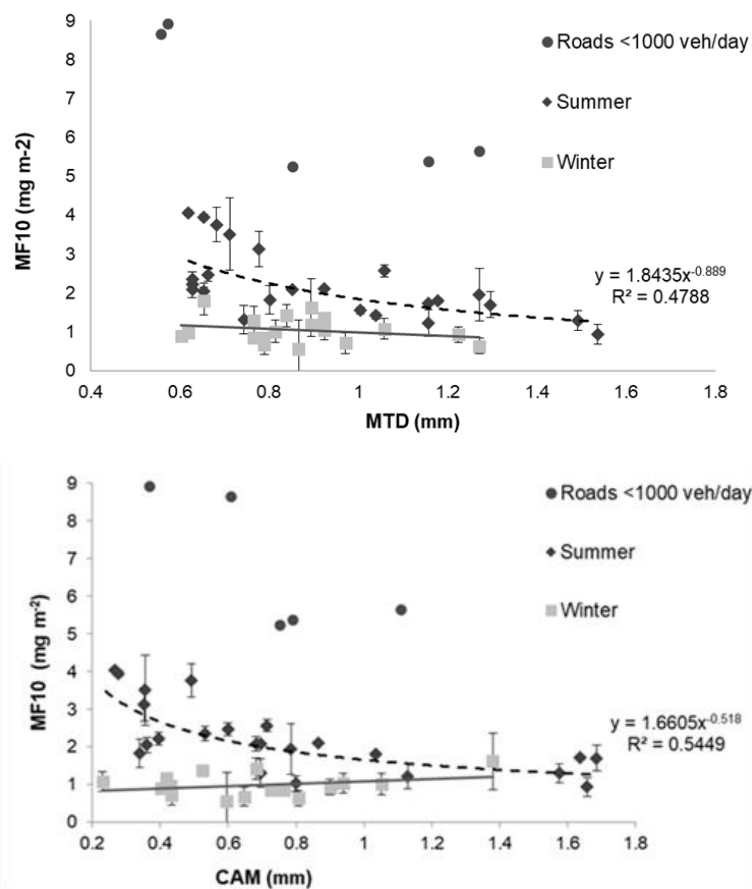


Figure 5.6 Relationship between MF10 and MTD (above) and CAM of aggregates. All samples have been used; red dots belong to sites where traffic intensity was below 1000 vehicles day⁻¹, and have been excluded from calculations.

Recently, review studies on non-exhaust emissions (Amato et al., 2014b; Denier van der Gon et al., 2013) have suggested the possibility of the use asphalt with coarser texture to improve air quality by inhibiting road dust resuspension, and our study offer experimental evidence, covering two different urban scenarios. Given that the observed range of MTD variability is high (Table 5.1), even within the same urban area, there is space for improvement since, currently, the surface texture is not regulated in cities. These results suggest that asphalts that are more porous and with coarser textures could, therefore, be not only designed to reduce noise emissions and to improve water drainage, but also to reduce the emissions from paved roads.

5.3.4 Predicting model

Our predicting model aims to estimate MF10 loading contributions from traffic sources, not from external sources (e.g. construction dust, soil resuspension or African deposition). Therefore, only the spatial variability could be assessed, as the temporal variability needs to be parametrized afterwards, using, for example, the method proposed by Amato et al. (2012).

Based on the results and the relationships discussed above, a multiple linear regression analysis was developed to predict the maximum MF10 loading from the CAM, the traffic intensity (TR) and the distance (DIST) from the closest braking zone. Independently, each parameter showed an inverse relationship with the MF10, thus we tried different linear regressions with two or three variables using exponential or potential equations. Our results show that the equation with the best prediction of MF10 was:

$$RD10 = e^{2.901 \pm 0.855} \times CAM^{-0.264 \pm 0.123} \times TR^{-0.218 \pm 0.105} \times DIST^{-0.145 \pm 0.076}$$

The model performed well, reporting the 74% of the variance of the dataset and reported no systematical bias in calculated values (Figure 5.7). During the development, we removed from the dataset samples below 1000 vehicles day⁻¹, for the above-depicted rationale, and samples where not all the data were available.

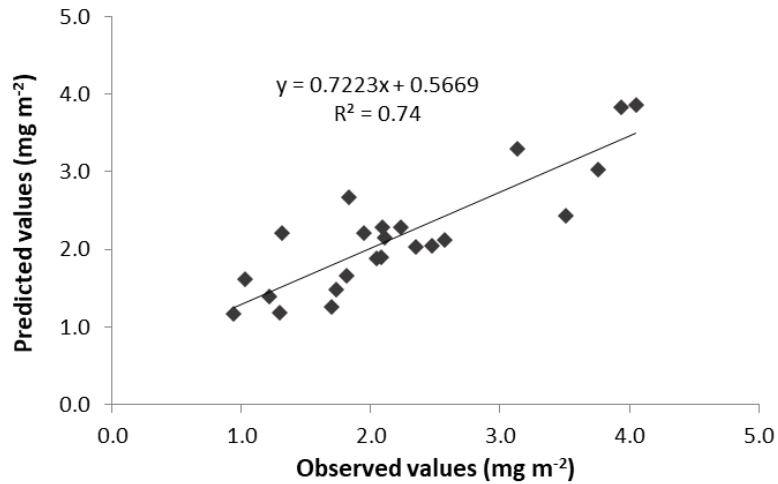


Figure 5.7 Observed versus predicted MF10 values, calculated using the linear regression presented in equation 3. Sites where traffic intensity was below 1000 vehicles day⁻¹ have been excluded from the calculations.

The validation of the method (performed with the leave-one-out method due to the low number of samples) gave also encouraging results, with an RPE value of 22% and a cross-validated coefficient of determination (Q^2) of 0.65, that indicate a good fit of the data. To have a better idea of the fit maintaining the original data scale, the cross-validated standard error (SECV) was 0.52 mg m⁻². Converted as an error on emission factors, it corresponds to 7 mg VKT⁻¹, a very encouraging result on maxima emission potentials, as we started from mostly non-parametrized or city-averaged inventories.

Our model can be therefore used for predicting road dust loadings for multiple objectives: bottom-up emission inventory, road maintenance for air quality management and air quality measures in general.

5.4 Conclusions

In this study, we explored the influence of road characteristics such as pavement macro-texture, traffic intensity and distance to braking zones on real-world road dust loading that can be mobilized and resuspended (i.e. emission factor) in two contrasting environments such as the cities of Turin and Barcelona. Our results showed good inverse relationship between MF10 and i) macro-texture, ii) traffic intensity and iii) distance from braking zone, although with a lower correlation. These results allowed building an empirical mode, able to predict suspendable road dust and emission factors based on the aforementioned road data. This model can

significantly improve bottom-up emission inventory for spatial allocation of emissions and air quality management to select those roads with higher emissions for mitigation measures. We also found a clear seasonal effect of road dust emissions, with higher emission in summer likely due to the lower pavement moisture, indicating that our model could be used only for predicting spatial variability of maxima emissions, which then need to be scaled for meteorological effect, using methods accounting for weather and pavement moisture.

5.5 Acknowledgements

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6. Physico-chemical characterization of playground sand dust, inhalable and bioaccessible fractions

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Abstract

Dust is a mixture of natural and anthropogenic particles originated from multiple sources, which can represent an hazard for human health. Playgrounds are a site of particularly concern, due to sand dust ingestion by toddlers and inhalation. In this study, 37 sands used in public playgrounds in the city of Barcelona were physico-chemically characterized also in relation to routine maintenance activities such as disinfection and sand renewal. The analyzed sands show a felsic mineralogy dominated by Na-feldspar, quartz, and, to a lesser extent, K-feldspar, with minor amounts of clay minerals, carbonates and hematite. Particle fractions below 10, 2.5 and 1 μm represent, on average, 0.65%, 0.17% and 0.07% of bulk volume, respectively, although, due to the human grinding, these initial fractions increased every year by a 18%, 5% and 2% respectively. Disinfection of sands effectively reduced only the NH_4^+ concentration, among inorganic species. The average metal content was anthropogenically enriched, with respect to the upper continental crust,

only for Sb and As. Both elements show high spatial variation indicating local sources such as road traffic for Sb (contributing mostly to the total concentration), and industry for As (also contributing with highly bioaccessible Sb, Cu and Zn). A clear inverse relationship between total concentrations of some elements and their leachable (Sb) and bioaccessible (Sb and Cr) fractions is observed. The most bioaccessible elements were Ca>Ni>Cu>Sr>Cd>Pb, all above the 25% of the total concentration. Bioaccessibility was higher for the carbonate-bearing particles and for the anthropic emitted metals (>50% of Ba, Cu, K, Pb and Zn).

6.1 Introduction

Dust is a mixture of natural and anthropogenic particles originated from multiple sources, which can represent a hazardous pollutant for human health via inhalation, ingestion, and, to a lesser extent, dermal contact (Paustenbach, 2000). A particularly sensible population is children, due to their higher inhalation rate and to the unintentional or deliberate ingestion of significant quantities of dust through hand-to-mouth contact (Acosta et al., 2009; Banerjee, 2003; Calabrese et al., 1997; Ljung et al., 2007; Ruby and Lowney, 2012). Incidental ingestion provides the primary pathway for human exposure; Shi et al. (2011) calculated that ingestion contributed 97.5% and 81.7% to the total exposure doses of non-carcinogenic and carcinogenic elements for children, and 91.7% and 52.9% for adults. The average amount of soil/sand dust ingested by a children has been calculated in various studies between 39 and 271 mg day⁻¹, with a central estimate of 100 mg day⁻¹, representing the average dust intake for children within 1-6 years (U.S. EPA, 2011). In addition, particle inhalation has been found to cause increased risk for respiratory and cardio-vascular disease and to affect the neurodevelopment of children (Sunyer et al., 2015). In urban environment, children exposure to dust occurs mostly during playground activities, as most of playgrounds are unpaved and sand particles are continuously ground by playing activities.

Particle size distribution is relevant for inhalation and ingestion processes. Inhalation involves mostly particles below hundreds of microns, although 10 microns (thoracic fraction) is the most common cut-off size for defining hazardous atmospheric particulate matter (PM). Incidental ingestion requires soil particles that can adhere to human hands, being finer particles (generally <63 µm in diameter) the more efficient in this behavior (Choate et al., 2006; Yamamoto et al., 2006; Ruby and Lowney, 2012).

As stated by the last report of air quality in Europe (EEA, 2015), PM limit values are often exceeded in Europe, mostly due to road traffic, industrial and biomass burning emissions. In addition, power generation, soil dust and shipping are also significant sources of PM. In the Barcelona Metropolitan Area the PM10 daily limit

value was exceeded until 2013, due to the high concentrations observed at specific sites such as the Sants (in 2012) and El Prat de Llobregat (in 2013) monitoring sites. In both stations, the exceedances were mainly due to the high concentrations of the mineral component of PM, namely mineral dust, which consists of primary particles, generally coarser than 1 μm , and composed mainly by Al, Si, Ca, Fe, K and Ti, among other typical crustal species. Mineral dust can be emitted by multiple sources, including local soil resuspension, African dust outbreaks, construction works, and traffic-induced resuspension. Soil resuspension can increase considerably PM10 levels also in school environment with sandy playgrounds (Amato et al., 2014c).

Concerning the ingestion pathway, only a part of the ingested particles can be adsorbed and reach the systemic circulation (i.e. the bioavailable fraction), and the oral bioaccessibility is defined as the fraction that is soluble in the gastrointestinal environment and available for absorption (Ruby et al., 1999). Therefore, in vitro tests of bioaccessibility are useful tools to predict the relative bioavailability, improving the accuracy of risk assessments in a cost-effective manner. In last years, bioaccessibility tests for soils have been developed and validated through comparison to the results of in vivo tests for specific metals (Oomen et al., 2002; Zia et al., 2011).

In this study we investigated the physico-chemical properties of sand dust in 37 public playgrounds in the city of Barcelona in relation to the risk for inhalation and ingestion for children, with the aim of: i) understanding the impact of sand use (two years period) on particle size distribution and metal contents; ii) understanding the impact of the regular maintenance activities (sand replacement and disinfection); iii) quantify the oral bioaccessibility of metals and their main sources.

6.2 Material and methods

6.2.1. Sampling and analytical treatment

Thirty-seven parks within the city of Barcelona (NE, Spain) were selected and sampled on 11-12 December 2014 based on the:

- Time past from the last sand replacement (samples labelled as 01R to 12R). Replacement is performed with a 2-years frequency by the City Council. This selection allowed evaluating the impact of sand aging/grinding from December 2012 to October 2014. In order to minimize possible confounders due to disinfection and spatial variability, the selected playgrounds of this first batch were disinfected nearly at the same time and were located within the same district.
- Time past from the last disinfection (consisting in a cleaning of the top 10 cm layer with water at 90°C) (samples labelled as 01D to 08D). Disinfection is

performed with 2-months frequency by the City Council. The selected playgrounds were disinfected from 6th October to 29th November 2014 and, in order to minimize possible confounders due to renewal and spatial variability, the selected parks of this second batch had similar time past from the last renewal and were located as close as possible.

– Location. Playgrounds located across the municipal terrain, with sand replaced at the same time (February 2014). Samples labelled as 01E to 13E.

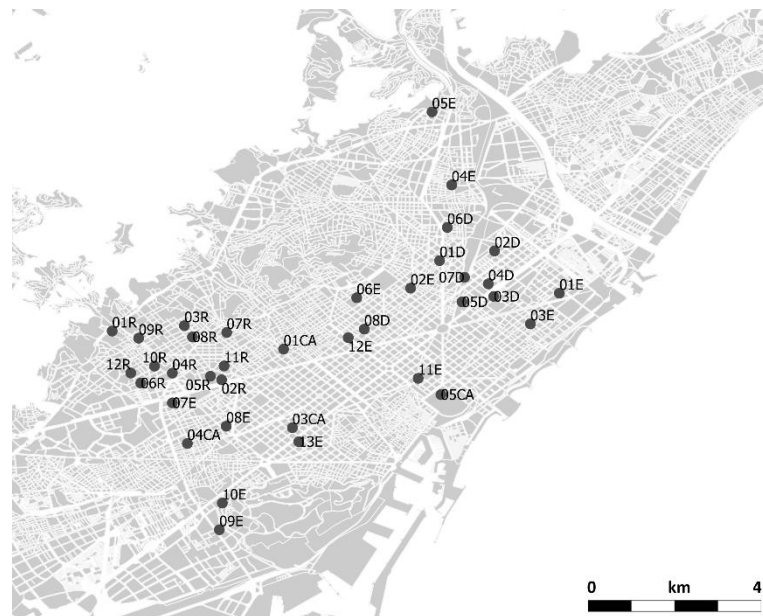


Figure 6.1 Map of playgrounds sampled across the city of Barcelona.

The sand sampling was performed within the top layer at 37 playgrounds using a PVC ring (5 cm height and 10 cm diameter), at two points of the playground (U.S. EPA, 1992) not covered by the treetops, not at the edge of the playground or near to vegetation or urban furniture and visibly dry. Each of the two subsamples allowed the collection of 393 cm³ of sand. In addition, one unexposed sand sample, not previously used for other purposes (blank), was collected from the stock of the provider in charge of the sand replacement. Once collected in a plastic bottle, samples were brought to the laboratory. Collected subsamples were mixed, homogenized and quartered to the final mass needed for laboratory analysis (Fernández, 2006; VMGA, 2014). Sand humidity and porosity were calculated gravimetrically, after drying the samples during 24h in a heater at 60°C and adding Milli-Q water until saturation (Asensio et al., 2012). For each sample, 200 g of sand

were then dried in plastic Petrie dishes in the stove at 60°C during 24h, and sieved at 63 µm by means of a mechanic sieve during 15 minutes.

Once sieved, the (<63 µm) sample was divided into several fractions for different laboratory analyses:

- 5 g were leached in Milli-Q water for the determination of water soluble ions. To determine the leaching potential of major and trace elements, we applied the European Standard leaching test EN-12457 (according to Council decision 2003/33/EC), using a ratio liquid/solid (Milli Q water/sample) of 10:1 under shaking for 24h. Then, the leachate was filtered using a syringe (BRAUN Injekt 10ml) and a 0.45µm PVDF Whatman filter and the liquid part was analyzed: selective electrode for NH₄⁺, High Performance Liquid Chromatography (HPLC Waters 1525) (for Cl⁻, NO₃⁻, and SO₄²⁻), Inductively Coupled Plasma- Mass Spectrometry (ICP-MS, Thermo Fischer Scientific X-Series II), for trace elements) and Atomic Emission Spectrometry (ICP-AES, Thermo Fischer Scientific iCAP 6500 Radial) for major elements. The samples sent to both ICPs were acidified to 2% HNO₃. Besides that, the pH and ionic conductivity were determined by means of Thermo Scientific pHmeter and Ultrameter MyronL respectively.

- 150 mg were used for the grain size analysis, by means of a Malvern Mastersizer 2000 with Hydro 2000G. The sample was dispersed in Milli Q water and analyzed between 0.01 and 2000 µm. From the spectrometric pattern acquired, the particle size distribution is calculated using the model of Mie's scattering theory.

- 1.5 g of each sample were milled for: 1 g for X-Ray Diffraction (XRD), 0.1 g for acid digestion and 0.1 g to determine Total Carbon (TC) by means of an elemental LECO analyzer.

The powder XRD data were collected by a Bruker D8 A25 Advance X-ray diffractometer θ - θ , with CuK α 1 radiation, Bragg-Brentano geometry and a lineal LynxEyeXE detector. The XRD spectra were obtained from 4° to 60° of 2-Theta with a step of 0.015° and a counting time of 0.1s and the sample rotation. The quantitative analyses on 9 samples were instead performed from 4° to 120° of 2-Theta with a step of 0.015° and a counting time of 0.5s and the sample in rotation. The crystalline phase identification was carried out by standard Joint Committee on Powder Diffraction Standards (JCPDS) file by the computer program "EVA" (Bruker).

For elemental composition, the samples (<63µm) were acid-digested adapting a protocol used for PM samples (Querol et al., 2001), using 5 ml HF, 2.5 ml HNO₃ and 2.5 ml HClO₄. For quality assurance, reference materials were also digested to determine the accuracy of the analytical and digestion methods: SRM 1633b (Trace Elements in Coal Fly Ash) and CANMET SO-2 and SO-4.

