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Effect of agronomic management on risk of suspended solids and phosphorus losses from soil to waters

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Potential phosphorus losses from soil as affected by fertilisation practices in two agronomic

systems

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Abstract

Phosphorus, through agriculture that is considered the principal non-point source of P, largely contributes to eutrophication which compromises the ecosystem and services associated to the fresh water environment favouring the algae growth. The agronomic management and the fertilisation practices affect the risk of soil and P losses during a runoff event modifying the behaviour of soil components.

Generally the impact of fertilisation management practices is focused on nitrogen losses in line with environmental directives. However in many European countries still scant attention has been devoted to the effect these practices may have on P accumulation and losses, although the unbalanced N/P ratio in manure and slurry compared to that required by crops.

The fertilisation practices, modifying the equilibrium between nutrient in soil, may induce some important effect on the accumulation of P in different forms, on the soil and finest particles degree of saturation and, in general, on the soil behaviour during a mobilization processes. Considered the particulate P (PP) as the major form that represents at least the 70% of the amount of total P lost, the study focus on evaluating the different kind of fertilisation, inorganic or organic, on the potential soil and P losses to water via runoff. Special aims is devoted to understand if the fertilisation could affect the dispersive processes in soil involving only selected soil particles.

Key words: phosphorus, suspended sediment, fertilisation, eutrophication

Introduction

Phosphorus is the limiting element to growth of blue-green algae and can contribute to eutrophication compromising the quality of freshwater environments (Sharpley and Rekolainen, 1997). Agriculture is considered as principal non point P source and its management is the most cause of soil P enrichment (Mainstone et al., 2008). On the other hand, the intensification of livestock production has led to increase the soil P concentration in localised areas, and manure application represents one of the greatest threats to water quality in agricultural regions (Sims et al., 2000).

Soils subjected to long-term and continuous agricultural fertilisation may accumulate high amounts of P, both inorganic and organic, depending on the type of fertiliser and agricultural management. After long term P application, Sharpley and Smith (1995) found that the increase in P was greater for inorganic P than organic P on plots where slurry and manure have been applied up 35 years. Rubaek and Sibbesen (1995), in contrast, found no difference in the amounts of total organic P between plots receiving NPK fertiliser and plots receiving slurry for 100 years. In general, organic fertiliser application has been shown to increase soil total, available and soluble P levels, but may reduce soil P adsorption capacity and increase biologically-mediated turnover of organic P due to stimulation of microbial and enzyme activities (Tiessen et al., 1994). Thus the organic P added with animal manure is quickly mineralised and the level

of total organic P depends more on the cropping system and tillage rather than on P source (Rubaek and Sibbesen, 1995).

It should be also considered that the environmental concerns linked to agriculture and livestock production have led many European member states to promote the voluntary or mandatory use of agricultural practices that limit water pollution and enhance soil quality, especially with the aim of reducing nitrogen surpluses in livestock farms (Goodlass et al., 2003; Hanegraaf and den Boer, 2003; Swensson, 2003) and in particular to direct the management action Programmes that the European Community Nitrate Directive has imposed in vulnerable zones (EEC, 1991). Several experimental trials have been assessed to evaluate the impact of fertilisation management practices on nitrogen losses following the application of organic fertilisers in line with those directives (i.e. Grignani et al., 2007, Lugato et al., 2006). However in many European countries still scant attention has been devoted to the effect these practices may have on P accumulation and losses, although the unbalanced N/P ratio in manure and slurry compared to that required by crops.

Both inorganic and organic P fertilisers may increase P losses through leaching and runoff. However, the most significant part of P losses occurs through horizontal pathway, as erosion and runoff movements (Gburek et al., 2005), following storm flow events or irrigation practices. Phosphorus is transferred to waters as particulate P (PP) or soluble P (RP) (Uusitalo et al., 2003), the former representing more than 80% of total transferred P (Borda et al., in press). The amount of P lost as particulate is related to different soil properties and to the various P forms which affect the accumulation in the finest soil particles and the equilibrium between particle dispersion and aggregation (Borda et al., in press), although the extent and mechanisms of these effects are still unknown.