A widely used and tested method was used to assess the oral bioaccessibility: the Simple Bioaccessibility Extraction Method (SBET), consisting in an extraction with glycine at a buffered pH miming the conditions on the gastrointestinal tract of children (Drexler and Brattin, 2007; Oomen et al., 2002). Oral bioaccessible (SBET method) contents were determined mixing 0.25 g with 25 ml of extractant, a glycine 0.4 M solution with pH adjusted to 1.5 with concentrated HCl. Samples have been horizontally shaken at 37°C and 140 rpm for 1 h (Ruby et al., 1999; U.S. EPA, 2013). The mixture was then centrifuged at 3000 rpm for 10 min and the supernatant filtered through 0.45µm PVDF (Whatman) filters prior to analysis. The extract was analyzed for trace and major elements as above described, except for P, S, As and V, not analyzed as the first two were present as impurities in the extracting solution and the last were highly interfered from the chloride.

6.2.3 Source apportionment of metals

Source apportionment techniques are used to apportion pollutants mass contributions to different source/factors which are able to explain most of the variance of observed pollutants concentrations. Source apportionment studies are generally performed by receptor models that are based on the mass conservation principle:

$$x_{ij} = \sum_{k=1}^p g_{ik} f_{jk} + e_{ij} \quad (1)$$

Where x_{ij} is the i th concentration of the species j , g_{ik} is the i th contribution of the source k and f_{jk} is the concentration of the species j in source k , while e_{ij} are the residuals. Equation (1) can be also expressed in matrix form as $X=GFT$. If f_{jk} are known for all the sources then the Chemical Mass Balance (CMB) can be applied (Watson et al., 1984). For this model, the experimental profiles of all major sources are needed. When both g_{ik} and f_{jk} are unknown, factor analysis (FA) techniques such as Principal Components Analysis (PCA) (Henry and Hidy, 1979; Thurston and Spengler, 1985) and Positive Matrix Factorization (PMF) (Paatero and Tapper, 1994) are used for solving (1).

PMF solves equation (1) minimizing the object function Q :

$$Q = \sum_{i=1}^n \sum_{j=1}^m (e_{ij} / s_{ij})^2 \quad (2)$$

where s_{ij} are the individual data uncertainties. For all elements with concentrations above the detection limit the uncertainty was expressed as 10% of the element concentration plus one third of the detection limit. For elements with concentration

below or equal to the detection limit, uncertainty was expressed as 0.83 times the detection limit. The PMF was applied using U.S. EPA's PMF software, Version 5.0 (Norris et al., 2014). A total (dependent) variable was set as a constant value (106 mg/kg) for all samples. The input data matrix contained the 33 most significant elements/components concentrations, based on their signal-to-noise ratio (Paatero and Hopke, 2003), the percentage of data above the detection limit and importance in tracing specific sources. The distribution of residuals, G-space plots, Fpeak values and Q values were explored for solutions with number of factors varying between 3 and 7.

The PMF method was also applied to the bioaccessible fraction of metals ($\mu\text{g/g}$) as independent variables, setting the sum of analyzed species as total variable. The input data contained the 18 most significant analyzed elements (excluding ions, As, P, S and V due to the extraction matrix and Ce, La, Li, Mo, Rb, Se, Sn, Ti and Zr, with high percentage of values below detection limit).

6.3 Results and discussion

6.3.1 Physico-chemical characteristics

The chemical characterization of sand samples (fraction below 63 μm) of playgrounds in the city of Barcelona is reported in Table 6.1, and shows a main aluminum-silicate composition (Al_2O_3 represents within 5.2-17.9 % of mass) followed by Ca-Mg carbonates ($\text{CaO} + \text{MgO}$ sums within 0.5-10.1 % of mass). Significant fractions of mass consist also of total carbon (TC), Fe_2O_3 , K_2O , Na_2O and P_2O_5 ($1.1\pm 0.9\%$, $4.0\pm 0.9\%$, $5.2\pm 1.1\%$, $4.0\pm 1.0\%$, $0.21\pm 0.15\%$, respectively). The sum of SO_4^{2-} , NO_3^- , NH_4^+ and Cl^- represents only 0.003-0.3% of the mass, while trace elements sum 0.2-1.0% of the mass. The most abundant trace elements are Ti, Mn, Ba, Zr, Zn, Rb, and Sr, with mean concentrations of 3130, 894, 562, 369, 166, 158, and 80 $\mu\text{g/g}$, respectively.

Table 6.1 Total concentrations ($\mu\text{g/g}$), bioaccessible fraction (%) and leachable fraction (%) of the analyzed metals. na: not analyzed

Element	Mean Total concentration ($\mu\text{g/g}$)	Mean bioaccessible fraction (%)	Mean leachable fraction (%)
Al	75571	1	<0.1
As	12	Na	0.2
Ba	561	8	<0.1
Ca	15954	64	2
Cd	0.97	30	0.2
Co	3.7	21	0.1
Cr	19	20	<0.1
Cu	26	36	0.2
Fe	27852	1	<0.1
K	37670	1	<0.1
La	57	8	<0.1
Li	27	2	0.4
Mg	4496	17	0.6
Mn	887	24	0.1
Mo	1.4	4	6
Na	26846	1	<0.1
Ni	9.3	44	<0.1
P	0.05	Na	1
Pb	62	27	<0.1
Rb	158	<1	<0.1
S	93	na	7
Sb	2.2	14	3
Se	1.1	41	0.3
Sn	18	< 0.1	<0.1
Sr	81	28	1
Ti	3147	0.5	<0.1
U	10	4	<0.1
V	40	na	<0.1
W	14	22	2
Zn	166	16	<0.1
Zr	361	<0.1	<0.1

We calculated the Enrichment Factors (EFs) for all elements, normalizing the concentration of the element with the concentration of Al in the average Earth upper-crust (Taylor and McLennan, 1995). Mean values for samples are reported

in Figure 6.2 together with values for the unexposed sand sample (blank). The majority of the elements appear not to be significantly enriched in sands, averaging all samples, while only As, Cd and Sb showed EFs around 10 (9, 10 and 12, respectively). With respect to the unexposed sample, however, only As and Sb showed enrichment, which is noteworthy considering the little time of exposure of sand to the atmospheric metals deposition. The sand particle grain size (% in volume) shows a typically coarse size distribution being the inhalable fraction (below 63 μm) 3.72% on average. The presence of clay minerals and mica is likely responsible for the significant fraction of particles below 2 μm . The thoracic fraction (<10 μm) accounted typically for 0.65% of bulk volume (or mass, assuming constant particle density), while the fraction below 2.5 and 1 μm are in average 0.17% and 0.07%, respectively.

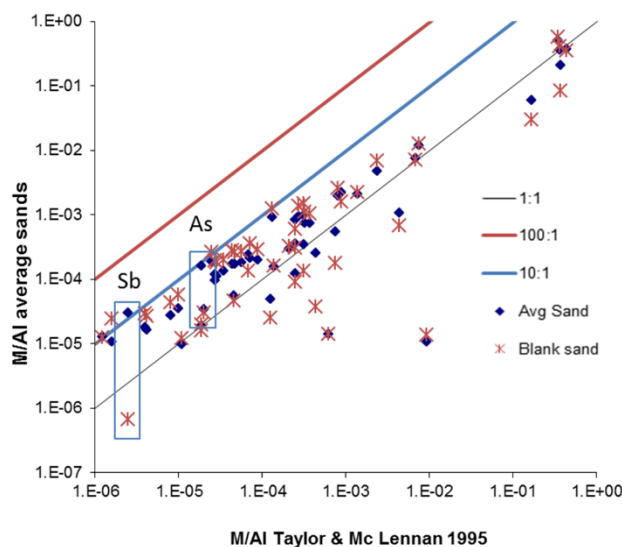


Figure 6.2 Average Enrichment Factors for the elements in sand samples collected in Barcelona and for one unexposed (blank) sand with respect to Earth crust average composition (Taylor and Mc Lennan, 1995).

6.3.2 Mineralogy

The XRD results (Table 6.2) show a felsic mineralogy dominated by Na-feldspar, quartz, and, to a lesser extent, K-feldspar, with minor amounts of clay minerals (illite>chlorite), carbonates (mostly calcite) and traces of hematite. According to the quantitative estimate of relative amounts on 9 samples (batch D: samples with same time of use and the unexposed sample), Na-feldspar is the most common mineral present (27-48%), followed by K-feldspar (13-23%) and quartz (9-23%).

Illite and chlorite amounts range within 11-27% and 6-11% respectively. In addition, dolomite and calcite were also detected although not in all the samples and up to 6% and 4% of total mass, while hematite was only in trace content. The source for these feldspathic sandstones is likely to be mainly from weathered granites (possibly with some influence from metamorphic materials). Much of the illite could derive from altered muscovite mica, the chlorite and hematite from altered biotite mica, and the calcite from the minor amount of calcium present in Na-feldspar.

Table 6.2 XRD Quantitative analysis of batch D samples (results as % of weight).

	1D	2D	3D	4D	5D	6D	7D	8D	unexposed
Quartz	17	20	11	23	10	9	18	17	10
Na-Feldspar	37	37	39	34	40	48	27	43	46
Dolomite	5	2	3	2			6		
Calcite	4	3	1	2	3		3		
Illite	11	12	13	15	14	12	27	13	14
K-Feldspar	20	19	23	18	22	21	13	20	22
Chlorite	6	7	10	6	11	10	6	7	8

With regard to the geology surrounding Barcelona, there is more exposure of the Palaeozoic granitoid basement around the River Besos valley than the Llobregat (although there is granodiorite exposed at least as far SW as the hill of Sant Pere Martir, and this may have fed granitic material into the Llobregat at least since Plio-Pleistocene times). The thick Pleistocene sediments flanking the Collserola hills generally contain much weathered granitic detritus. The abundance of feldspar makes these sandstones sedimentologically immature, so it is likely that they are sourced from mostly local materials deposited fluvially.

The mineralogy affects particle size distribution as when the percentage of quartz increases, the fraction (in volume) of soil particles below 10 microns decreases ($R^2 = 0.56$), due to the coarser size distribution of quartz particles (the same was expected for the fractions below 2.5 and 1 microns, but the trend was not so clear). The potential impact on emissions due to resuspension is therefore lower for quartz-rich sands, rather than for typical fluvial sands, enriched in feldspars and fine clay minerals.

6.3.3 Effects of maintenance activities

One of the main goals of the study was to evaluate the impact of sand use (i.e. time past from the last sand replacement) on the physico-chemical characteristics. Regarding the particle size distribution, it can be observed a general increasing proportion of respirable fractions with the time of use. Sands become therefore finer over time, by an average rate of 17.7%, 4.7% and 2.0%, for the fractions <10 μm , <2.5 μm and <1 μm respectively, per year.

Figure 6.3 shows the full size distribution of particle volume for three samples collected after 6, 14 and 21 months of use, respectively. It can be clearly observed the increase in fraction below 20 μm (from the “youngest” (less used sand: 20%) to the “oldest” sample (more used sand: 49%)) in terms of their use in public playgrounds.

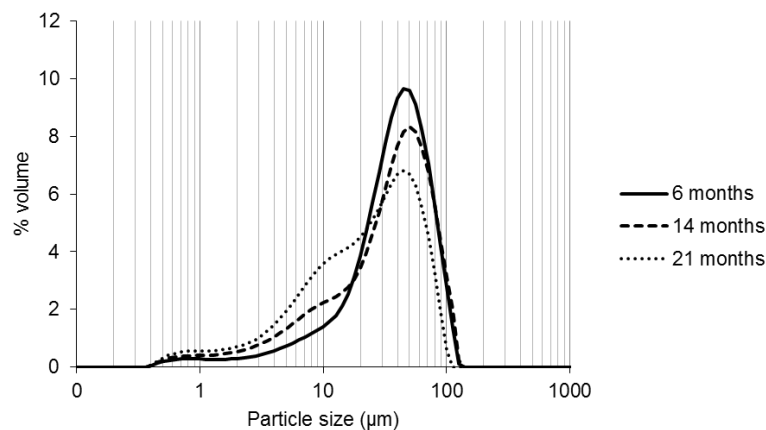


Figure 6.3 Size distribution of particle volume in sand samples collected after 6, 14 and 21 months of use.

Concerning the metal content, results show no clear impact of time of use on the buildup of metals, probably due to the relatively little time of exposure (<2 years). Unexpectedly, some metals such as Cr, Ni and Pb show higher concentrations in sands newly replaced, suggesting a relevant contribution from bedrock materials such as carbonates (Cr and Ni, see paragraph 6.3.5) and feldspars (Pb, see paragraph 6.3.5). Similarly, neither TC nor soluble compounds showed higher concentrations in the “oldest” samples.

Regarding the treatment of disinfection that is carried out every 2 months in the playgrounds, it can be observed that the effect on the inorganic fraction of sand is limited to a decreasing trend on the concentration of NH_4^+ (Figure 6.4). The NH_4^+ concentration seems to increase exponentially with time after the last disinfection

($R^2=0.58$), probably due to the atmospheric deposition of ammonium salts. No clear effect on other soluble components, such as SO_4^{2-} , NO_3^- or Cl^- was found. Neither metals seem to have been affected by this treatment, due to their low solubility in water (<6%). No effect on particle size distribution was found.

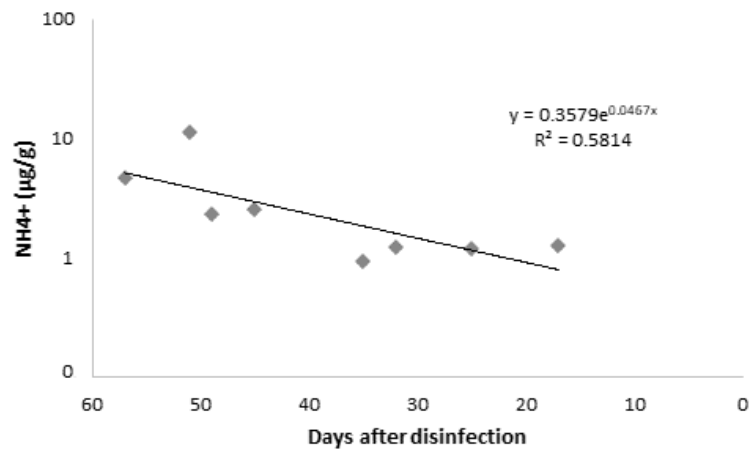


Figure 6.4 Relationship between the days after disinfection and ammonium content.

6.3.4 Spatial variability

Enrichment factors were explored in the spatial domain of the city. Cadmium, as shown earlier, was enriched by a factor of 9 with respect to the Earth crust, but not enriched with respect to the local unexposed sand. The range of enrichment variability was low across the city (Figure 6.5), showing a maximum EF of 1.6 (with respect to the unexposed sand). Conversely As showed a clearer spatial pattern in the anthropogenic signature across the city, displaying maxima enrichments towards the coastal part of the city, although no clear association to specific sources can be drawn. Antimony, mainly emitted from non-exhaust sources (Schauer et al., 2006), showed also little variation across the city, however no correlation was found between metals concentrations and time of exposure or traffic density.

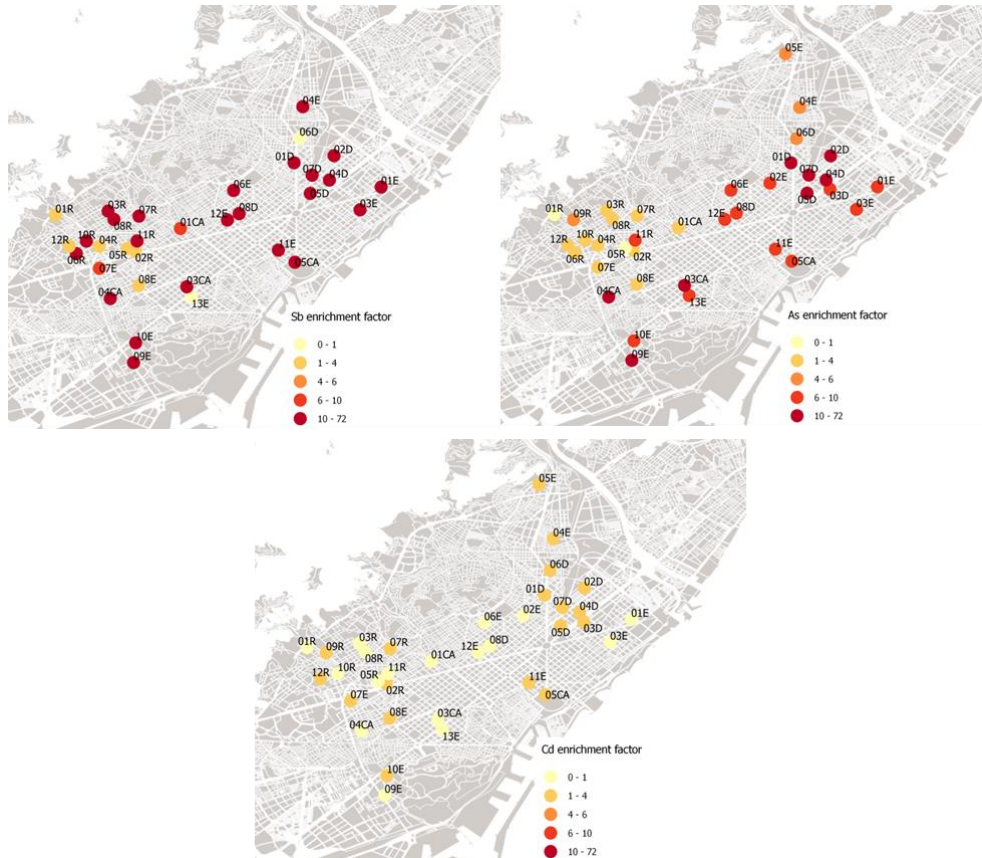


Figure 6.5 Maps of Enrichment factors calculated for Sb, As and Cd with respect to the unexposed sand.

Spatial Distribution analysis revealed also higher levels of NO_3^- and NH_4^+ in parks located in the NE part of the city (Figure 6.6), next to a methane-fueled power plant, although this part of the city, which is at the lowest altitude and a shallow top layer of the phreatic zone, can be also influenced by leaking from sewage system.

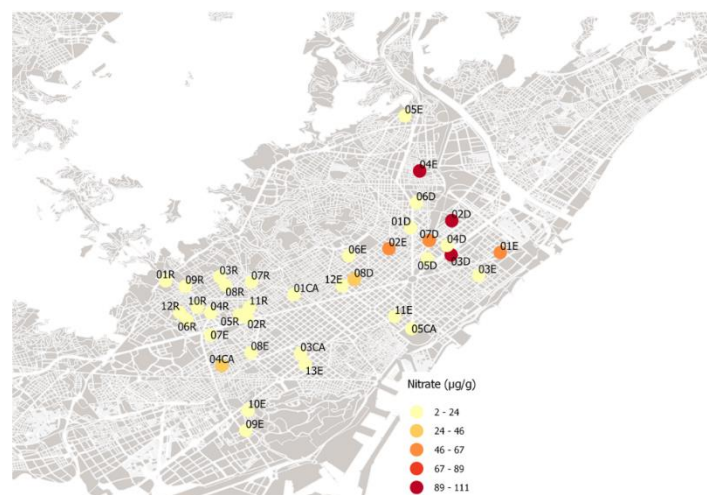


Figure 6.6 Spatial distribution of nitrate concentration in sands.

6.3.5 Source apportionment of metals

The PMF solution for total metal concentrations (<63 µm) revealed four factors/sources, namely Anthropogenic, Al-Silicates, Salts and Carbonates (Figure 6.7). These sources contributed, in average, 4.3%, 57.6%, 10.6% and 27.5% to the sand material below 63 µm.

The Anthropogenic source was identified from the high share of Sb, As, Cu explained by this source. Sb and Cu are commonly used as brake wear tracers (Schauer et al., 2006), but can also be emitted by metallurgical industry (Amato et al., 2009), as for As. The chemical profile of this factor is dominated by Fe₂O₃, C, S, Al₂O₃ and CaO. It is also noteworthy the significant share of Sn, Cr, Pb and Mn explained by this source.

The Al-Silicates source is the main responsible for the total composition, explaining most of the variation of Al₂O₃, Na₂O, K₂O, Fe₂O₃, Rb, Ti and Mn, which are related to clay minerals (illite, and chlorite) and feldspars (microcline and albite). This factor also shows the majority of Zr, Sn and Pb, which all have affinity to aluminum silicates.

The third factor, labelled as Salts, explained most of Cl⁻ and NO₃⁻ variation, and (to a lesser extent) NH₄⁺, suggesting the presence of ammonium salts and sea salt from atmospheric deposition.

The fourth factor is clearly related to carbonates, showing high loading of CaO, MgO, C, but also Sr, Ba and Ni, which are quite common in calcite and dolomite. The presence of S and Ba may indicate also the presence of barite.

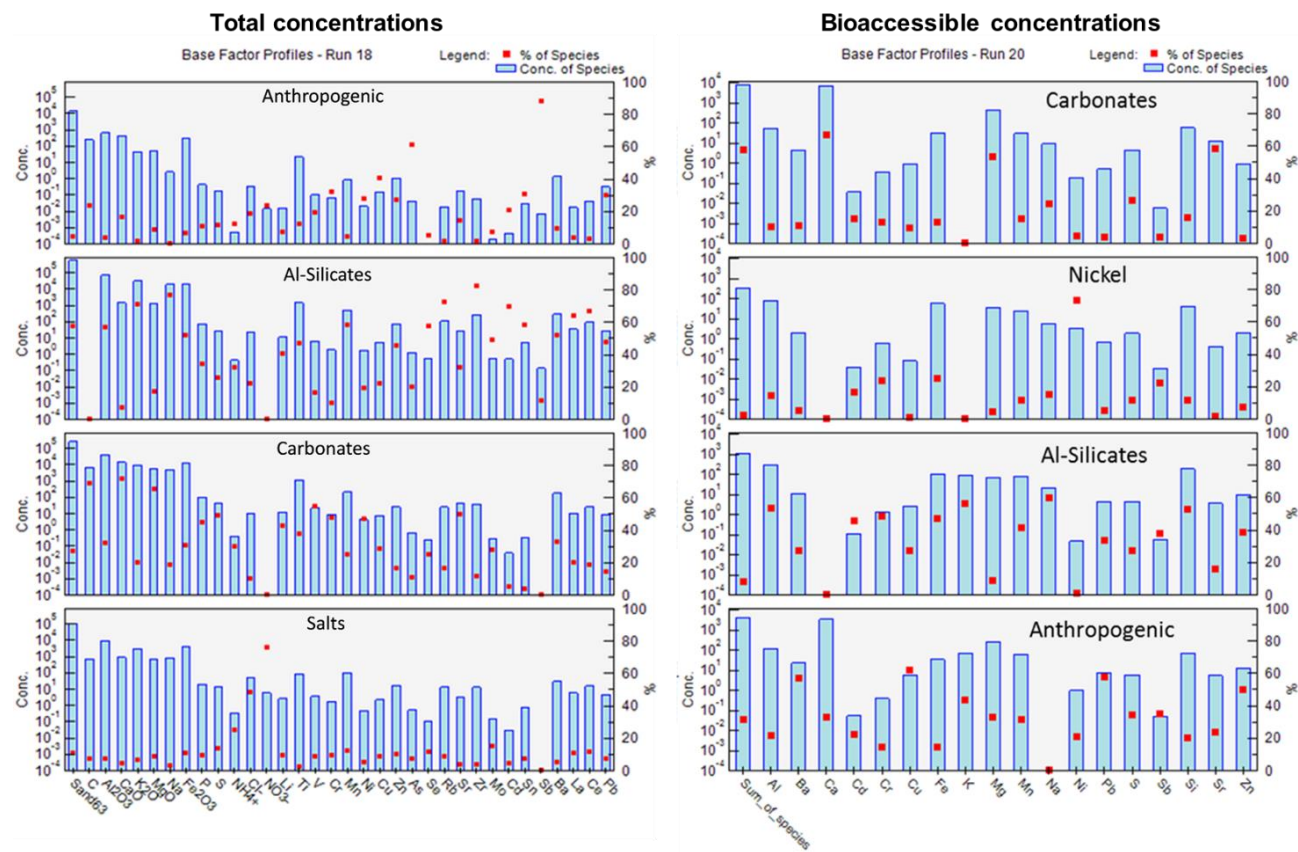


Figure 6.7 PMF factor profiles for total (left) and bioaccessible (right) concentrations. Blue bars indicate average absolute species concentration (mg/kg, left axis), red dots indicate % of specie due to each source.

According to PMF results, more than 50% of S, Cu, Sb, and As in sands are originated from anthropogenic sources, although only As and Sb show high enrichment factors with respect to the average composition of Earth crust and the unexposed sand. In spite of the clear anthropogenic contribution (related, probably, mainly to traffic and industry), no correlation was found between the anthropogenic factor and the traffic density (vehicles m⁻², data provided from the Catalan Government), suggesting that the most relevant traffic contribution is from background rather than from street-level emissions.

6.3.6 Leachable and bioaccessible fractions

The pH of the leachates of the playground sands are slightly alkaline, with values ranging from 7.1 to 7.9. Mean leachable fraction of each element is listed in Table 6.1. The most soluble elements were S, Mo, Sb, Ca, and Sr, although their soluble fraction does not exceed 7%, 6%, 3%, 2% and 1%, respectively. Therefore, the solubility is not related to specific sources, as S and Mo are mostly explained from the Al-Silicates factor, Sb from the Anthropogenic and Ca and Sr from the Carbonates factor.

In several elements (i.e. Sb, Ca, Cd, Zn, Cr, Zr, Ni, Sr and Mg) it has been observed that the higher the total concentration of the element (µg/g), the lower the leachable fraction (%), which might suggest a different speciation and solubility of the metals emitted by the different sources. Antimony, for example (Figure 6.8), was found to be mostly anthropogenic (as shown by PMF results), showing a higher solubility at lower concentrations, especially in the SW part of the city, which suggests a more industrial (with high temperature process and finer size distribution) origin of the bioaccessible fraction.

Bioaccessibility extraction test is used to determine the metal fraction that would dissolve in the gastric environment and become available for absorption. Results for all analyzed elements are reported in Table 6.1 as percentage of the total content.

Average values of bioaccessibility varies from 0.002% of Zr to 64% of Ca, but some of the most harmful metals, such as Ni, Cu, Cd, Pb and Sb, were also among the most bioaccessible (from 14% to 41%), including Se. The leachable fraction of Sb and Cr showed lower bioaccessible percentages in samples with higher concentrations (Figure 6.8). As for total concentration, the relationship between the bioaccessible fraction with disinfection and time of use was explored but no significant relationships were seen.

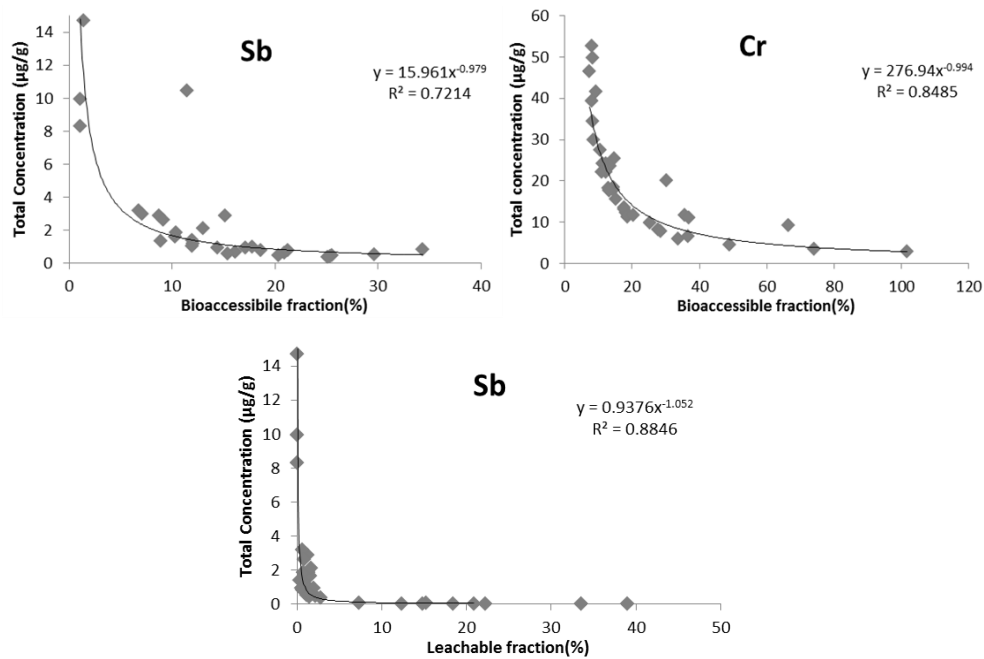


Figure 6.8 Relationship between total concentrations of Sb and Cr and their bioaccessible fractions (%) and between total concentration of Sb ($\mu\text{g/g}$) and its leachable fraction (%).

Spatial distribution of the bioaccessible contents was explored across the city. Cadmium, which showed the higher variability range for bioaccessibility, did not show a clear spatial pattern, coherently with the relatively low anthropogenic contribution. Antimony showed a higher bioaccessibility in the SW region of the city (Figure 6.9, although this does not exceed 35%, where also the lowest concentrations were found. Therefore road traffic, responsible for most (80%) of the Sb, produces probably less bioaccessible Sb than industrial processes. This is in agreement with studies indicating that natural and mechanical wear contribution is less bioaccessible than high temperature emission processes (Ljung et al., 2007; Madrid et al., 2008; Wang et al., 2015). In fact, no relationship was found between traffic density and bioaccessible relative (or absolute) concentrations of metals. Similarly to Sb, higher bioaccessibility in the SW of the city was found for Cu and Zn, which are emitted from both traffic and industrial combustion sources (Amato et al., 2009; Minguillón et al., 2012) but a higher bioaccessibility for the industrial emitted particles can be deduced (Wang et al., 2015).

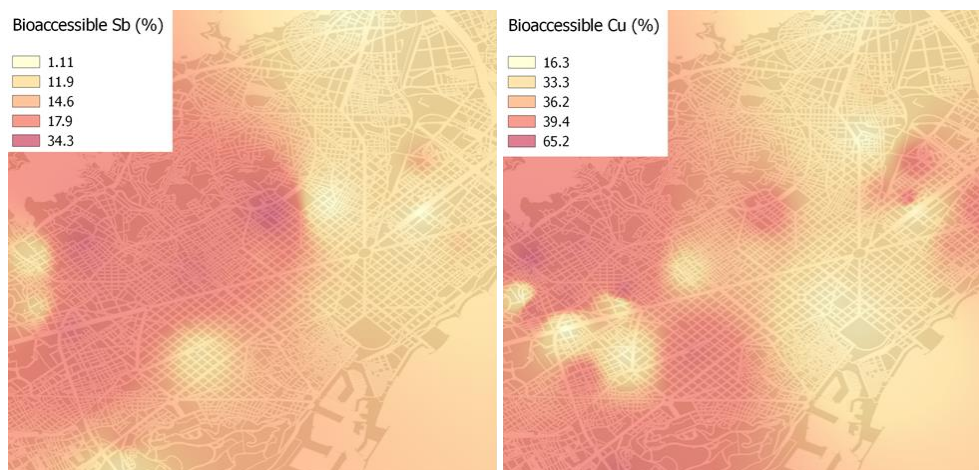


Figure 6.9 Spatial interpolation of the bioaccessible fraction (%) of Sb and Cu across the city of Barcelona.

The PMF analysis applied to the bioaccessible metal concentrations (Figure 6.7) revealed four factors, similarly to the solution found for the total metal concentration. The similar sources identified were Carbonates, Anthropogenic and Al-Silicates, while a Nickel factor (contributing very little to the sum of species) was found instead of the Salts factor. Relative contribution to the sum of bioaccessible species was, on average, 58%, 32%, 8% and 2%, respectively. These results are coherent with the first PMF if we consider that the Salts factor could not be resolved, as in the SBET solution ions were not analyzed. Factor profiles are reported in Figure 6.7, while in Figure 6.10 the contribution of each factor to the total concentration.

According to PMF results, bioaccessible Sr, Mg, Cd and Ca are mainly explained by the Carbonates factors and, as expected, are among the most available; as carbonates dissolve at gastric pH, while elements explained mostly from the Al-Silicates factor are the least bioavailable, in average. More in detail, after Ca, the most bioaccessible metal is Ni, associated mostly to the Nickel factor and to the Anthropogenic, and this value is higher than what found in literature (Ljung et al., 2007; Padoan et al., 2017). Elements mainly explained by the Anthropogenic factor, as Cu and Sb, have a bioaccessible fraction of 36% and 14%, respectively, and also some Al-Silicates bearing metals, like Cd, Pb and Zn, have significant bioaccessible fraction. The mass of the Anthropogenic factor is dominated by Ca, Mg and Al, and it explains most of the variation of Ba, Cu, K, Pb and Zn.

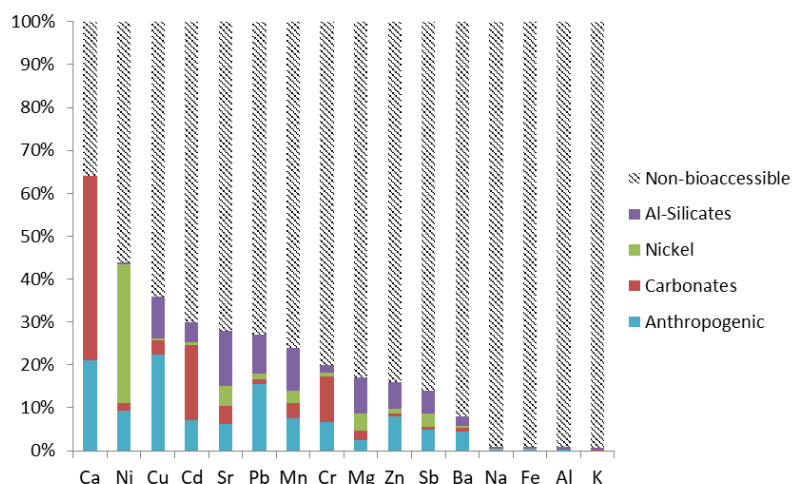


Figure 6.10 Share of bioaccessible metals explained from each factor, as fraction of the total concentration.

Comparing PMF results for bioaccessible and total metal concentrations, the variation of metals explained by the different factors is generally similar except for Ba and K, whose bioaccessible fraction derives more from the Anthropogenic factor rather than geogenic (as for the total concentration), indicating that the anthropic input for these metals is more bioaccessible than the natural one, which dominates the total concentration, and Cr, shifting from the Carbonates to Al-silicates factor. Also Cu and Zn have a clearer anthropic signature in the bioaccessible fraction, rather than the total concentration, which helps identifying spatial patterns (see Figure 6.9 for Cu). The Ni-factor also shows significant contributions of Fe and Cr, pointing to steel particles. However, the identification of this factor is not definitively clear.

6.4 Conclusions

Thirty-seven sands used in public playgrounds in the city of Barcelona were physico-chemically characterized in order to improve our understanding of their potential impact on risks due to dust ingestion by toddlers and inhalation. Routine maintenance activities were controlled, such as disinfection and sand replacement. The analyzed sands show a felsic mineralogy dominated by Na-feldspar, quartz, and, to a lesser extent, K-feldspar, with minor amounts of clay minerals (illite > chlorite), carbonates (mostly calcite) and traces of hematite. The particle size analysis shows a typically coarse distribution, although clay minerals are responsible for the significant fraction of particles below 2.5 μm . The fractions below 10, 2.5 and 1 μm represent, on average, 0.65%, 0.17% and 0.07% of the bulk

volume, respectively, although due to the human grinding through playing, these initial fractions increase every year by a 18%, 5% and 2% respectively, confirming the environmental concern for air quality due to dust resuspension, which may cause local exceedances of PM10 European limit standards. Bimonthly disinfection of sands was found to reduce significantly only the NH_4^+ concentration. The average metal content was anthropogenically enriched with respect to the upper continental crust, only for Sb (EF=12) and As (EF=10), while the enrichment of Cd (EF=9) may be linked to the local geology. Both Sb and As show high spatial variation, attributed to the anthropogenic source in PMF, although no clear separation can be done between industrial and road traffic contributions. The spatial distribution suggests background road traffic and industry as main sources of Sb (as no correlation was found with street level traffic density) and, less clearly, harbor and industry as main sources of As. A clear inverse relationship between total concentrations of some elements and their leachable (Sb) or bioaccessible (mostly Sb and Cr) fractions is observed. The most bioaccessible elements were $\text{Ca} > \text{Ni} > \text{Cu} > \text{Sr} > \text{Cd} > \text{Pb}$, all above the 25% of the total concentration. Bioaccessibility was higher for the carbonate-bearing particles and for the anthropic emitted metals, being more than 50% of the bioaccessible fraction of Ba, Cu, K, Pb and Zn originated from the anthropogenic source.