Other factors such as P sorption capacity may drive the fate of P in over fertilised soils (Borling et al., 2004). Degree of P saturation estimates how close the soil is to saturation (Sharpley, 1995) and provides possibilities to compare soils with varying P sorption capacities. It can be thus useful as an estimate of P source in risk assessment systems (van der Zee et al., 1989). However, the composition of the finest particles and their degree of P saturation may change the total amount of P lost as the association of strongly sorbing compounds such as phosphate with colloids may enhance their mobility (Kretzschmar et al., 1999; Siemens et al., 2004). Inorganic P attached to particulate matter eroded is affected by adsorption/desorption phenomena that influence the particle surface charge, and hence soil dispersion. At large degree of P saturation, a high fraction of P is reported to be sorbed to dispersed particles, mainly due to their large surface area (Kretzschmar et al., 1999). Phosphate sorption may cause a reversal of the positive charge of oxides, increasing the electrostatic repulsive forces. That means that a certain P saturation of the sorbent may mark a change point for the release of colloidal P, similar to the change point for the mobilisation of dissolved P (Puls & Powell, 1992). The increase of colloidal P concentrations with increasing degree of P saturation might be related to an increasing P concentration in the individual colloidal particles or to an additional release of colloids from the soil. Organic P forms may affect colloidal dispersion as well, dependent on their charge and on their charge/mass ratio (Celi & Barberis, 2005). However, little information exists on the reciprocal effects of the different P forms on P losses as affected by different fertilisation practices and on the characteristics of the dispersed particles.

The aim of this study was to evaluate the role of different fertilisation practices on the potential risk of P losses from soil to water bodies in a middle term experimental field with homogeneous soil properties. The systems have been subjected for 15 years to different maize-based crops and fertiliser management focused on risk of nitrogen losses. In this work we evaluated the changes on P build-up, the consequent P mobilisation with special emphasis to quantify particulate P forms and characterise the mobilised soil particles.

Material and methods

Site characteristics

The soils were sampled in Tetto Frati, the Agri-environment experimental station of the Department of "Agronomia, Selvicoltura e Gestione del Territorio" of the University of Turin (NW, Italy). The site is located in the western area of the river Po plain (229 m a.s.l.) at a latitude of 45°N, and is characterised by a scarcely weathered alluvial soil, classified as a Typic Udifluvent (USDA, 1998).

The climate is temperate, characterised by two main rainy periods. During the experimentation period, from 1992 to 2007, the mean annual precipitation was 792 mm and the mean annual temperature 11.8°C (Grignani et al., 2007).

Experimental trials and treatments

The experimental site was a randomised block with three replicates cultivated with maize (Zea mays, L.) for silage (MS) and for grain (MG) at high nitrogen fertilisation levels. The different trials were subjected to mineral treatments and to organic fertilisation, with solid manure (M) and slurry (S). The fertilisation levels were:

- 300 kg N ha⁻¹ like urea and 100 kg N ha⁻¹ as urea and 59 kg P ha⁻¹ at ridging (NPK) ✓
- No N addition and 59 kg P ha⁻¹ at ridging (PK) ✓
- ✓ 100 t ha⁻¹ bovine slurry, supplying in average 230 kg N ha⁻¹ and 74 kg P ha⁻¹, and 100 kg N ha⁻¹ as urea and 32 kg P ha⁻¹ at ridging (S)
- ✓ 40 t ha⁻¹ bovine solid manure, supplying in average 280 kg N ha⁻¹ and 113 kg P ha⁻¹, and 100 kg N ha⁻¹ as urea and 32 kg P ha⁻¹ at ridging (M).

The plots treated with organic fertilisers had a surface of 75 m² (7.5 x 10 m) while those treated with mineral fertilisers had a surface of 45 m² (4.5 x 10 m), to allow the use of common farm machines. The plots and treatments were established in 1992 and still ongoing. Nutrient balance

A simple P balance was calculated for each plot from the difference between the supply as organic or mineral fertilisers and removal as crop yields. This difference, called surplus, was either positive (input > output) or negative (output > input). Organic fertilisers were sampled just before spreading and were characterised, as reported in Grignani et al. (2007). Nutrients content, as organic carbon, total nitrogen and P, was higher in the manure than in the slurry. The amount of organic carbon resulted up to 84 kg t⁻¹ of fresh matter compared to the 20.9 kg t⁻¹ of fresh matter determined in average in the slurry. Total P was 2.2 kg t⁻¹ of fresh matter compared to 0.6 kg t⁻¹ for the slurry. It resulted important to consider the percentage of dry matter, that, as expected, was higher for the manure than for the other one (25.7 vs 5.7%, respectively) (Grignani et al., 2007).