6.5 Acknowledgements

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7. General conclusions

The work investigated the relations between size fractions, bioaccessibility and the HM concentrations in urban matrices, such as soils, road dust and urban sands. Soil and road dust samples were collected in Turin and in Barcelona, and the results will help the comprehension of the sources of HM in the urban environment and the interactions between soil, road dust and atmosphere.

The observed total concentrations of HM in RD and roadside soils of Turin were higher than reported in previous studies and were above the legislative limits. Particles with sizes $<2.5 \mu\text{m}$ and between 2.5 and $10 \mu\text{m}$ were enriched in Fe, Mn, Cd, Cu, Pb and Zn, while not in Cr and Ni, compared to the bulk samples, and the spatial variation was more pronounced for elements mostly emitted by traffic sources (Cu, Sb, Pb and Zn). In RD samples, the analysis of fractions identified two different sources for Zn, likely industrial for $<2.5 \mu\text{m}$ particles and tire wear for the 2.5 - $10 \mu\text{m}$ particles.

In the soil samples, the bioaccessibility of Fe, Mn, Cr and Ni increased in fine particles, likely due to their greater reactivity and the higher anthropic contribution with respect to coarser fractions, while Cu, Pb, Sb and Zn had almost constant bioaccessibility for all size fractions. In the RD samples, the bioaccessibility of fine particles was clearly greater than in soils for all metals. For Pb, Cu and Zn, the bioaccessible fraction reached the 90% of the total concentration in the $<2.5 \mu\text{m}$ fraction, which also showed the highest enrichment when compared to the earth's crust, so these results appear to be critical for the estimation of risk to human health in urban areas.

From the literature review on the impact of non-exhaust emissions on air quality, the road dust category was the most identified source. In PM_{2.5}, the road dust contribution is the highest (mean of 11% of PM_{2.5}) among non-exhaust ones (9% from brake wear and 2% from tire wear), but sensibly lower than vehicle exhaust (24%). Conversely, in PM₁₀ road dust had slightly higher contributions range (22% as mean) than vehicle exhaust (21%), and sensibly higher than brake wear (7%) and tire wear (4%). Thus, globally, road dust emissions are already at least as important as exhaust ones for PM₁₀.

For all sources, an increasing gradient of contribution (% of PM₁₀) from rural to traffic locations was observed, in spite of the limited number of observations for each land use. Regarding road dust, the largest increase step was found from sub-urban to urban locations. A climate-dependence was also found for road dust contribution: the lowest contributions of road dust relatively to exhaust emissions

were found in Oceanic sites, while the highest in Mediterranean and Tropical-Monsoon climates.

In the cities of Turin and Barcelona we explored the influence of road characteristics on the RD fraction that can be mobilized and resuspended (i.e. the emission factor). Our results showed good inverse relationship between RD and i) macro-texture, ii) traffic intensity and iii) distance from the braking zone. These results allowed building an empirical model able to predict resuspendable road dust and emission factors based on the aforementioned road data. This model can significantly improve bottom-up emission inventory for spatial allocation of emissions but also air quality management plans (helping prioritizing roads with higher emissions for the application of mitigation measures).

The characterization of the sands used in the public playgrounds of the city of Barcelona improved our understanding of their potential risk in case of ingestion by toddlers and inhalation. The analyzed sands showed a typically coarse size distribution, with fractions below 10, 2.5 and 1 μm representing a low percentage of the bulk volume (less than 1%). Yet we found that, due to the human grinding through playing, these initial fractions increase every year by an 18%, 5% and 2% respectively. Concerning the HM concentrations, only Sb (EF=12) and As (EF=10) resulted sensibly enriched with respect to the upper continental crust, while the enrichment of Cd (EF=9) may be linked to the local geology. Both Sb and As showed high spatial variation, attributed to anthropogenic sources from the PMF analysis. The spatial distribution suggests background road traffic and industry as the main sources of Sb and, although less clearly, harbor and industry as main sources of As. The most bioaccessible elements were $\text{Ca} > \text{Ni} > \text{Cu} > \text{Sr} > \text{Cd} > \text{Pb}$, all above the 25% of the total concentration. Bioaccessibility was higher for the carbonate-bearing particles and for the anthropic metals, being >50% of the bioaccessible fraction of Ba, Cu, K, Pb and Zn due to anthropogenic source.

Finally, the heavy metal(loid)s concentrations and the bioaccessibility were pointed out to be influenced strongly from the size of the particles, with fine particles of soil, road dust and sand resulting to be not only the most enriched in heavy metal(loid)s, but also the most bioaccessible. Thus, the bulk sample concentrations should not be considered as reliable indicator for the heavy metal(loid)s risk. Size fractionation appears to be an important need in studies aiming to elucidate risks in urban environments.

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9. References

- Aatmeeyata, Kaul, D.S., Sharma, M. (2009). Traffic generated non-exhaust particulate emissions from concrete pavement: A mass and particle size study for two-wheelers and small cars. *Atmospheric Environment*, 43(35), 5691-5697.
- Abu-Allaban, M., Gillies, J.A., Gertler, A.W., Clayton, R., Proffitt, D. (2003). Tailpipe, resuspended road dust, and brake-wear emission factors from on-road vehicles. *Atmospheric Environment*, 37 (37), 5283-5293. <http://doi.org/10.1016/j.atmosenv.2003.05.005>
- Achilleos, S., Wolfson, J.M., Ferguson, S.T. ... Koutrakis, P. (2016). Spatial variability of fine and coarse particle composition and sources in Cyprus. *Atmospheric Research*, 169, 255–270. doi:10.1016/j.atmosres.2015.10.005
- Acosta, J.A., Cano, A.F., Arocena, J.M., Debela, F., Martínez-Martínez, S. (2009). Distribution of metals in soil particle size fractions and its implication to risk assessment of playgrounds in Murcia City (Spain). *Geoderma*, 149, 101–109. Doi:10.1016/j.geoderma.2008.11.034.
- Acosta, J.A., Faz, Á., Kalbitz, K., Jansen, B., Martínez-Martínez, S., 2011. Heavy metal concentrations in particle size fractions from street dust of Murcia (Spain) as the basis for risk assessment. *J. Environ. Monit.* 13, 3087. doi:10.1039/c1em10364d
- Adaishi, K., Tainosho, Y. (2004). Characterization of heavy metal particles embedded in tire dust. *Environment International*, 30, 1009– 1017.
- Aimar, S.B., Mendez, M.J., Funk, R., Buschiazzo, D.E., 2012. Soil properties related to potential particulate matter emissions (PM10) of sandy soils. *Aeolian Res.* 3, 437–443. doi:10.1016/j.aeolia.2010.12.001
- AIRUSE LIFE 11 ENV/ES/584, PM10 trends in the AIRUSE cities, Action B1 (2015). http://airuse.eu/wp-content/uploads/2013/11/R03_AIRUSE-PM10-trends-in-AIRUSE-cities.pdf (accessed 12.12.2016)
- Ajmone Marsan, F., Biasioli, M., 2010. Trace Elements in Soils of Urban Areas. *Water. Air. Soil Pollut.* 213, 121–143. doi:10.1007/s11270-010-0372-6
- 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. doi:10.1016/j.envpol.2007.05.020
- Aldrin, M., Hobæk Haff, I., Rosland, P. (2008). The effect of salting with magnesium chloride on the concentration of particular matter in a road tunnel. *Atmos. Environ.*, 42, 1762–1776.
- Alloway B.J. (2013). Heavy metals in soils. Trace metals and metalloids in soils and their bioavailability. Springer, Reading, UK. <https://doi.org/10.1007/978-94-007-4470-7>
- Almeida, S.M., Pio, C.A., Freitas, M.C., Reis, M.A., Trancoso, M.A. (2005). Source apportionment of fine and coarse particulate matter in a sub-urban area at the Western European Coast. *Atmospheric Environment*, 39, 3127–3138.
- Amato, F., Pandolfi, M., Viana, M., Querol, X., Alastuey, A., and Moreno, T. (2009). Spatial and chemical patterns of PM10 in road dust deposited in urban environment. *Atmospheric Environment*, 43(9), 1650–1659. <https://doi.org/10.1016/j.atmosenv.2008.12.009>

- Amato, F., Pandolfi, M., Escrig, A., Querol, X., Alastuey, A., Pey, J., Perez, N., Hopke, P.K. (2009). Quantifying road dust resuspension in urban environment by Multilinear Engine: A comparison with PMF2. *Atmospheric Environment*, 43 (17), pp. 2770-2780. Doi: 10.1016/j.atmosenv.2009.02.039.
- Amato, F., Nava, S., Lucarelli, F., Querol, X., Alastuey, A., Baldasano, J., Pandolfi, M. (2010). A comprehensive assessment of PM emissions from paved roads: real-world emission factors and intense street cleaning trials. *Sci. Total Environ.*, 408, 4309-4318. <http://doi.org/10.1016/j.scitotenv.2010.06.008>
- Amato, F., Querol, X., Johansson, C., Nagl, C., Alastuey, A. (2010). A review on the effectiveness of street sweeping, washing and dust suppressants as urban PM control methods. *Sci. Total Environ.*, 408, 3070–3084.
- Amato, F., Pandolfi, M., Moreno, T., Furger, M., Pey, J., Alastuey, A., Bukowiecki, N., Prevot, A.S.H., Baltensperger, U., Querol, X. (2011). Sources and variability of inhalable road dust particles in three European cities. *Atmos. Environ.*, 45, 6777–6787. <https://doi.org/10.1016/j.atmosenv.2011.06.003>
- Amato, F., Schaap, M., Gon, H.A.C.D. van der, Pandolfi, M., Alastuey, A., Keuken, M., Querol, X. (2012). Effect of rain events on the mobility of road dust load in two Dutch and Spanish roads. *Atmos. Environ.*, 62, 352–358. <http://doi.org/10.1016/j.atmosenv.2012.08.042>
- Amato, F., Pandolfi, M., Alastuey, A., Lozano, A., Contreras González, J., Querol, X. (2013). Impact of traffic intensity and pavement aggregate size on road dust particles loading. *Atmos. Environ.*, 77, 711–717. <http://doi.org/10.1016/j.atmosenv.2013.05.020>
- Amato, F., Cassee, F. R., Denier van der Gon, H. A. C., Gehrig, R., Gustafsson, M., Hafner, W., ... Querol, X. (2014). Urban air quality: The challenge of traffic non-exhaust emissions. *Journal of Hazardous Materials*, 275, 31–36. <https://doi.org/10.1016/j.jhazmat.2014.04.053>
- Amato, F., Alastuey, A., de la Rosa, J., Gonzalez-Castanedo, Y., Sánchez de la Campa, A.M., Pandolfi, M., Lozano, A., Contreras González, J., Querol, X. (2014b). Trends of road dust emissions contributions on ambient air particulate levels at rural, urban and industrial sites in southern Spain. *Atmospheric Chemistry and Physics*, 14, 3533-3544.
- Amato, F., Rivas, I., Viana, M., Moreno, T., Bouso, L., Reche, C., Álvarez-Pedrerol, M., Alastuey, A., Sunyer, J., Querol, X. (2014c). Sources of indoor and outdoor PM2.5 concentrations in primary schools. *Sci. Total Environ.*, 490, 757–765. Doi:10.1016/j.scitotenv.2014.05.051.
- Amato, F., Alastuey, A., Karanasiou, A., Lucarelli, F., ... Querol, X. (2016a). AIRUSE-LIFEC: a harmonized PM speciation and source apportionment in five southern European cities. *Atmospheric Chemistry and Physics*, 16, 3289-3309. <http://dx.doi.org/10.5194/acp-16-3289-2016>
- Amato, F., Zandveld, P., Keuken, M., Jonkers, S., Querol, X., Rche, C., Denier van der Goh, H.A.C., Schaap, M. (2016b). Improving the modeling of road dust levels for Barcelona at urban scale and street level. *Atmospheric Environment*, 125(A), 231-242. <https://doi.org/10.1016/j.atmosenv.2015.10.078>

- Amato, F., Favez, O., Pandolfi, M., Alastuey, A., ... Sciare, J. (2016c). Traffic induced particle resuspension in Paris: Emission factors and source contributions. *Atmospheric Environment*, 129, 114-124. <http://dx.doi.org/10.1016/j.atmosenv.2016.01.022>
- Amato F., Editor (2017). *Non-Exhaust Emissions: An Urban Air Quality Problem for Public Health*. Elsevier, San Diego, CA. <http://www.elsevier.com/books/non-exhaust-emissions/amato/978-0-12-811770-5>
- ARPA Piemonte (2015). *Relazione sullo stato dell'ambiente in Piemonte*. <http://relazione.ambiente.piemonte.gov.it/2014/it> (accessed 15.03.17)
- ARPA Piemonte (2016). *Uno sguardo all'aria, relazione annuale sui dati rilevati dalla rete metropolitana di monitoraggio della qualità dell'aria*. <http://www.arpa.piemonte.gov.it/approfondimenti/territorio/torino/aria/Pubblicazioni/uno-sguardo-allaria-2016-anteprima> (accessed 06.07.17).
- Asensio, I., Moreno, S., Blanquer, H.G., Manuel, J. (2012). Técnicas de medida del espacio poroso del suelo. <http://hdl.handle.net/10251/16872> (in Spanish).
- ASPB, Agencia de Salut Publica de Barcelona. *Informe d'avaluació de la qualitat de l'aire a la ciutat de Barcelona Any 2012* (2013). http://www.aspb.cat/quefem/docs/Qualitat_aire_2012.pdf (in Spanish).
- ASTM E965-15, 2015. *Standard Test Method for Measuring Pavement Macrotexture Depth Using a Volumetric Technique*, ASTM International, West Conshohocken, PA. <http://doi.org/10.1520/E0965-15>
- Athanasopoulou, E., Tombrou, M., Russell, A. G., Karanasiou, A., Eleftheriadis, K., Dandou, A. (2010). Implementation of road and soil dust emission parameterizations in the aerosol model CAMx: Applications over the greater Athens urban area affected by natural sources. *Journal of Geophysical Research*, 115(D17), 301. <http://dx.doi.org/10.1029/2009JD013207>
- Banerjee, A.D. (2003). Heavy metal levels and solid phase speciation in street dusts of Delhi, India. *Environ. Pollut.*, 123, 95–105. doi: 10.1016/S0269-7491(02)00337-8
- Barnpadimos, I., Keller, J., Oderbolz, D., Hueglin, C., and Prévôt, A. S. H. (2012). One decade of parallel fine (PM 2.5) and coarse (PM 10-PM 2.5) particulate matter measurements in Europe: Trends and variability. *Atmospheric Chemistry and Physics*, 12(7), 3189–3203. <https://doi.org/10.5194/acp-12-3189-2012>
- Basta, N.T., Ryan, J.A., Chaney, R.L. (2005). Trace element chemistry in residual-treated soil: key concepts and metal bioavailability. *J. Environ. Qual.*, 34, 49-63.
- Baumann, K., Jayanty, R.K.M., Flanagan, J.B. (2008). Fine Particulate Matter Source Apportionment for the Chemical Speciation Trends Network Site at Birmingham, Alabama, Using Positive Matrix Factorization. *Journal of the Air and Waste Management Association*, 58(1), 27-44. <http://dx.doi.org/10.3155/1047-3289.58.1.27>
- Beddows, D.C.S., Dall'Osto, M., Olatunbosun, O.A., Harrison, R.M. (2016). Detection of brake wear aerosols by aerosol time-of-flight mass spectrometry. *Atmospheric Environment*, 129, 167-175. <http://dx.doi.org/10.1016/j.atmosenv.2016.01.018>
- Beevers, S.D., Kitwiroon, N., Williams, M.L., Kelly, F.J., Anderson, H.R., Carslaw, D.C. (2013). Air pollution dispersion models for human exposure predictions in London. *Journal of Exposure Science and Environmental Epidemiology*, 23, 647–653.

- Begum, B.A., Kim, E., Biswas, S.K., Hopke, P.K. (2004). Investigation of sources of atmospheric aerosol at urban and semi-urban areas in Bangladesh. *Atmospheric Environment*,
- Begum, B.A., Biswas, S.K., Nasiruddin, M., Monsur Showkot Hossain, A., Hopke, P.K. (2009). Source Identification of Chittagong Aerosol by Receptor Modeling. *Environmental Engineering Science*, 26(3), 679-689. <http://dx.doi.org/10.1089/ees.2008.0055>
- Behera, S.N., Sharma, M., Dikshit, O., Shkula, S.P. (2001). GIS-Based Emission Inventory, Dispersion Modeling, and Assessment for Source Contributions of Particulate Matter in an Urban Environment. *Water, Air and Soil Pollution*, 218, 423-436.
- Belis, C.A., Cancelinha, J., Duane, M., Forcina, V., Pedroni, V., Passarella, R., ... Larsen, B.R. (2011). Sources for PM air pollution in the Po Plain, Italy: I. Critical comparison of methods for estimating biomass burning contributions to benzo(a)pyrene. *Atmospheric Environment*, 45, 7266-7275. <http://doi.org/10.1016/j.atmosenv.2011.08.061>
- Bell, M.L., Belanger, K., Ebisu, K., Gent, J.F., Lee, H.J., Koutrakis, P., Leaderer, B.P. (2010). Prenatal exposure to fine particulate matter and birth weight: Variations by particulate constituents and sources. *Epidemiology*, 21(6), 884-891.
- Berger, J., Denby, B. (2011). A generalised model for traffic induced road dust emissions. Model description and evaluation. *Atmospheric Environment*, 45 (22), 3692-3703.
- Beuck, H., Quass, U., Klemm, O., Kuhlbusch, T.A.J. (2011). Assessment of sea salt and mineral dust contributions to PM10 in NW Germany using tracer models and positive matrix factorization. *Atmospheric Environment*, 45, 5813-5821. <http://dx.doi.org/10.1016/j.atmosenv.2011.07.010>
- Bi, X., Li, Z., Sun, G., Liu, J., Han, Z., 2015. In vitro bioaccessibility of lead in surface dust and implications for human exposure: A comparative study between industrial area and urban district. *J. Hazard. Mater.* 297, 191-197. doi:10.1016/j.jhazmat.2015.04.074
- Biasioli, M., Ajmone Marsan, F., 2007. Organic and inorganic diffuse contamination in urban soils: the case of Torino (Italy). *J. Environ. Monit.* 9, 862. doi:10.1039/b705285e
- Biasioli, M., Barberis, R., Ajmone Marsan, F., 2006. The influence of a large city on some soil properties and metals content. *Sci. Total Environ.* 356, 154-164. doi:10.1016/j.scitotenv.2005.04.033
- Bolan, N.S., Kunhikrishnan, A., Thangarajan, R., Kumpiene, J., Park, J., Makino, T., Kirkham, M.B., Scheckel, K. (2014). Remediation of heavy metal (loid)s contaminated soils, to mobilize or to immobilize? *J. Hazard. Mater.* 266, 141-166. <https://doi.org/10.1016/j.jhazmat.2013.12.018>
- Bonifacio, E., Falsone, G., Piazza, S., 2010. Linking Ni and Cr concentrations to soil mineralogy: does it help to assess metal contamination when the natural background is high? *J Soils Sediments*. 10: 1475-1486. doi:10.1007/s11368-010-0244-0
- Borm, P.J.A., Kelly, F., Kunzli, N., Schins, R.P.F., Donaldson, K. (2007). Oxidant generation by particulate matter: from biologically effective dose to a promising, novel metric. *Occupational and Environmental Medicine*, 64(2), 73-74.

- Brines, M., Dall'Osto, M., Amato, F., Minguillón, M.C., Karanasiou, A., Alastuey, A., Querol, X. (2016). Vertical and horizontal variability of PM₁₀ source contributions in Barcelona during SAPUSS. *Atmospheric Chemistry and Physics*, 16, 6785-6804. <http://dx.doi.org/10.5194/acp-16-6785-2016>
- Brown, J.S., Gordon, T., Price, O., Asgharian, B. (2013). Thoracic and respirable particle definitions for human health risk assessment. Part. *Fibre Toxicol.*, 10, 1. <http://dx.doi.org/10.1186/1743-8977-10-12>
- 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](http://dx.doi.org/10.1016/S0140-6736(02)11274-8)
- Brunekreef, B., Forsberg, B. (2005). Epidemiological evidence of effects of coarse airborne particles on health. *Eur. Respir. J.* 26, 309–318.
- Bukowiecki, N., Gehrig, R., Lienemann, P., Hill, M., Figi, R., Buchmann, B., Furger, M., Richard, A., Mohr, C., Weimer, S., Prévôt, A., Baltensperger, U. (2009a). PM₁₀ emission factors of abrasion particles from road traffic (APART). Swiss Association of Road and Transportation Experts (VSS).
- Bukowiecki, N., Lienemann, P., Hill, M., Figi, R., Richard, A., Furger, M., Rickers, K., Falkenberg, G., Zhao, Y., Cliff, S., Prevot, A., Baltensberger, U., Buchmann, B., Gehrig, R. (2009b). Real-world emission factors for antimony and other brake wear related trace elements: size segregated values for light and heavy duty vehicles. *Environmental Science and Technology*, 43,8072–8078.
- Bukowiecki, N., Lienemann, P., Hill, M., Furger, M., Richard, A., Amato, F., Prévôt, A.S.H., Baltensperger, U., Buchmann, B., Gehrig, R. (2010). PM₁₀ emission factors for non-exhaust particles generated by road traffic in an urban street canyon and along a freeway in Switzerland. *Atmospheric Environment*, 44, 2330-2340. <http://dx.doi.org/10.1016/j.atmosenv.2010.03.039>
- Buzcu, B., Fraser, M.P., Kulkarni, P., Chellam, S. (2003). Source Identification and Apportionment of Fine Particulate Matter in Houston, TX, Using Positive Matrix Factorization. *Environmental Engineering Science*, 20(6), 533-545.
- Calabrese, E.J., Stanek, E.J., James, R.C., Roberts, S.M. (1997). Soil ingestion: A concern for acute toxicity in children. *Environ. Health Perspect.*, 105, 1354–1358.
- Cesari, D., Donato, A., Conte, M., Contini, D. (2016). Inter-comparison of source apportionment of PM₁₀ using PMF and CMB in three sites nearby an industrial area in central Italy. *Atmospheric Research*, 182, 282-293.
- Chalbot, M.C., McElroy, B., Kavouras, I.G. (2013). Sources, trends and regional impacts of fine particulate matter in southern Mississippi valley: significance of emissions from sources in the Gulf of Mexico coast. *Atmospheric Chemistry and Physics*, 13, 3721-3732. <http://dx.doi.org/10.5194/acp-13-3721-2013>
- Chan, Y.C., Simpson, R.W., Mctainsh, G.H., Vowles, P.D., Cohen, D.D., Bailey, G.M. (1999). Source apportionment of PM_{2.5} and PM₁₀ aerosols in Brisbane (Australia) by receptor modelling. *Atmospheric Environment*, 33, 3251-3268.
- Chan, Y.C., Cohen, D.D., Hawas, O., Stelcer, E., Simpson, R., Denison, L., Carswell, S. (2008). Apportionment of sources of fine and coarse particles in four major Australian cities by positive matrix factorisation. *Atmospheric Environment*, 42(2), 374-389. <http://dx.doi.org/10.1016/j.atmosenv.2007.09.030>

- Charlesworth, S.M., Lees, J.A., 1999. Particulate-associated heavy metals in the urban environment: their transport from source to deposit, Coventry, UK. *Chemosphere* 39, 833-848.
- Chen, Y., Zheng, M., Edgerton, E.S., Ke, L., Sheng, G., Fu, J., (2012). PM2.5 source apportionment in the southeastern U.S.: Spatial and seasonal variations during 2001–2005. *Journal of Geophysical Research*, 117, D08304. <http://dx.doi.org/10.1029/2011JD016572>
- Cheng, Y., Lee, S.C., Gu, Z.L., Ho, K.F., Zhang, Y.W., Huang, Y., Chow, J.C., Weston, J.G., Cao, J.J., Zhang, R.J. (2015). PM2.5 and PM10–2.5 chemical composition and source apportionment near a Hong Kong roadway. *Particuology*, 18, 96-104. <https://doi.org/10.1016/j.partic.2013.10.003>
- China, S., James, D.E. (2012). Influence of pavement macrotexture on PM10 emissions from paved roads: A controlled study. *Atmos. Environ.*, 63, 313–326. <http://doi.org/10.1016/j.atmosenv.2012.09.018>
- Choate, L.M., Ranville, J.F., Bunge, A.L., Macalady, D.L. (2006). Dermal adhered soil: 1. Amount and particle-size distribution. *Integr. Environ. Assess. Manag.*, 2, 375–384. doi: 10.1002/ieam.5630020409
- Christoforidis, A., Stamatis, N., 2009. Heavy metal contamination in street dust and roadside soil along the major national road in Kavala's region, Greece. *Geoderma* 151, 257–263. doi:10.1016/j.geoderma.2009.04.016
- Colombo, C., Miano, T. (eds), 2015. *Metodi di Analisi chimica del suolo*, third ed. Società Italiana della Scienza del Suolo, Pubblicità and Stampa, Modugno (BA).
- Crespi, A., Bernardoni, V., Calzolari, G., Lucarelli, F., Nava, S., Valli, G., Vecchi, R. (2016). Implementing constrained multi-time approach with bootstrap analysis in ME-2: An application to PM2.5 data from Florence (Italy). *Science of the Total Environment*, 541, 502–511. <http://dx.doi.org/10.1016/j.scitotenv.2015.08.159>
- Crilley, L.R., Lucarelli, F., Bloss, W.J., Harrison, R.M., Beddows, D.C., Calzolari, G., ... Vecchi, R. (2017). Source apportionment of fine and coarse particles at a roadside and urban background site in London during the 2012 summer ClearfLo campaign. *Environmental Pollution*, 220, 766-778. <https://doi.org/10.1016/j.envpol.2016.06.002>
- Dahl, A., Gharibi, A., Swietlicki, E., Gudmundsson, A., Bohgard, M., Ljungman, A., Blomqvist, G., Gustafsson, M. (2006). Traffic-generated emissions of ultrafine particles from pavement-tire interface. *Atmospheric Environment*, 40(7), 1314-1323. <https://doi.org/10.1016/j.atmosenv.2005.10.029>
- Dall'Osto, M., Beddows, D.C.S., Gietl, J.K., Olatunbosun, O.A., Yang, X., Harrison, R.M. (2014). Characteristics of tyre dust in polluted air: Studies by single particle mass spectrometry (ATOFMS). *Atmospheric Environment*, 94, 224-230. <https://doi.org/10.1016/j.atmosenv.2014.05.026>
- Denby, B.R., Sundvor, I., Johansson, C., Pirjola, L., Ketzler, M., Norman, M., Kupiainen, K., Gustafsson, M., Blomqvist, G., Omstedt, G. (2013a). A coupled road dust and surface moisture model to predict non-exhaust road traffic induced particle emissions (NORTRIP). Part 1: Road dust loading and suspension modelling. *Atmospheric Environment*, 77, 283-300. <https://doi.org/10.1016/j.atmosenv.2013.04.069>

- Denby, B.R., Sundvor, I., Johansson, C., Pirjola, L., Ketzler, M., Norman, M., Kupiainen, K., Gustafsson, M., Blomqvist, G., Kauhaniemi, M., Omstedt, G., (2013b). A coupled road dust and surface moisture model to predict non-exhaust road traffic induced particle emissions (NORTRIP). Part 2: Surface moisture and salt impact modelling. *Atmospheric Environment*, 81, 485-503.
- Denier van der Gon, H. A. C., Gerlofs-Nijland, M. E., Gehrig, R., Gustafsson, M., Janssen, N., Harrison, R. M., ... Cassee, F. R. (2013). The Policy Relevance of Wear Emissions from Road Transport, Now and in the Future—An International Workshop Report and Consensus Statement. *Journal of the Air and Waste Management Association*, 63(2), 136–149. <https://doi.org/10.1080/10962247.2012.741055>
- Denys, S., Caboche, J., Tack, K., Rychen, G., Wragg, J., Cave, M., Jondreville, C., Feidt, C. (2012). In-vivo validation of the unified BARGE method to assess the bioaccessibility of arsenic, antimony, cadmium, and lead in soils. *Environ. Sci. Technol.*, 46, 6252–6260.
- Dongarra, G., Manno, E., Varrica, D. (2009). Possible markers of traffic related emissions. *Environmental Monitoring and Assessment*, 154, 117–125.
- Drexler, J.W., Brattin, W.J. (2007). An In Vitro Procedure for Estimation of Lead Relative Bioavailability: With Validation. *Hum. Ecol. Risk Assess. Int. J.*, 13, 383–401. <http://dx.doi.org/10.1080/10807030701226350>
- Driver, J.H., Konz, J.J., Whitmyre, G.K. (1989). Soil adherence to human-skin. *Bull. Environ. Contam. Toxicol.*, 43, 814–820.
- Ducret-Stich, R.E., Tsai, M.Y., Thimmaiah, D., Künzli, N., Hopke, P.K., Phuleria, H.C. (2013). PM10 source apportionment in a Swiss Alpine valley impacted by highway traffic. *Environmental Science and Pollution Research*, 20, 6496–6508. <http://dx.doi.org/10.1007/s11356-013-1682-1>
- Duong, T. T. T., and Lee, B.-K. (2011). Determining contamination level of heavy metals in road dust from busy traffic areas with different characteristics. *Journal of Environmental Management*, 92(3), 554–562. <https://doi.org/10.1016/j.jenvman.2010.09.010>
- Duvall, R.M., Norris, G.A., Burke, J.M., Olson, D.A., Vedantham, R., Williams, R. (2012). Determining spatial variability in PM2.5 source impacts across Detroit, MI. *Atmospheric Environment*, 47, 491-498. <https://doi.org/10.1016/j.atmosenv.2011.09.071>
- Edwards R.D., Liroy, P.J. (1999). The EL sampler: a press sampler for the quantitative estimation of dermal exposure to pesticides in housedust. *J. Expo. Anal. Environ. Epidemiol.*, 9, 521–529.
- European Commission (Ed.), 2011. *Cities of tomorrow: challenges, visions, ways forward*, Oct. 2011. ed, European Union - Regional Policy. Publ. Office of the European Office, Luxembourg.
- EEA (2015). *Air quality in Europe — 2015 report*. European Environment Agency, EEA Report No 5/2015.
- European Commission, Joint Research Centre (2012). *The State of Soil in Europe*. EUR Report 25186 EN.

http://eusoils.jrc.ec.europa.eu/ESDB_Archive/eusoils_docs/other/EUR25186.pdf
(accessed 12/12/2017)

- Eeftens, M., Tsai, M., Ampee, C., Anwanderf, B., Beelen, R., et al., 2012. Spatial variation of PM_{2.5}, PM₁₀, PM_{2.5} absorbance and PM coarse concentrations between and within 20 European study areas and the relationship with NO₂ – Results of the ESCAPE project. *Atmos. Environ.* 62, 303-317. doi:10.1016/j.atmosenv.2012.08.038
- Etyemezian, V., Kuhns, H., Gilles, J., Chow, J., Hendrickson, K., McGown, M., Pitchford, M. (2003). Vehicle-based road dust emission measurement: III effect of speed, traffic volume, location and season on PM₁₀ road dust emission in the Treasure Valley, ID. *Atmospheric Environment*, 37, 4583-4593. [https://doi.org/10.1016/S1352-2310\(03\)00530-2](https://doi.org/10.1016/S1352-2310(03)00530-2)
- Fabretti, J.F., Sauret, N., Gal, J.F., Maria, P.C., Schärer, U. (2009). Elemental characterization and source identification of PM_{2.5} using positive matrix factorization: the Malraux road tunnel, Nice, France. *Atmospheric Research*, 94(2), 320-329. <https://doi.org/10.1016/j.atmosres.2009.06.010>
- Fausser, P. (1999). Particulate air pollution with emphasis on traffic generated aerosols. Riso, 1999: ALL.
- Fernández, L. et al. (2006). Manual de técnicas de análisis de suelos aplicadas a la remediación de sitios contaminados. Instituto Mexicano del Petróleo, Secretaría de Medio Ambiente y Recursos Naturales, Instituto Nacional de Ecología, México. (in Spanish)
- Ferreira-Baptista, L., De Miguel, E. (2005). Geochemistry and risk assessment of street dust in Luanda, Angola: a tropical urban environment. *Atmos. Environ.*, 39, 4501–4512. <http://dx.doi.org/10.1016/j.atmosenv.2005.03.026>
- Figi, R., Nagel, O., Tuchschnid, M., Lienemann, P., Gfeller, U., Bukowiecki, N. (2010). Quantitative analysis of heavy metals in automotive brake linings: a comparison between wet-chemistry based analysis and insitu screening with a handheld X-ray fluorescence spectrometer. *Analytica Chimica Acta*, 676(1–2, :46–52.
- Font, A., and Fuller, G.W. (2016). Did policies to abate atmospheric emissions from traffic have a positive effect in London?. *Environmental Pollution*, 218, 463-474. <https://doi.org/10.1016/j.envpol.2016.07.026>
- Fujiwara, F., Rebagliati, R.J., Dawidowski, L., Gómez, D., Polla, G., Pereyra, V., Smichowski, P., 2011. Spatial and chemical patterns of size fractionated road dust collected in a megacity. *Atmos. Environ.* 45, 1497–1505. doi:10.1016/j.atmosenv.2010.12.053
- Furusjö, E., Sternbeck, J., Cousins, A.P. (2007). PM₁₀ source characterization at urban and highway roadside locations. *Science of the Total Environment*, 387, 206–219.
- Garg, B.D., Cadle, S.H., Mulawa, P.A., Groblicki, P.J. (2000). Brake wear particulate matter emissions. *Environmental Science and Technology*, 34, 4463–4469.
- Gasser, M., Riediker, M., Mueller, L., Perrenoud, A., Blank, F., Gehr, P., Rothen-Rutishauser, B. (2009). Toxic effects of brake wear particles on epithelial lung cells in vitro. *Particle and Fibre Toxicology*, 6(30).
- GBD 2013 Risk Factors Collaborators, Forouzanfar, M. H., Alexander, L., Anderson, H. R., Bachman, V. F., Biryukov, S., ... Murray, C. J. (2015). Global, regional, and

- national comparative risk assessment of 79 behavioural, environmental and occupational, and metabolic risks or clusters of risks in 188 countries, 1990-2013: a systematic analysis for the Global Burden of Disease Study 2013. *Lancet* (London, England), 386(10010), 2287–2323. [http://dx.doi.org/10.1016/S0140-6736\(15\)00128-2](http://dx.doi.org/10.1016/S0140-6736(15)00128-2)
- Gee, G.W. and Bauder, J.W., 1986. Particle-size analysis, in Klute, A. (Ed.), *Methods of soil analysis, Part 1*, 2nd ed., Agron. Monogr. 9, ASA and SSSA, Madison, W, pp. 383–411.
- Gehrig, R., Huglin, C., Hofer, P. (2001). Contributions of Road Traffic to Ambient PM10 and PM2.5 concentrations. 1st Swiss Transport Research Conference, Monte Verita/Ascona.
- Gehrig, R., Hill, M., Buchmann, B., Imhof, D., Weingartner, E., Baltensperger, U. (2004). Separate determination of PM10 emission factors of road traffic for tailpipe emissions and emissions from abrasion and resuspension processes. *International Journal of Environment and Pollution*, 22 (3), 312-325.
- Gehrig, R., Zeyer, K., Bukowiecki, N., Lienemann, P., Poulidakos, L.D., Furger, M., Buchmann, B. (2010). Mobile load simulators – A tool to distinguish between the emissions due to abrasion and resuspension of PM10 from road surfaces. *Atmospheric Environment*, 44, 4937–4943. <https://doi.org/10.1016/j.atmosenv.2010.08.020>
- Gietl, J. K., Lawrence, R., Thorpe, A. J., and Harrison, R. M. (2010). Identification of brake wear particles and derivation of a quantitative tracer for brake dust at a major road. *Atmospheric Environment*, 44(2), 141–146. <https://doi.org/10.1016/j.atmosenv.2009.10.016>
- Green, M.C., Antony Chen, L.W., DuBois, D.W., Molenar, J.V. (2012). Fine particulate matter and visibility in the Lake Tahoe Basin: Chemical characterization, trends, and source apportionment. *Journal of the Air and Waste Management Association*, 62(8), 953-965. <http://dx.doi.org/10.1080/10962247.2012.690362>
- Grigoratos, T., and Martini, G. (2015). Brake wear particle emissions: a review. *Environmental Science and Pollution Research*, 22(4), 2491–2504. <https://doi.org/10.1007/s11356-014-3696-8>
- Gu, J., Pitz, M., Schnelle-Kreis, J., Diemer, J., Reller, A., Zimmermann, R., ... Cyrus, J. (2011). Source apportionment of ambient particles: Comparison of positive matrix factorization analysis applied to particle size distribution and chemical composition data. *Atmospheric Environment*, 45(10), 1849–1857. <https://doi.org/10.1016/j.atmosenv.2011.01.009>
- Gualtieri, M., Rigamonti, L., Galeotti, V., Camatini, M. (2005). Toxicity of tire debris extracts on human lung cell line A549. *Toxicology In Vitro*, 19(7), 1001–1008.
- Gualtieri, M., Mantecca, P., Cetta, F., Camatini, M. (2008). Organic compounds in tire particle induce reactive oxygen species and heat-shock proteins in the human alveolar cell line A549. *Environment International*, 34(4) 437–442.
- Gummeneni, S., Yusup, Y.B., Chavali, M., Samadi, S.Z. (2011). Source apportionment of particulate matter in the ambient air of Hyderabad city, India. *Atmospheric Environment*, 45(3), 752-764. <https://doi.org/10.1016/j.atmosres.2011.05.002>