The above-ground crop biomass production was assessed each year in a 18 m² sampling area. In the case of maize for grain, the plant was divided into kernel and crop residues, including stalks, leaves, cobs and bracts. Productions were expressed as oven dried matter (Grignani et al., 2007) and total P was measured (microwave acid digestion followed by determination with ICP spectrometry).

Soil characterisation and dispersion test

The soil (Typic Udifluvent) is deep with a loam texture in the Ap horizon, silty loam in the AC, C1, and C2 horizons, and sandy loam in the deeper C horizons. The pH is subalkaline due to the presence of calcium carbonate, the cation exchange capacity low as well as the content of exchangeable K. Soils were sampled from the Ap horizons of each plot, air dried, and sieved at <2 mm.

Total C and total N contents were determined using a CN analyser (CE Instruments, NA2100 Protein, Milan, Italy). Carbonates were determined volumetrically. Organic C was obtained by difference between total and organic C. Total phosphorus was determined after soil H_2SO_4 -HClO₄ digestion (Kuo, 1996) by measuring the amount of P in solution as described by Ohno and Zibilske (1991). Available P was extracted according to Olsen et al. (1954) and determined colorimetrically by the ascorbic acid molybdate blue method. Organic P content as determined by the NaOH-EDTA extraction was done following the method of Bowman and Moir (1993) and modified by Turner et al. (2003).

The soil dispersion simulation was carried out using a gentle water dispersion test (hereafter called DESPRAL test) as described in Withers et al. (2007), shaking 20 g of soil (< 2 mm) in 1 L of water and collecting, following the sedimentation time, 25 mL of soil suspensions containing particles < 20 µm. The amount of total suspended solid (TSS) was determined by UV-vis absorption at 420 nm in the collected suspensions (Hitachi U-2000 Uv-vis spectrophotometer, Tokyo, Japan).

Determination of P forms in the suspended solid

On the obtained suspensions total phosphorus (TP) was determined after and before sulpho-perchloric digestion (Martin et al., 1999). Total dissolved phosphorus concentration (TDP) and Reactive P (RP) were determined after filtration of the samples through Albert RC-membrane 0.45 µm filters. Phosphorus content on the different solutions was measured using the Ohno and Zibilske (1991) method as modified by Martin et al. (1999).

The particulate P concentration (PP) was calculated subtracting TDP from TP and the unreactive P concentration (UP) was calculated as difference between TDP and RP, as suggested by Haygarth and Sharpley (2000).

All results were expressed as average of two analytical replicates for the three soil replicates.

Bulk soil and suspended solid Phosphorus Saturation Indexes on the maize for grain system

The degree of P saturation index (DPS), expressed as percentage of soil P saturation, was calculated following the method by van der Zee et al. (1989):

$DPS = P_{ox} / 0.5 * (Fe_{ox} + AI_{ox})$

The amount of poorly crystalline Fe and AI (hydr)oxides (Fe_{ox}, Al_{ox}) was determined by treating 1 g of soil samples with an ammonium oxalate solution (1:50 w/v) buffered at pH 3 (Schwertmann, 1964) and the Fe and AI contents were measured by atomic absorption spectrometry. The amount of P in the same extracts, released from Fe and AI oxides, was determined.

The Phosphorus Saturation Index (PSI) using a single point as described by Bache and Williams (1971) and modified by Borling et al. (2001) was used only to characterise the soil samples. Two grams of airdried soil (<2 mm) were equilibrated with 20 mL 0.01 M CaCl₂ containing a single maximum amount of KH_2PO_4 (50 mmol P kg⁻¹ soil) in plastic centrifuge tubes. Two drops of toluene were added to inhibit microbial activity. The tubes were shaken at 20°C for 20 h. The suspensions were centrifuged at *1600 g* for 10 min and filtered, and P was determined colorimetrically. The amount of sorbed P (Qa) was obtained by subtracting the amount of P remained in the solution (Ce) to the added P. The Phosphorus Saturation Index (PSI) was calculated as:

PSI= Qa/ log₁₀ Ce

Characterisation of total suspended soils

The suspended solid collected after the application of the DESPRAL test, as simulation of the potential amount of soil-P lost during a runoff event is characterised for the total C and total N contents, determined using a CN analyser (CE Instruments, NA2100 Protein, Milan, Italy). The concentration of total P (TP) was determined, as described above, after sulpho-percloric digestion.