- Gunawardana, C., Goonetilleke, A., Egodawatta, P., Dawes, L., Kokot, S. (2012). Source characterisation of road dust based on chemical and mineralogical composition. *Chemosphere*, 87, 163–170. doi:10.1016/j.chemosphere.2011.12.012
- Gunawardana J., Ziyath A.M., Egodawatta P., Ayoko G.A., Goonetilleke A. (2014). Mathematical relationships for metal build-up on urban road surfaces based on traffic and land use characteristics. *Chemosphere*, 99, 267-271. <https://doi.org/10.1016/j.chemosphere.2013.10.068>
- Guney, M., Zagury, G.J., 2016. Bioaccessibility and other key parameters in assessing oral exposure to PAH-contaminated soils and dust: A critical review. *Human and Ecological Risk Assessment: An International Journal*, 22, 6, 1396-1417. doi: 10.1080/10807039.2016.1185691
- Gupta. A.K., Karar, K., Srivastava, A. (2007). Chemical mass balance source apportionment of PM10 and TSP in residential and industrial sites of an urban region of Kolkata, India. *Journal of Hazardous Materials*, 142, 279–287.
- Gupta, I., Salunkhe, A., Kumar, R. (2012). Source Apportionment of PM10 by Positive Matrix Factorization in Urban Area of Mumbai, India. *The Scientific World Journal*, 2012, 585791. <http://dx.doi.org/10.1100/2012/585791>
- Gustafsson, M., Blomqvist, G., Gudmundsson, A., Dahl, A., Swietlicki, E., Bohgard, M. et al. (2008). Properties and toxicological effects of particles from the interaction between tyres, road pavement and winter traction material. *Science of the Total Environment*, 393(2–3), 226–240.
- Gustafsson M, Blomqvist G, Gudmundsson A, Dahl A, Jonsson P, Swietlicki E. (2009). Factors influencing PM10 emissions from road pavement wear. *Atmospheric Environment*, 43, 4699-4702. <https://doi.org/10.1016/j.atmosenv.2008.04.028>
- Guttikunda, S.K., and Calori, G. (2013). A GIS based emissions inventory at 1 km 1 km spatial resolution for air pollution analysis in Delhi, India. *Atmospheric Environment*, 67, 101-111. <https://doi.org/10.1016/j.atmosenv.2012.10.040>
- Guttikunda, S.K., Kopakka, R.V., Dasari, P., Gertler A.W. (2013). Receptor model-based source apportionment of particulate pollution in Hyderabad, India. *Environmental Monitoring and Assessment*, 185, 5585-5593. <http://dx.doi.org/10.1007/s10661-012-2969-2>
- Hagino, H., Oyama, M., Sasaki, S., 2016. Laboratory testing of airborne brake wear particle emissions using a dynamometer system under urban city driving cycles. *Atmos. Environ.* 131, 269–278. doi:10.1016/j.atmosenv.2016.02.014
- Happo, M.S., Salonen, R.O., Hlinen, A.I., Jalava, P.I., Pennanen, A.S., Dor-mans, J.A.M.A. et al. (2010). Inflammation and tissue damage in mouse lung by single and repeated dosing of urban air coarse and fine particles collected from six European cities. *Inhalation Toxicology*, 22(5), 402–416.
- Harrison, R.M., Laxen, D.P.H., Wilson, S.J. (1981). Chemical Associations of Lead, Cadmium, Copper, and Zinc in Street Dusts and Roadside Soils. *Environmental Science and Technology*, 15, 1378-1383.
- Harrison, R.M., Smith, D.J.T., Piou, C.A., Castro, L.M. (1997). Comparative receptor modelling study of airborne particulate pollutants in Birmingham (United Kingdom), Coimbra (Portugal) and Lahore (Pakistan). *Atmospheric Environment*, 31(20), 3309-3321. [https://doi.org/10.1016/S1352-2310\(97\)00152-0](https://doi.org/10.1016/S1352-2310(97)00152-0)

- Harrison, R.M., Beddows, D.C.S., Dall'Osto, M. (2011). PMF Analysis of Wide-Range Particle Size Spectra Collected on a Major Highway. *Environmental Science and Technology*, 45, 5522–5528. <http://dx.doi.org/10.1021/es2006622>
- Harrison, R.M., Jones, A.M., Gietl, J., Yin, J., Green, D.C. (2012). Estimation of the contributions of brake dust, tire wear, and resuspension to nonexhaust traffic particles derived from atmospheric measurements. *Environmental Science and Technology*, 46(12), 6523-6529. <http://dx.doi.org/10.1021/es300894r>
- Hedberg, E., Johansson, C., Johansson, L., Swietlicki, E., and Brorström-Lundén, E. (2012). Is Levoglucosan a Suitable Quantitative Tracer for Wood Burning? Comparison with Receptor Modeling on Trace Elements in Lycksele, Sweden. *Journal of the Air and Waste Management Association*, 56(12), 1669-1678. <http://dx.doi.org/10.1080/10473289.2006.10464572>
- Held, T., Ying, Q., Kleeman, M.J., Schauer, J.J., Fraser, M.P. (2005). A comparison of the UCD/CIT air quality model and the CMB source–receptor model for primary airborne particulate matter. *Atmospheric Environment*, 39(12), 2281-2297. <https://doi.org/10.1016/j.atmosenv.2004.12.034>
- Henry, R.C., Hidy, G.M. (1979). Multivariate analysis of particulate sulfate and other air quality variables by principal components-Part I. *Atmospheric Environ.* [http://dx.doi.org/10.1016/0004-6981\(79\)90068-4](http://dx.doi.org/10.1016/0004-6981(79)90068-4)
- Henry, J.J. (2000). NCHRP Synthesis 291, Evaluation of Pavement Friction Characteristics, TRB. National Research Council, Washington, DC.
- Hjortenkrans, D.S.T., Bergback, B.G., Haggerud, A.V. (2007). Metal emissions from brake linings and tires: case studies of Stockholm, Sweden 1995/1998 and 2005. *Environmental Science and Technology*, 41, 5224–5230.
- Hu, X., Zhang, Y., Luo, J., Wang, T., Lian, H., Ding, Z., 2011. Bioaccessibility and health risk of arsenic, mercury and other metals in urban street dusts from a mega-city, Nanjing, China. *Environ. Pollut.* 159, 1215–1221. <http://dx.doi.org/10.1016/j.envpol.2011.01.037>
- Huang, L., Wang, K., Yuan, C.S., Wang, G. (2010). Study on the Seasonal Variation and Source Apportionment of PM10 in Harbin, China. *Aerosol and Air Quality Research*, 10, 86–93. <http://dx.doi.org/10.4209/aaqr.2009.04.0025>
- Hulskotte, J. H. J., Roskam, G. D., and Denier van der Gon, H. A. C. (2014). Elemental composition of current automotive braking materials and derived air emission factors. *Atmospheric Environment*, 99, 436–445. <https://doi.org/10.1016/j.atmosenv.2014.10.007>
- ICH. 2005. Harmonized Tripartite Guideline, Validation of Analytical Procedure: Text and Methodologies, Q2 (R1), Parent guidelines on methodology dated November 6: 1996, incorporated in November 2005. http://www.ich.org/fileadmin/Public_Web_Site/ICH_Products/Guidelines/Quality/Q2_R1/Step4/Q2_R1__Guideline.pdf (accessed March 29, 2017).
- Iijima, A., Sato, K., Yano, K., Kato, M., Tago, H., Kato, M., Kimura, H., Furuta, N. (2007). Particle size and composition distribution analysis of automotive brake abrasion dusts for the evaluation of antimony sources of airborne particulate matter. *Atmospheric Environment*, 41, 4908–4919.

- Iijima, A., Sato, K., Yano, K., Kato, M., Kozawa, K., Furuta, N. (2008). Emission factor for antimony in brake abrasion dusts as one of the major atmospheric antimony sources. *Environmental Science and Technology*, 42(8), 2937-2942. doi: 10.1021/es702137g
- IREA, *Inventario Regionale delle Emissioni in Atmosfera* (2010). <http://www.sistemapiemonte.it/fedwinemar/elenco.jsp> (accessed 14.07.17)
- Ivošević, T., Stelcer, E., Orlic, I., Bogdanović Radović, I., Cohen, D. (2016). Characterization and source apportionment of fine particulate sources at Rijeka, Croatia from 2013 to 2015. *Nuclear Instruments and Methods in Physics Research B*, 371, 376–380. <https://doi.org/10.1016/j.nimb.2015.10.023>
- Jacobson T, Wågberg L. (2007). Developing and Upgrading of a Prediction Model of Wear Caused by Studded Tyres and an Overview of the Knowledge of the Factors Influencing the Wear. VTI report 7. Swedish National Road and Transport Research Institute, Linköping, Sweden. (In Swedish)
- Jeong, C.H., McGuire, M.L., Herod, D., Dann, T., ... Evans, G. (2011). Receptor model based identification of PM_{2.5} sources in Canadian cities. *Atmospheric Pollution Research*, 2(2), 158-171. <https://doi.org/10.5094/APR.2011.021>
- Juhasz, A.L., Smith, E., Weber, J., Rees, M., Rofe, A., Kuchel, T., Sansom, L., Naidu, R. (2007). Comparison of in vivo and in vitro methodologies for the assessment of arsenic bioavailability in contaminated soils. *Chemosphere*, 69, 961–966.
- Juhasz, A.L., Weber, J., Smith, E. (2011). Impact of soil particle size and bioaccessibility on children and adult lead exposure in peri-urban contaminated soils. *Journal of Hazardous Materials*, 186, 1870–1879. <http://dx.doi.org/10.1016/j.jhazmat.2010.12.095>
- Kara, M., Hopke, P.K., Dumanoglu, Y., Altioğ, H., Elbir, T., Odabasi, M., Bayram, A. (2015). Characterization of PM Using Multiple Site Data in a Heavily Industrialized Region of Turkey. *Aerosol and Air Quality Research*, 15, 11–27. <https://doi.org/10.4209/aaqr.2014.02.0039>
- Kelly, F.J. (2003). Oxidative stress: its role in air pollution and adverse health effects. *Occupational and Environmental Medicine*, 60(8), 612–616.
- Karanasiou, A.A., Siskos, P.A., Eleftheriadis, K. (2009). Assessment of source apportionment by Positive Matrix Factorization analysis on fine and coarse urban aerosol size fractions. *Atmospheric Environment*, 43(21), 3385-3395. <https://doi.org/10.1016/j.atmosenv.2009.03.051>
- Karanasiou, A., Moreno, T., Amato, F., Lumbreiras, J., Narros, A., ... Reche, C. (2011). Road dust contribution to PM levels – Evaluation of the effectiveness of street washing activities by means of Positive Matrix Factorization. *Atmospheric Environment*, 45(13), 2193-2201. <https://doi.org/10.1016/j.atmosenv.2011.01.067>
- Karar, K., Gupta, A.K. (2007). Source apportionment of PM₁₀ at residential and industrial sites of an urban region of Kolkata, India. *Atmospheric Research*, 84, 30–41.
- Kastury, F., Smith, E., Juhasz, A. L. (2017). A critical review of approaches and limitations of inhalation bioavailability and bioaccessibility of metal(loid)s from ambient particulate matter or dust. *Science of The Total Environment*, 574, 1054–1074. <http://dx.doi.org/10.1016/j.scitotenv.2016.09.056>

- Kavouras, I.G., DuBois, D.W., Nikolich, G., Etyemezian, V. (2015). Monitoring, Source Identification and Health Risks of Air Toxics in Albuquerque, New Mexico, U.S.A. *Aerosol and Air Quality Research*, 15, 556–571. <https://doi.org/10.4209/aaqr.2014.04.0075>
- Ke, L., Liu, W., Wang, Y., Russell, A.G., Edgerton, E.S., Zheng, M. (2008). Comparison of PM_{2.5} source apportionment using positive matrix factorization and molecular marker-based chemical mass balance. *Science of The Total Environment*, 394, 290–302. <https://doi.org/10.1016/j.scitotenv.2008.01.030>
- Ketzel M., Omstedt G., Johansson C., During I., Pohjola M., Oettl D., Gidhagen L., ... Berkowicz R. (2007). Estimation and validation of PM_{2.5}/PM₁₀ exhaust and non-exhaust emission factors for practical street pollution modelling. *Atmospheric Environment*, 41 (40), 9370-9385. <https://doi.org/10.1016/j.atmosenv.2007.09.005>
- Keuken M., Denier van der Gon H., van der Valk K. (2010). Non-exhaust emissions of PM and the efficiency of emission reduction by road sweeping and washing in the Netherlands. *Science of the Total Environment*, 408 (20), 4591-4599. <https://doi.org/10.1016/j.scitotenv.2010.06.052>
- Keuken, M. P., Roemer, M. G. M., Zandveld, P., Verbeek, R. P., and Velders, G. J. M. (2012). Trends in primary NO₂ and exhaust PM emissions from road traffic for the period 2000-2020 and implications for air quality and health in the Netherlands. *Atmospheric Environment*, 54, 313–319. <https://doi.org/10.1016/j.atmosenv.2012.02.009>
- Kong S., Lu B., Ji Y., Zhao X., Bai Z., Xu Y., Liud Y. and Jiang H. (2012). Risk assessment of heavy metals in road and soil dusts within PM_{2.5}, PM₁₀ and PM₁₀₀ fractions in Dongying city, Shandong Province, China. *J. Environ. Monit.*, 14, 791. doi:10.1039/C1EM10555H
- Kousoulidou, M., Ntziachristos, L., Mellios, G., and Samaras, Z. (2008). Road-transport emission projections to 2020 in European urban environments. *Atmospheric Environment*, 42(32), 7465–7475. <https://doi.org/10.1016/j.atmosenv.2008.06.002>
- Kreider, M. L., Panko, J. M., McAtee, B. L., Sweet, L. I., and Finley, B. L. (2010). Physical and chemical characterization of tire-related particles: Comparison of particles generated using different methodologies. *Science of The Total Environment*, 408(3), 652–659. <https://doi.org/10.1016/j.scitotenv.2009.10.016>
- Kuenen, J. J. P., Visschedijk, A. J. H., Jozwicka, M., Denier van der Gon H. A. C. (2014). TNO-MACC_II emission inventory; a multi-year (2003–2009) consistent high-resolution European emission inventory for air quality modeling. *Atmospheric Chemistry and Physics*, 14, 10963–10976. <https://doi.org/10.5194/acp-14-10963-2014>
- Kukutschová, J., Moravec, P., Tomášek, V., Matějka, V., Smolík, J., Schwarz, J., ... Filip, P. (2011). On airborne nano/micro-sized wear particles released from low-metallic automotive brakes. *Environmental Pollution*, 159(4), 998–1006. <https://doi.org/10.1016/j.envpol.2010.11.036>
- Kumar, M., Furumai, H., Kurisu, F., Kasuga, I. (2013). Tracing source and distribution of heavy metals in road dust, soil and soakaway sediment through speciation and isotopic fingerprinting. *Geoderma*, 211–212, 8–17. doi:10.1016/j.geoderma.2013.07.004

- Kupiainen, K. J., Tervahattu, H., Räisänen, M., Mäkelä, T., Aurela, M., and Hillamo, R. (2005). Size and composition of airborne particles from pavement wear, tires, and traction sanding. *Environmental Science and Technology*, 39(3), 699–706.
- Kupiainen, K., Ritola, R., Stojiljkovic, A., Pirjola, L., Malinen, A., and Niemi, J. (2016). Contribution of mineral dust sources to street side ambient and suspension PM10 samples. *Atmospheric Environment*, 147, 178–189. <https://doi.org/10.1016/j.atmosenv.2016.09.059>
- Kuwayama, t., Ruehl, C.R., Kleeman, M.J. (2013). Daily Trends and Source Apportionment of Ultrafine Particulate Mass (PM0.1) over an Annual Cycle in a Typical California City. *Environmental Science and Technology*, 47, 13957-13966. <http://dx.doi.org/10.1021/es403235c>
- Kwak, J.H., Kim, H., Lee, J., Lee, S. (2013). Characterization of non-exhaust coarse and fine particles from on-road driving and laboratory measurements. *Science of the Total Environment*, 458-460, 273-282.
- Lawrence, S., Sokhi, R., Ravindra, K., Mao, H., Prain, H.D., Bull, I.D. (2013). Source apportionment of traffic emissions of particulate matter using tunnel measurements. *Atmospheric Environment*, 77, 548-557. <https://doi.org/10.1016/j.atmosenv.2013.03.040>
- Lee, H.J., Gent, J.F., Leadere, B.P., Koutrakis, P. (2011). Spatial and temporal variability of fine particle composition and source types in five cities of Connecticut and Massachusetts. *Science of the Total Environment*, 409, 2133-2142. <https://doi.org/10.1016/j.scitotenv.2011.02.025>
- Lee, S., Kwak, J., Kim, H., Lee, J. (2013). Properties of roadway particles from interaction between the tire and road pavement. *International Journal of Automotive Technology*, 14(1), 163–173.
- Li, Z., Hopke, P.K., Husain, L., Qureshi, S., Dutkiewicz, V.A., Schwab, J.J., Drewnick, F., Demerjian, K.L. (2004). Sources of fine particle composition in New York city. *Atmospheric Environment*, 38, 6521-6529. <https://doi.org/10.1016/j.atmosenv.2004.08.040>
- Li, H., Qian, X., Hu, W., Wang, Y., Gao, H. (2013). Chemical speciation and human health risk of trace metals in urban street dusts from a metropolitan city, Nanjing, SE China. *Sci. Total Environ.*, 456–457, 212–221. doi:10.1016/j.scitotenv.2013.03.094
- Li, H., Wang, Q., Yang, M., Li, F., Wang, J., Sun, Y., Wang, C., ... Qian, X. (2016). Chemical characterization and source apportionment of PM2.5 aerosols in a megacity of Southeast China. *Atmospheric Research*, 181, 288-299. <https://doi.org/10.1016/j.atmosres.2016.07.005>
- Lim, J.M., Lee, J.H., Moon, J.H., Chung, Y.S., Kim, K.H. (2010). Source apportionment of PM10 at a small industrial area using Positive Matrix Factorization. *Atmospheric Research*, 95, 88-100. <https://doi.org/10.1016/j.atmosres.2009.08.009>
- Lim, S.S., Vos, T., Flaxman, A.D., Danaei, G., Shibuya, K., Adair-Rohani, H., Amann, M., Anderson, H.R., Andrews, K.G., Aryee, M., Atkinson, C., Bacchus, L.J., Bahalim, A.N., Balakrishnan, K., Balmes, J., Barker-Collo, S., Baxter, A., Bell, M.L., Blore, J.D., Blyth, F., Bonner, C., Borges, G., Bourne, R., Boussinesq, M., Brauer, M., Brooks, P., Bruce, N.G., Brunekreef, B., Bryan-Hancock, C., Bucello, C. et al. (2012). A comparative risk assessment of burden of disease and injury attributable