To determine the poorly crystallised Fe and Al hydro(oxides), the amount of P released from the oxides the 25 mL of collected sample was ultra-centrifuged at *2600 g* for 10 min to separate the suspended solid. Ammonium oxalate buffered at pH 3 (Schwertmann, 1964) was added to the collected solid (1/50 w/v). Fe_{ox} and Al_{ox} were determined reading the atomic absorbance, while P_{ox} contents was analysed colorimetrically.

The concentration of total Ca on the suspended solid was determined after 16 h of extraction in HCI (1M) and by reading the atomic absorbance.

The degree of P saturation (DPS), as for the soil sample, was determined considering the amount of P as related to the amount of Fe and AI extracted in ammonium oxalate and corrected for a 0.5 value.

The index of suspended solid C and P enrichment, compared to the amount of soil C and P, the CER (Carbon enrichment ratio) and the PER (Phosphorus enrichment ratio) was calculated.

The electrophoretic mobility was measured by Laser Doppler Velocimetry coupled with Photon Correlation Spectroscopy using a DELSA 440 spectrometer (Beckman Coulter Electronics, Hialeah, FL) equipped with a 5-mW HeNe laser (632.8 nm). The electrophoretic mobility of the solid suspension, obtained by DESPRAL test, was measured at four different angles (8.6, 17.1, 25.6 and 34.2°) and the data were converted to zeta potential (ζ) using the Smoluchowski equation (Hunter, 1998). *Statistical evaluation*

The effect of agronomic systems and fertilisation management on soil dispersibility, P losses and P forms were tested by analysis of variance (ANOVA). If the F-test was significant (p < 0.05), the means were compared using Bonferroni's test. Data were compared using Pearson correlation to see the relationship between soil properties and soil and P losses.

Results

Nutrient balance, soil characteristics and dispersion test

Different agronomic systems and fertiliser management considerably affected nutrient balance and some soil properties during the 15 years of experiment (Table 1). The nutrient balance showed that maize for grain (MG) in all fertiliser systems led to a larger P surplus compared to maize for silage (MS), as a large part of P returned into soil with crop remains, although the higher P uptake by the maize for grain. In

both agronomic systems the lowest P surplus in the nutrient balance was observed in the plot with NPK fertilisation. In the plot where the same amount of P fertiliser was applied but no N (PK fertiliser), a larger P surplus in the nutrient balance was found, as a result of the lower P output by plants. Where slurry or manures were applied, always keeping constant N application, P surplus was more than doubled after 15 years of treatment, especially in the manured plot but not statistically differences were found between the organic fertilisers.

The soil (Ap horizon, 0-30 cm) presented a pH around 8 in all plots, a low CEC (in average 10 cmol₍₊₎/kg) and a loamy texture (data not shown). The soil trials differed instead with a wide range in total P, bioavailable phosphorus and organic matter (Table 1).

Soil total P was directly affected by agronomic systems and fertiliser management. Mean values ranged from 855 - 1023 mg kg⁻¹ in mineral trials to 978 - 1135 mg kg⁻¹ in organic treated trials. In both systems the amount of total P following slurry or manure application increased and was statistically different compared to that in the mineral fertiliser plots (p < 0.05).

Olsen P was tightly related to the nutrient balance with lower values in the MS systems (from 5.0 to 42.9 mg kg⁻¹) compared to the MG ones (from 11.3 to 52.3 mg kg⁻¹). For both systems Olsen P levels increased in the order: PK < NPK < S < M (p < 0.05). Organic P, as estimated by difference between total and inorganic P in the NaOH-EDTA extraction, ranged, in average, from 87 in PK to 172 mg kg⁻¹ in manured treated plots, accounting in all plots for less than 15% of soil total P. The amount of organic P increased in order PK < NPK < S < M, but not significant differences were observed.

The same was observed for the soil organic matter content: higher values were found in the MG plots compared to MS ones (p < 0.05); in 15 years organic fertilisation increased the SOM level of about 10% in the MG plots and of 18% in the MS plots but no statistical differences were found between manure and slurry application. The TOC/TN ratio did not vary between systems and fertiliser management and the mean values were around 10.

In Table 2, DESPRAL test showed similar amounts of the total suspended solid (TSS) in the MS (from 0.86 to 1.26 g L⁻¹) and MG systems (from 0.89 to 1.15 g L⁻¹). Soil dispersibility was statistically higher in the mineral fertilised plots than in the organic treated ones (p < 0.05), but no differences were found between NPK and PK plots or between manure and slurry applied plots. The amount of soil dispersed led to a solid /solution ratio of 1/800 in average with the higher values in the mineral plots.

The amount of total P lost in the dispersion soil test (TP) followed the same trend in the two agronomic systems (from 1.58 to 2.01 mg L⁻¹ in MG and from 1.59 to 1.98 mg L⁻¹ in MS), increasing in plots where manure and slurries were applied (p < 0.05). The same behaviour was observed for particulate P. The particulate P lost during the soil dispersion test was the highest form of total P, accounting in average for 92%. The reactive P fraction was from 0.03 to 0.25 mg L⁻¹ in MG and from 0.01 to 0.17 mg L⁻¹ in MS, with a sharp increase in manured plots (p < 0.05). The soluble un-reactive fraction (UP), that roughly corresponds to the organic forms, did not differ between agronomic systems or kind of fertilisation and ranged in MG system from 0.01 to 0.05 mg L⁻¹. No differences were observed among the fertiliser treatments in the MS system.

The particulate P bound to the dispersed solid (PP/TSS) ranged from 1.41 - 1.53 to 1.84 - 2.18 mg g⁻¹ in MG and MS systems, respectively. Low and similar ratios were found in both mineral and slurry treated plots, while much higher values were observed in the manured plots (p < 0.05).

Bulk soil and suspended solid characterisation on a maize for grain system

Bulk soil saturation P indexes

The extraction of Fe, AI and P in ammonium oxalate is reported in Table 3. The contents of Fe_{ox} and AI_{ox} were not statistically different among the plots while P_{ox} ranged from 268 in NPK treated soil to 420 mg kg⁻¹ in the manured plot. Only the continuous application of manure increased significantly the amount of P bound to (hydro)oxides (p < 0.05).

The degree of P saturation in soil (DPS_{soil}) increased in the order NPK < PK = S < M (p < 0.05) following the same trend of P_{ox}. This index was compared to P sorption index (PSI) to obtain an estimate of the residual P buffer capacity of soil. Results showed that mean values ranged between 0.07 and 0.22 with the lowest value in the manured soil and the highest in the PK fertilised soil.

Suspended solid characterisation

The type of fertilisation affected some chemical properties of the suspended solid responsible for P mobilisation.

In the dispersed solid, the amount of P supposed to be bound to (hydro)oxides did not vary depending on fertiliser treatments and no differences were observed (in average 996 mg P kg⁻¹ solid), while Fe and Al extracted in oxalate decreased in the order NPK > PK > S > M. The application of manure rather than other fertilisers decreased significantly the amount of poorly crystallised iron and aluminium forms in the dispersed solid (p < 0.05). The degree of P saturation in the dispersed solid (DPS_{solid}) increased from 36% in the NPK fertilised plots to 52% in the manured plots, but not statistical differences were found.

The suspended solid was characterised by different content of TP, C and N increasing, statistically significant (p < 0.05), in the order NPK < PK = S < M (Table 4). The amount of organic C and N resulted, as expected, well correlated to total P. Moreover, results showed a significant relationship between the solid PER and solid CER ($r^2 = 0.983$), indicating that P enrichment was related to organic matter accumulation in the dispersed particles. The amount of total Ca ranged from 1052 mg kg⁻¹ in the PK mineral plot to 2224 mg kg⁻¹ in the slurried treated one.

The ζ potential was highly negative on the dispersed particles obtained from the NPK (-27 mV) and, to a less extent, PK (-20 mV) dispersed solids, while it was closer to neutrality in the slurried (-18 mV) and in the manured solids (-16 mV) where the amount of total Ca was higher.