- to 67 risk factors and risk factor clusters in 21 regions, 1990-2010: a systematic analysis for the Global Burden of Disease Study 2010. *Lancet*, 380, 2224–2260. [http://dx.doi.org/10.1016/S0140-6736\(12\)61766-8](http://dx.doi.org/10.1016/S0140-6736(12)61766-8)
- Liu, A., Gunawardana, C., Gunawardena, J., Egodawatta, P., Ayoko, G.A., Goonetilleke, A. (2016). Taxonomy of factors which influence heavy metal build-up on urban road surfaces. *Journal of Hazardous Materials*, 310, 20–29. <https://doi.org/10.1016/j.jhazmat.2016.02.026>
- Liu, Z., Wang, Y., Hu, B., Ji, D., Zhang, J., Wu, F., Wan, X., Wang, Y. (2016). Source appointment of fine particle number and volume concentration during severe haze pollution in Beijing in January 2013. *Environmental Science and Pollution Research*, 23(7), 6845–60. <http://dx.doi.org/10.1007/s11356-015-5868-6>.
- Ljung, K., Oomen, A., Duits, M., Selinus, O., Berglund, M. (2007). Bioaccessibility of metals in urban playground soils. *J. Environ. Sci. Health Part A*, 42, 1241–1250. doi:10.1080/10934520701435684
- Luo, X., Yu, S., Li, X. (2011). Distribution, availability, and sources of trace metals in different particle size fractions of urban soils in Hong Kong: Implications for assessing the risk to human health. *Environ. Pollut.*, 159, 1317–1326. doi:10.1016/j.envpol.2011.01.013
- Madrid, L., Díaz-Barrientos, E., Ruiz-Cortés, E., Reinoso, R., Biasioli, M., Davidson, C. M., ... Ajmone Marsan, F. (2006). Variability in concentrations of potentially toxic elements in urban parks from six European cities. *Journal of Environmental Monitoring*, 8, 1158–1165. <http://dx.doi.org/10.1039/B607980F>
- Madrid, F., Biasioli, M., Ajmone-Marsan, F. (2008). Availability and bioaccessibility of metals in fine particles of some urban soils. *Arch. Environ. Contam. Toxicol.*, 55, 21–32. doi:10.1007/s00244-007-9086-1
- Maenhaut, W., Vermeylen, R., Claeys, M., Vercauteren, J., Roekens, E. (2016). Sources of the PM10 aerosol in Flanders, Belgium, and re-assessment of the contribution from wood burning. *Science of the Total Environment*, 562, 550–560. <https://doi.org/10.1016/j.scitotenv.2016.04.074>
- Manoli, E., Voutsas, D., Samara, C. (2002). Chemical characterization and source identification/apportionment of fine and coarse air particles in Thessaloniki, Greece. *Atmospheric Environment*, 36(6), 949–961. [https://doi.org/10.1016/S1352-2310\(01\)00486-1](https://doi.org/10.1016/S1352-2310(01)00486-1)
- Manousakas, M., Diapouli, E., Papaefthymiou, H., Migliori, A., Karydas, A.G., ... Eleftheriadis, K. (2015). Source apportionment by PMF on elemental concentrations obtained by PIXE analysis of PM10 samples collected at the vicinity of lignite power plants and mines in Megalopolis, Greece. *Nuclear Instruments and Methods in Physics Research Section B: Beam Interactions with Materials and Atoms*, 349, 114–124. <https://doi.org/10.1016/j.nimb.2015.02.037>
- Mansha, M., Ghauri, B., Rahman, S., Amman, A. (2012). Characterization and source apportionment of ambient air particulate matter (PM2.5) in Karachi. *Science of the Total Environment*, 425, 176–183. <https://doi.org/10.1016/j.scitotenv.2011.10.056>
- Mantecca, P., Sancini, G., Moschini, E., Farina, F., Gualtieri, M., Rohr, A., et al. (2009). Lung toxicity induced by intratracheal instillation of size-fractionated tire particles. *Toxicology Letters*, 189(3), 206–214.

- Mantecca, P., Farina, F., Moschini, E., Gallinotti D., Gualtieri M., Rohr A., et al. (2010). Comparative acute lung inflammation induced by atmospheric PM and size-fractionated tire particles, *Toxicology Letters*, 198(2), 244–254.
- Marcazzan, G.M., Ceriani, M., Valli, G., Vecchi, R. (2003). Source apportionment of PM10 and PM2.5 in Milan (Italy) using receptor modelling. *Science of The Total Environment*, 317, 137-147.
- Masri, S., Kang C.M., Koutrakis, P., (2015). Composition and sources of fine and coarse particles collected during 2002–2010 in Boston, MA. *Journal of the Air and Waste Management Association*, 65(3), 287-297. <http://dx.doi.org/10.1080/10962247.2014.982307>
- Mathissen, M., Scheer, V., Vogt, R., Benter, T. (2011). Investigation on the potential generation of ultrafine particles from the tire–road interface. *Atmospheric Environment*, 45, 6172–6179.
- 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.
- Mbengue, S., Alleman, L.Y., Flament, P. (2017). Metal-bearing fine particle sources in a coastal industrialized environment. *Atmospheric Research*, 183, 202-211. <https://doi.org/10.1016/j.atmosres.2016.08.014>
- McKenzie, E.R., Wong, C.M., Green, P.G., Kayhanian, M., Young, T.M. (2008). Size dependent elemental composition of road-associated particles. *Science of the Total Environment*, 398(1-3), 145-153.
- Meuser, H. (2010). *Contaminated urban soils*. Springer. <https://doi.org/10.1007/978-90-481-9328-8>
- Ming, H., He, W., Lamb, D.T., Megharaj, M., Naidu, R. (2012). Bioavailability of lead in contaminated soil depends on the nature of bioreceptor. *Ecotoxicol. Environ. Saf.*, 78, 344–350. <http://dx.doi.org/10.1016/j.ecoenv.2011.11.045>
- Minguillón, M.C., Schembari, A., Triguero-Mas, M., de Nazelle, A., Dadvand, P., ... Querol, X. (2012). Source apportionment of indoor, outdoor and personal PM2.5 exposure of pregnant women in Barcelona, Spain. *Atmospheric Environ.*, 59, pp. 426-436. doi: 10.1016/j.atmosenv.2012.04.052
- Mooibroek, D., Staelens, J., Cordell, R., Panteliadis, P., ... Roekens, E. (2016). PM10 Source Apportionment in Five North Western European Cities—Outcome of the Joaquin Project. In R.E. Hester, R.M. Harrison and X. Querol (Eds.), *Airborne Particulate Matter: Sources, Atmospheric Processes and Health* (pp. 264-292. Royal Society of Chemistry. <http://dx.doi.org/10.1039/9781782626589-00264>
- Mosleh, M., Blau, P.J., Dumitrescu, D. (2004). Characteristics and morphology of wear particles from laboratory testing of disc brake materials. *Wear*, 256, 1128–1134.
- Mukhtar, A., Limbeck, A. (2013). Recent developments in assessment of bio-accessible trace metal fractions in airborne particulate matter: a review. *Anal. Chim. Acta*, 774, 11–25. <https://doi.org/10.1016/j.aca.2013.02.008>
- Ng, J.C., Juhasz, A., Smith, E., Naidu, R. (2015). Assessing the bioavailability and bioaccessibility of metals and metalloids. *Environmental Science and Pollution Research*, 22, 8802–8825. <http://dx.doi.org/10.1007/s11356-013-1820-9>

- Norris, G., Duvall, R., Brown, S., Bai, S. (2014). EPA Positive Matrix Factorization (PMF) 5.0 Fundamentals and User Guide, EPA/600/R-14/108. Environ. Prot. Agency Off. Researc Dev. Publusing House Whashington DC 20460.
- Nosko, O., Olofsson, U. (2017). Quantification of ultrafine airborne particulate matter generated by the wear of car brake materials. *Wear*, 374–375, 92-96. <https://doi.org/10.1016/j.wear.2017.01.003>
- Oomen, A.G., Hack, A., Minekus, M., Zeijdner, E., Cornelis, C., Schoeters, G., Verstraete, W., Van de Wiele, T., Wragg, J., Rompelberg, C.J.M., Sips, A.J.A.M., Van Wijnen, J.H. (2002). Comparison of five in vitro digestion models to study the bioaccessibility of soil contaminants. *Environ. Sci. Technol.*, 36, 3326–3334. doi:10.1021/es010204v
- Ostro, B., Tobias, A., Querol, X., Alastuey, A., Amato, F., Pey, J., Pérez, N., Sunyer, J. (2011). The effects of particulate matter sources on daily mortality: A case-crossover study of Barcelona, Spain. *Environmental Health Perspectives*, 119(12), 1781-1787.
- Paatero, P., Hopke, P.K. (2003). Discarding or downweighting high-noise variables in factor analytic models. *Analytica Chimica Acta*. 277–289. doi:10.1016/S0003-2670(02)01643-4
- Paatero, P., Tapper, U. (1994). Positive Matrix Factorization - A Nonnegative Factor Model with Optimal Utilization of Error Estimates of Data Values. *Environmetrics*, 5, 111–126. Doi:10.1002/env.3170050203
- Padoan, E., Malandrino, M., Giacomino, A., Grosa, M.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. doi:10.1016/j.chemosphere.2015.11.094
- Padoan, E., Romè, 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. doi:10.1016/j.scitotenv.2017.05.180
- Panko, J.M., Chu, J., Kreider, M.L., Unice, K.M. (2013). Measurement of airborne concentrations of tire and road wear particles in urban and rural areas of France, Japan, and the United States. *Atmospheric Environment*, 72, 192-199. <https://doi.org/10.1016/j.atmosenv.2013.01.040>
- Pant, P., Harrison, R. M. (2013). Estimation of the contribution of road traffic emissions to particulate matter concentrations from field measurements: A review. *Atmospheric Environment*, 77, 78–97. <https://doi.org/10.1016/j.atmosenv.2013.04.028>
- Pant, P., Baker, S.J., Shukla, A., Maikawa, C., Godri Pollitt, K.J., Harrison, R.M. (2015). The PM10 fraction of road dust in the UK and India: characterization, source profiles and oxidative potential. *Sci. Total Environ.*, 530-531, 445–452. <https://doi.org/10.1016/j.scitotenv.2015.05.084>
- Patinha, C., Durães, N., Sousa, P., Dias, A.C., Reis, A.P., Noack, Y., Silva, E.F. da (2015). Assessment of the influence of traffic-related particles in urban dust using sequential selective extraction and oral bioaccessibility tests. *Environ. Geochem. Health*, 37, 707–724. doi:10.1007/s10653-015-9713-0
- Paustenbach, D.J. (2000). The practice of exposure assessment: a state-of-the-art review. *J. Toxicol. Environ. Health Part B*, 3, 179–291. doi:10.1080/10937400050045264

- Pay, M.T., Jimenez-Guerrero, P., Baldasano, J.M. (2011). Implementation of resuspension from paved roads for the improvement of CALIOPE air quality system in Spain. *Atmospheric Environment*, 45(3), 802-807. <https://doi.org/10.1016/j.atmosenv.2010.10.032>
- Peel, M.C., Finlayson, B.L., McMahon, T.A. (2007). Updated world map of the Köppen-Geiger climate classification. *Hydrology and Earth System Sciences*, 11, 1633-1644.
- Perrone, M.G., Larsen, B.R., Ferrero, L., Sangiorgi, G., De Gennaro, G., Udisti, R., Zangrando, R., Gambaro, A., Bolzacchini E. (2012). Sources of high PM2.5 concentrations in Milan, Northern Italy: Molecular marker data and CMB modelling. *Science of the Total Environment*, 414, 343-355. <https://doi.org/10.1016/j.scitotenv.2011.11.026>
- Pietroangelo, 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. Atmos. Environ.*, 69, 1–14. <https://doi.org/10.1016/j.atmosenv.2012.11.059>
- Pipalatkhar, P., Khaparde, V.V., Gajghate, D.G., Bawase, M.A. (2014). Source Apportionment of PM2.5 Using a CMB Model for a Centrally Located Indian City. *Aerosol and Air Quality Research*, 14, 1089–1099. <https://doi.org/10.4209/aaqr.2013.04.0130>
- Poggio, L., Vrscaj, B., Schulin, R., Hepperle, E., Ajmone Marsan, F. (2009). Metals pollution and human bioaccessibility of topsoils in Grugliasco (Italy). *Environmental Pollution*, 157, 680–689.
- Pokorná, P., Hovorka, J., Kroužek, J., Hopke, P.K. 2013. Particulate matter source apportionment in a village situated in industrial region of Central Europe, *Journal of the Air and Waste Management Association*, 63(12), 1412-1421. <http://dx.doi.org/10.1080/10962247.2013.825215>
- Pokorná, P., Hovorka, J., Klan, M., Hopke, P.K. (2015). Source apportionment of size resolved particulate matter at a European air pollution hot spot. *Science of the Total Environment*, 502, 172-183. <https://doi.org/10.1016/j.scitotenv.2014.09.021>
- Praticò, F.G. and Vaiana, R. (2015). A study on the relationship between mean texture depth and mean profile depth of asphalt pavements. *Construction and Building Materials*, 101 (Part 1), 72-79. <https://doi.org/10.1016/j.conbuildmat.2015.10.021>
- Putaud, J.-P., Van Dingenen, R., Alastuey, A., Bauer, H., Birmili, W., Cyrys, J., Flentje, H., Fuzzi, S., Gehrig, R., Hansson, H.-C., et al. (2010). A European aerosol phenomenology–3: Physical and chemical characteristics of particulate matter from 60 rural, urban, and kerbside sites across Europe. *Atmos. Environ.*, 44, 1308–1320.
- Qadir, R.M., Schnelle-Kreis, J., Abbaszade, G., Arteaga-Salas, J.M., Diemer, J., Zimmermann, R. (2014). Spatial and temporal variability of source contributions to ambient PM10 during winter in Augsburg, Germany using organic and inorganic tracers. *Chemosphere*, 103, 263-273. <https://doi.org/10.1016/j.chemosphere.2013.12.015>
- Querol, X., Alastuey, A., Rodriguez, S., Plana, F., Mantilla, E., Ruiz, C.R. (2001). Monitoring of PM10 and PM2.5 around primary particulate anthropogenic emission sources. *Atmos. Environ.*, 35, 845–858. doi:10.1016/S1352-2310(00)00387-3
- Querol, X., Alastuey, A., Ruiz, C.R., Artiñano, B., Hansson, H.C., Harrison, R.M., Buringh, E., ten Brink, H.M., Lutz, M., Bruckmann, P., Straehl, P., Schneider, J. (2004).

- Speciation and origin of PM10 and PM2.5 in selected European cities. *Atmos. Environ.*, 38, 6547–6555. doi:10.1016/j.atmosenv.2004.08.037
- Quevauviller, Ph., Lachica, M., Barahona, M.E., Rauret, G., Ure, A., Gomez, A., Muntau, H. (1997). The Certification of the EDTA-Extractable Contents (Mass Fractions) of Cd, Cr, Ni, Pb and Zn and of the DTPA-Extractable Contents (Mass Fractions) of Cd and Ni in Calcareous Soil by the Extraction Procedures Given, CRM 600. Report EUR 17555 EN. European Commission, Brussels.
- Räisänen M, Kupiainen K, Tervahattu H. (2005). The effect of mineralogy, texture and mechanical properties of anti-skid and asphalt aggregates on urban dust, stages II and III. *Bulletin of Engineering Geology and the Environment*, 64, 247-256.
- Rexeis, M., and Hausberger, S. (2009). Trend of vehicle emission levels until 2020 - Prognosis based on current vehicle measurements and future emission legislation. *Atmospheric Environment*, 43(31), 4689–4698. <https://doi.org/10.1016/j.atmosenv.2008.09.034>
- Riediker M, Devlin RB, Griggs TR, Herbst MC, Bromberg PA, Williams RW, Casci WE (2004) Cardiovascular effects in patrol officers are associated with fine particulate matter from brake wear and engine emissions. *Particle and Fibre Toxicology* 1(2)
- Rogge, W.F., Hildemann, L.M., Mazurek, M.A., Cass, G.R., Simoneit, B.R.T. (1993). Sources of Fine Organic Aerosol. 3. Road Dust, Tire Debris, and Organometallic Brake Lining Dust: Roads as Sources and Sinks. *Environmental Science and Technology*, 27(9), 1892-1904.
- Ruby, M.V., Schoof, R., Brattin, W., Goldade, M., Post, G., Harnois, M., Mosby, D.E., Casteel, S.W., Berti, W., Carpenter, M., Edwards, D., Cragin, D., Chappell, W. (1999). Advances in evaluating the oral bioavailability of inorganics in soil for use in human health risk assessment. *Environ. Sci. Technol.*, 33, 3697–3705. doi:10.1021/es990479z
- Ruby, M.V., Lowney, Y.W. (2012). Selective soil particle adherence to hands: implications for understanding oral exposure to soil contaminants. *Environ. Sci. Technol.*, 46, 12759–12771. doi:10.1021/es302473q
- Samara, C., Kouimtzi, T., Tsiouridou, R., Kaniyas, G., Simeonov, V. (2003). Chemical mass balance source apportionment of PM10 in an industrialized urban area of Northern Greece. *Atmospheric Environment*, 37, 41–54.
- Samek, L., Stegowski, Z., Furman, L., Fiedor, J. (2017). Chemical content and estimated sources of fine fraction of particulate matter collected in Krakow. *Air Quality, Atmosphere and Health*, 10(1), 47-52. <https://doi.org/10.1007/s11869-016-0407-2>
- Sanders, P.G., Xu, N., Dalka, T.M., Maricq, M.M. (2003). Airborne brake wear debris: size distributions, composition, and a comparison of dynamometer and vehicle tests. *Environmental Science and Technology*, 37, 4060–4069.
- Santoso, M., Lestiani, D.D., Mukhtar, R., Hamonangan, E., Syafrul, H., Markwitz, A., Hopke, P.K. (2011). Preliminary study of the sources of ambient air pollution in Serpong, Indonesia. *Atmospheric Pollution Research*, 2, 190-196. <https://doi.org/10.5094/APR.2011.024>
- Schaap, M., Manders, A.M.M., Hendriks, E.C.J., Cnossen, J.M., Segers, A.J.S., ... Builtjes, P.J.H. (2009). Regional Modeling of Particulate Matter for the Netherlands. <http://www.rivm.nl/bibliotheek/rapporten/500099008.pdf> (accessed 06.07.17).