Discussion

In the experimental field under study where management was based on N fertiliser efficiency without considering the unbalance between the N/P ratio in the organic fertilisers and that required by plant, the P surplus derived from balance between P input and output was more than 2-fold higher in the slurried plot and even 3-fold higher in the manured plot compared to the mineral treated ones after 15 years of continuous applications. This is in line with other studies (i.e. Takahashi et al. 2007; Monaco et al., 2009; Vogeler et al., 2009) that showed a large increase of nutrients (P, C, N) following long term organic waste application or P fertilisation, inorganic and organic, but a modest increase of organic P form nevertheless the high amount of organic fertiliser applied.

The P balance showed immediately a picture of nutrient disequilibrium obtained by irrational fertilisation compared to N budges evaluated in a previous study (Grignani et al., 2007). The P surplus provoked a P increase in soil both as total and bio-available forms. However, the excess of P in the sewaged soils was not consistent with the relatively lower increase in soil total P, indicating that a part of the nutrient applied remained unaccounted. An estimate of P unaccounted in the 0-30 cm layers was obtained by evaluating the increment of P surplus and of soil total P in each treatment with respect to the values in the NPK plot, considered as the control system because nearly balanced (Table 5). From this assumption it appeared that, in 15 years, P unaccounted was 7, 41, and 33% of P surplus in the MG mineral PK, slurried, and manured plots, respectively. In the maize for silage system the values were similar, except in the manured plot where the P unaccounted was only 11% of P surplus. Phosphorus unaccounted may be considered as a P mobility index in relation with the agronomic management and showed that, as expected, a high percentage of P was lost from the Ap horizon in the slurry treated plots. This resulted in agreement with many studies showing that organic fertiliser application, especially as slurry, may enhance the translocation into depth as related to the level of soil P saturation (Ulen, 2003; Chardon et al., 2007).

The different fertilisation and, at a less extent, agronomic management affected soil disperdibility and then P losses (Tarkalson et al., 2004; Sharpley & Withers, 1994). The major P losses found in the soil suspension were in the particulate form (90% of total P lost) as often observed during runoff events (Withers et al., 1999; Uusitalo et al., 2001; Udeigwe et al., 2007). The two crop systems produced similar amounts of particulate P expressed as percentage of total P lost in the soil dispersion test, while the fertiliser management induced significant differences (p < 0.05). The percentage of particulate P relative to total P dispersed increased in the order M < S < NPK < PK. Thus, manure application produced a lower amount of PP than the other fertilisers, but a higher P soil particle enrichment, indicating that the plots receiving organic fertilisers were less dispersible, but their particles were more P enriched. This suggested a preferential accumulation of total P on the particles < 20 μ m favoured by the sandy-loamy texture, as the P enrichment ratio (PER) exponentially increases with declining of clay content (Gburek et al., 2005).

The relationship between Olsen P and soluble P (RP) (Figure 1a) was linear indicating that this soil P test is a good predictor to estimate the losses of soluble P (Siemens et al., 2008; Vadas et al., 2009; Borda et al., in press). However the RP was the less representative fraction of the total P lost, nevertheless the high P surplus in the sewaged treatments, and it was below the P_{Olsen} change point (Heckrath et al., 1995). Soluble P was affected by the fertilisation management with the higest values in the slurried and manured plots. This means that in soils where continuous application of organic wastes or manures has raised an excessive soil P content and has decreased its P sorption capacity, the risk of P losses via leaching becomes more relevant (Heckrath et al., 1995; Sims et al., 1998; Hooda et al., 2001).

Particulate P was not directly related to Olsen P content and, even if the soil was homogeneous, seemed independent of soil fertilisation or agronomic management (Figure 1b). This pointed out that organic and mineral fertilisation may contribute to soil dispersion and P losses through different mechanisms. Particulate P losses may be first controlled by the amount of soil dispersed ($r^2 = 0.648$, Figure 2) as reported by Uusitalo et al. (2000) and Withers et al. (2007). When organic fertilisation is used, the amount of disperdible particles may decrease as organic matter incorporation into soil favours aggregation processes. This may explain why the amount of soil easily dispersible was lower in the manured plot than in the other plots and first dependent on bulk soil organic matter. The use of organic fertilisers led in 15 years to significant C increase in the bulk soil which may favour aggregate stability (Auerswald, 1995) and then limit particle dispersibility (Withers et al., 2007). However, the negative relationship between total suspended solid (TSS) and the soil organic matter content, even if significant, showed a low linearity coefficient ($r^2 = 0.24$), considering both systems and improved ($r^2 = 0.51$) when only the MG system was taken into account. In our case, where an unbalanced N/P fertilisation occurred, the high amount of P added in the manured and slurried soils contrasted the aggregation effect determined by addition of organic fertilisers and crop residues.