- Schauer, J.J., Rogge, W.F., Hildemann, L.M., Mazurek, M.A., Cass, G.R., Simoneit, B.R.T. (1996). Source apportionment of airborne particulate matter using organic compounds as tracers. *Atmospheric Environment*, 30(22), 3837-3855.
- Schauer, J.J., Fraser, M.P., Cass, G.R., Simoneit, B.R.T. (2002). Source Reconciliation of Atmospheric Gas-Phase and Particle-Phase Pollutants during a Severe Photochemical Smog Episode. *Environmental Science and Technology*, 36, 3806-3814. <https://doi.org/10.1021/es011458j>
- Schauer, J.J., Lough, G.C., Shafer, M.M., Christensen, W.F., Arndt, M.F., DeMinter, J.T., Park, J.-S. (2006). Characterization of metals emitted from motor vehicles. *Res. Rep. Health Eff. Inst.*, 1-76-88.
- Seneviratne, M.C.S., Waduge, V.A., Hadagiripathira, L., Sanjeevani, S., Attanayake, T., Jayaratne, N., Hopke, P.K. (2011). Characterization and source apportionment of particulate pollution in Colombo, Sri Lanka. *Atmospheric Pollution Research*, 2(2), 207-212. <https://doi.org/10.5094/APR.2011.026>
- Sharma, S., Patil, K.V. (2016). Emission Scenarios and Health Impacts of Air Pollutants in Goa. *Aerosol and Air Quality Research*, 16, 2474–2487. <https://doi.org/10.4209/aaqr.2015.12.0664>
- Shi, G., Chen, Z., Bi, C., Wang, L., Teng, J., Li, Y., Xu, S. (2011). A comparative study of health risk of potentially toxic metals in urban and suburban road dust in the most populated city of China. *Atmos. Environ.*, 45, 764–771. doi:10.1016/j.atmosenv.2010.08.039
- Siciliano, S.D., James, K., Zhang, G., Schafer, A.N., Peak, J.D. (2009). Adhesion and enrichment of metals on human hands from contaminated soil at an arctic urban brownfield. *Environ. Sci. Technol.*, 43, 6385–6390. doi:10.1021/es901090w
- Snipes, M.B. (1989). Long-Term Retention and Clearance of Particles Inhaled by Mammalian Species. *Critical Reviews in Toxicology*, 20, 175-211. <http://dx.doi.org/10.3109/10408448909017909>
- Song, Y., Zhang, Y., Xie, S., Zeng, L., Zheng, M., Salmon, L.G., Shao, M., Slanina, S. (2006). Source apportionment of PM_{2.5} in Beijing by positive matrix factorization. *Atmospheric Environment*, 40(8), 1526-1537. <https://doi.org/10.1016/j.atmosenv.2005.10.039>
- Sowlat, M.H., Naddafi, K., Yuneslan, M., Jackson, P.L., Lotfi, S., Shahsavani, A. (2013). PM₁₀ Source Apportionment in Ahvaz, Iran, Using Positive Matrix Factorization. *Clean – Soil, Air, Water*, 41(12), 1143–1151.
- Sowlat, M.H., Hasheminassab, S., Sioutas, C. (2016). Source apportionment of ambient particle number concentrations in central Los Angeles using positive matrix factorization (PMF). *Atmospheric Chemistry and Physics*, 16(8), 4849-4866. <http://dx.doi.org/10.5194/acp-16-4849-2016>
- Srimuruganandam, B., Shiva Nagendra, S.M. (2012a). Application of positive matrix factorization in characterization of PM₁₀ and PM_{2.5} emission sources at urban roadside. *Chemosphere*, 88, 120–130. <http://dx.doi.org/10.1016/j.chemosphere.2012.02.083>
- Srimuruganandam, B., Shiva Nagendra, S.M. (2012b). Source characterization of PM₁₀ and PM_{2.5} mass using a chemical mass balance model at urban roadside. *Science of the Total Environment*, 433, 8–19. <https://doi.org/10.1016/j.scitotenv.2012.05.082>

- Srivastava, A., Jain, V.K. (2007). Seasonal trends in coarse and fine particle sources in Delhi by the chemical mass balance receptor model. *Journal of Hazardous Materials*, 144, 283–291.
- Sternbeck, J., Sjodin, A., Andreasson, K. (2002). Metal emissions from road traffic and the influence of resuspension—results from two tunnel studies. *Atmospheric Environment*, 36, 4735–4744.
- Sturtz, T.M., Adar, S.D., Gould, T., Larson T.V. (2014). Constrained source apportionment of coarse particulate matter and selected trace elements in three cities from the multi-ethnic study of atherosclerosis. *Atmospheric Environment*, 84, 65-77. <http://dx.doi.org/10.1016/j.atmosenv.2013.11.031>
- Sunyer, J., Esnaola, M., Alvarez-Pedrerol, M., Forns, J., Rivas, I., López-Vicente, M., et al. (2015). Association between traffic-related air pollution in schools and cognitive development in primary school children: a prospective cohort study. *PLoS Med*, 12, e1001792. doi: 10.1371/journal.pmed.1001792
- Sutherland, R.A., Tack, F.M.G., Ziegler, A.D. (2012). Road-deposited sediments in an urban environment: A first look at sequentially extracted element loads in grain size fractions. *J. Hazard. Mater.*, 225–226, 54–62. doi:10.1016/j.jhazmat.2012.04.066
- Taylor, S.R., McLennan, S.M. (1995). The geochemical evolution of the continental crust. *Rev. Geophys.*, 33, 241–265. doi: 10.1029/95RG00262
- Thorpe, A.J., Harrison, R.M., Boulter, P.G., McCrae, I.S. (2007). Estimation of particle resuspension source strength on a major London Road. *Atmospheric Environment*, 41, 8007–8020.
- Thorpe, A.J., and Harrison, R. M. (2008). Sources and properties of non-exhaust particulate matter from road traffic: A review. *Science of The Total Environment*, 400(1–3), 270–282. <https://doi.org/10.1016/j.scitotenv.2008.06.007>
- Thurston, G.D., Spengler, J.D. (1985). A quantitative assessment of source contributions to inhalable particulate matter pollution in metropolitan Boston. *Atmospheric Environ.*, 19, 9–25. doi:10.1016/0004-6981(85)90132-5
- Tian, S.L., Pan, Y.P., Wang, Y.S. (2016). Size-resolved source apportionment of particulate matter in urban Beijing during haze and non-haze episodes. *Atmospheric Chemistry and Physics*, 16(1). <https://doi.org/10.5194/acp-16-1-2016>
- Todeschini, R. (1998). *Introduzione alla chemiometria*. Naples, EdiSES s.r.l. (in Italian)
- Tositti, L., Brattich, E., Masiol, M., Baldacci, D., Ceccato, D., Parmeggiani, S., Stracquandano, M., Zappoli, S. (2014). Source apportionment of particulate matter in a large city of southeastern Po Valley (Bologna, Italy). *Environmental Science and Pollution Research*, 21, 872–890.
- Turner, A., Ip, K.-H. (2007). Bioaccessibility of metals in dust from the indoor environment: Application of a physiologically based extraction test. *Environ. Sci. Technol.*, 41, 7851–7856. doi:10.1021/es071194m
- United Nations, Department of Economic and Social Affairs, Population Division (2015). *World Urbanization Prospects: The 2014 Revision*, (ST/ESA/SER.A/366).
- U.S. EPA (1992). *Preparation of soil sampling protocols: Sampling techniques and strategies*. U.S. Environmental Protection Agency, EPA/600/R-92/128.
- U.S. EPA (2011). *Exposure Factors Handbook 2011 Edition (Final)*, EPA/600/R-09/052F. <http://www.epa.gov/ncea/efh>

- U.S. EPA (2013). Method 1340, In vitro bioaccessibility assay for lead in soil. U.S. Environmental Protection Agency, SW-846 Update VI.
- van Kamp, I., Leidelmeijer, K., Marsmana, G., de Hollander, A. (2003). Urban environmental quality and human well-being. Towards a conceptual framework and demarcation of concepts. A literature study. *Landscape and Urban Planning*, 65, 5–18.
- Varrica, D., Dongarrà, G., Sabatino, G., Monna, F. (2003). Inorganic geochemistry of roadway dust from the metropolitan area of Palermo, Italy. *Environ. Geol.*, 44, 222–230. doi:10.1007/s00254-002-0748-z
- Violante, A., Cozzolino, V., Perelomov, L., Caporale, A.G., Pigna, M. (2010). Mobility and bioavailability of heavy metals and metalloids in soil environments. *J. Soil Sci. Plant Nutr.*, 10, 268–292. <http://dx.doi.org/10.4067/S0718-95162010000100005>
- Visser, S., Slowik, J. G., Furger, M., Zotter, P., Bukowiecki, N., Canonaco, F., Flechsig, U., Appel, K., Green, ... Prévôt, A.S.H. (2015). Advanced source apportionment of size-resolved trace elements at multiple sites in London during winter. *Atmospheric Chemistry and Physics*, 15, 11291–11309. <http://dx.doi.org/10.5194/acp-15-11291-2015>
- VMGA (2014). Vice Ministerio de Gestión Ambiental, D.G. de C.A., 2014. Guía para muestreo de suelos. (in Spanish)
- Von Uexküll, O., Skerfving, S., Doyle, R., Braungart, M. (2005). Antimony in brake pads—a carcinogenic component? *Journal of Cleaner Production*, 13(1), 19–31. doi: 10.1016/j.jclepro.2003.10.008
- Wahlin, P., Berkowicz, R., Palmgren, F. (2006). Characterisation of traffic-generated particulate matter in Copenhagen. *Atmospheric Environment*, 40, 2151–2159.
- Wahlström, J., Söderberg, A., Olander, L., Jansson, A., Olofsson, U. (2010). A pin-on-disc simulation of airborne wear particles from disc brakes. *Wear*, 268, 763–769.
- Wang, H., and Shooter, D. (2005). Source apportionment of fine and coarse atmospheric particles in Auckland, New Zealand. *Science of the Total Environment*, 340, 189–198.
- Wang, Q., Ma, Y., Tan, J., Zheng, N., Duan, J., Sun, Y., He, K., Zhang, Y. (2015). Characteristics of size-fractionated atmospheric metals and water-soluble metals in two typical episodes in Beijing. *Atmospheric Environ.*, 119, 294–303. Doi:10.1016/j.atmosenv.2015.08.061
- Wang, Y., Hopke, P.K. (2013). A ten-year source apportionment study of ambient fine particulate matter in San Jose, California. *Atmospheric Pollution Research*, 4, 398–404.
- Watson, J.G., Cooper, J.A., Huntzicker, J.J. (1984). The effective variance weighting for least squares calculations applied to the mass balance receptor model. *Atmospheric Environ.*, 18, 1347–1355. doi:10.1016/0004-6981(84)90043-X
- Watson, J.G., Chow, J.C., Lu, Z., Fujita, E.M., Lowenthal, D.H., Lawson, D.R., Ashbaugh, L.L. (1994). Chemical Mass Balance Source Apportionment of PM₁₀ during the Southern California Air Quality Study. *Aerosol Science and Technology*, 21(1), 1–36. <https://dx.doi.org/10.1080/02786829408959693>
- Watson, J.G., Chow, J.C., Lowenthal, D.H., Antony Chen, L.W., Shaw, S., Edgerton, E.S., Blanchard, C.L. (2015). PM_{2.5} source apportionment with organic markers in the

- Southeastern Aerosol Research and Characterization (SEARCH) study. *Journal of the Air and Waste Management Association*, 65(9), 1104-1118. <http://dx.doi.org/10.1080/10962247.2015.1063551>
- Wedepohl, K.H. (1995). The composition of the continental crust, *Geochim. Cosmochim. Ac.*, 59, 1217–1232, doi:10.1016/0016-7037(95)00038-2,
- Wei, Z., Wang, L.T., Chen, M.Z., Zheng, Y. (2014). The 2013 severe haze over the Southern Hebei, China: PM_{2.5} composition and source apportionment. *Atmospheric Pollution Research*, 5, 759-768. <http://dx.doi.org/10.5094/APR.2014.085>
- Weinbruch, S., Worringer, A., Ebert, M., Scheuven, D., Kandler, K., Pfeffer, U., Bruckmann, P. (2014). A quantitative estimation of the exhaust, abrasion and resuspension components of particulate traffic emissions using electron microscopy. *Atmospheric Environment*, 99, 175-182. <https://doi.org/10.1016/j.atmosenv.2014.09.075>
- Werkenthin, M., Kluge, B., Wessolek, G. (2014). Metals in European roadside soils and soil solution - A review. *Environmental Pollution*, 189, 98-110. <http://dx.doi.org/10.1016/j.envpol.2014.02.025>
- West, J.J., Cohen, A., Dentener, F., Brunekreef, B., Zhu, T., Armstrong, B., Bell, M.L., Brauer, M., Carmichael, G., Costa, D.L., Dockery, D.W., Kleeman, M.I., Krzyzanowski, M., Künzli, N., Liou, C., Lung, S.-C.C., Martin, R.V., Pöschl, U., Pope, C.A., Roberts, J.M., Russell, A.G., Wiedinmyer, C. (2016). "what We Breathe Impacts Our Health: Improving Understanding of the Link between Air Pollution and Health". *Environmental Science and Technology*, 50(10), 4895-4904.
- Wiseman, C.L.S. (2015). Analytical methods for assessing metal bioaccessibility in airborne particulate matter: A scoping review. *Analytica Chimica Acta*, 877, 9–18. <http://dx.doi.org/10.1016/j.aca.2015.01.024>
- Wragg, J., Cave, M., Basta, N., Brandon, E., Casteel, S., Denys, S., Gron, C., Oomen, A., Reimer, K., Tack, K., van de Wiele, T. (2011). An inter-laboratory trial of the unified BARGE bioaccessibility method for arsenic, cadmium and lead in soil. *Sci. Total Environ.*, 409, 4016–4030.
- Xue, Y.H., Wu, J.H., Feng, Y.C., Dai, L., Bi, X.H., Li, X., Zhu, T., Tang, S.B., Chen, M.F. (2010). Source Characterization and Apportionment of PM₁₀ in Panzhihua, China. *Aerosol and Air Quality Research*, 10, 367–377. <http://dx.doi.org/10.4209/aaqr.2010.01.0002>
- Yamamoto, N., Takahashi, Y., Yoshinaga, J., Tanaka, A., Shibata, Y. (2006). Size distributions of soil particles adhered to children's hands. *Arch. Environ. Contam. Toxicol.*, 51, 157–163. doi:10.1007/s00244-005-7012-y
- Yanosky, J.D., Tonne, C.C., Beevers, S.D., Wilkinson, P., Kelly, F.J. (2012). Modeling exposures to the oxidative potential of PM₁₀. *Environmental Science and Technology*, 46 (14) 7612–7620.
- Yi, S.M., Hwang, I. (2014). Source Identification and Estimation of Source Apportionment for Ambient PM₁₀ in Seoul, Korea. *Asian Journal of Atmospheric Environment*, 8(3), 115-125. <http://dx.doi.org/10.5572/ajae.2014.8.3.115>
- Yu, B., Wang, Y., Zhou, Q. (2014). Human health risk assessment based on toxicity characteristic leaching procedure and simple bioaccessibility extraction test of toxic

- metals in urban street dust of Tianjin, China. *PLoS ONE*, 9, e92459. doi:10.1371/journal.pone.0092459
- Yu, L., Wang, G., Zhang, R., Zhang, L., Song, Y., Wu, B., Li, X., An, K., Chu, J. (2013). Characterization and Source Apportionment of PM_{2.5} in an Urban Environment in Beijing. *Aerosol and Air Quality Research*, 13, 574–583. <http://dx.doi.org/10.4209/aaqr.2012.07.0192>
- Zeng, F., Shi, G.L., Li, X., Feng, Y.C., Bi, X.H., Wu, J.H., Xue, Y.H. (2010). Application of a Combined Model to Study the Source Apportionment of PM₁₀ in Taiyuan, China. *Aerosol and Air Quality Research*, 10, 177–184. <http://dx.doi.org/10.4209/aaqr.2009.09.0058>
- Zhao, P., Feng, Y., Zhu, T., Wu, J. (2006) Characterizations of resuspended dust in six cities of North China. *Atmospheric Environment*, 40, 5807–5814. <https://doi.org/10.1016/j.atmosenv.2006.05.026>
- Zheng, N., Liu, J., Wang, Q., Liang, Z. (2010). Health risk assessment of heavy metal exposure to street dust in the zinc-smelting district, Northeast of China. *Sci. Total Environ.*, 408, 726–733. <http://dx.doi.org/10.1016/j.scitotenv.2009.10.075>
- Zhu, D., Gilles, J.A., Etyemezian, V., Nikolich, G., Shaw, W.J. (2015). Evaluation of the surface roughness effect on suspended particle deposition near unpaved roads. *Atmospheric Environment*, 122, 541–551. <https://doi.org/10.1016/j.atmosenv.2015.10.009>
- Zia, M.H., Codling, E.E., Scheckel, K.G., Chaney R.L. (2011). In Vitro and in Vivo Approaches for the Measurement of Oral Bioavailability of Lead (Pb) in Contaminated Soils. *Environmental Pollution*, 159, 2320–2327. doi:10.1016/j.envpol.2011.04.043