From these findings it appears that the amount of P lost as particulate is controlled by the opposite effect of P and organic matter on aggregation/dispersion phenomena and explains why only the amount of PP per unit of solid dispersed (PP/TSS) was related to Olsen P (Figure 3) (p < 0.05), in both MG and MS systems.

Slurry and manure application led to a relatively higher increase in inorganic P rather than in organic P forms. In these systems organic P added with animal manure and slurry was likely quickly mineralised due to the large amount of degradable SOM and to an active microbial biomass (Tiessen et al., 1994), as shown by previous basal respiration studies at the same site (Monaco et al., 2008). This is in agreement with several experiments comparing mineral and organic fertilisers (i.e., Sharpley and Smith, 1995), where the level of total organic P has been reported to be affected more by the cropping system and tillage than by the P source (Rubaek and Sibbesen, 1995).

In MG system, all plots presented a high degree of P saturation close to 40%, reported as the maximum level reachable in soil (van der Zee, 1989). The dispersed solid appeared always more saturated than the bulk soil, due to the larger reactive surfaces of the finest particles. As a result, the P enrichment ratio in the dispersed solid compared to the bulk soil was always higher than 1, but not proportional to the P surplus. Especially in the manured plot, where P surplus was very high, soil and dispersed solid were similarly saturated, confirming that this soil has reached the maximum P sorption capacity to buffer P addition. Moreover the finest particles detached were C enriched and depleted in poorly crystallised Fe and Al oxides. Particle composition and P sorption may affect surface electrical charge and hence soil disperdibility (Barrow, 2000; Celi et al., 1999). In our study disperdible particles from mineral plots were characterised by a higher negative charge compared to the organic treated ones. This may indicate that in mineral fertilised plots surface charge and then soil disperdibility is governed by P sorption (Lima et al., 2000) while in organic fertilised systems electrical charge is more difficult to predict due to the reciprocal effect of P and organic compounds reacting with the clay surfaces (Violante and Pigna 2002). In addition, manure and slurry application may have improved carbonate dissolution and consequent precipitation of Ca-phosphates, which can further neutralise the surface negative charge through bridging with phosphate or salt co-precipitation (Celi et al., 2000). However, the suspended solid showed only a slightly higher amount of exchangeable Ca in the organic than in mineral treatment and further investigations on Ca forms should be done to better understand the process.

Conclusions

The fertilisation management, mineral or organic, strongly modifies the P biogeochemical processes which drive soil P build-up and mobilisation. In this work a controlled experimental field where the soil properties were homogeneous was studied. From our findings we observed that manure and slurry application, focused on N for 15 years, has led to a very larger P soil surplus compared to a more balanced NPK mineral fertilisation. However, the contrasting effect of manure fertilisation on dispersion/aggregation processes resulted in minor losses of P in the particulate forms than those expected from the uncontrolled P increase and high Olsen P. In the slurry treated soil a large amount of P remained unaccounted in the 0-30 cm layer, due to vertical translocation of P forms into deeper horizons. The remaining P fraction in the topsoil behaved as that in the PK system, where mobilisation of P via runoff was affected by un-balanced nutrient ratio and different P plant uptake.

In both organic fertilised systems an important part of P was lost in the soluble form indicating that, in soils which have reached excessive P levels, the risk of P losses via leaching becomes more relevant than expected.

While soluble P may be predictable from Olsen P values, the amount of P lost in the particulate form was not estimated using soil properties. Intensive P addition, mineral vs organic fertilisation, and unbalanced nutrient ratio may cause important modifications in soil disperdibility, P cycling and then P mobilisation. Moreover, the different composition of the dispersed particles highlights that strong modifications may be determined by the type of fertilisation and affect the impact of particulate P on water quality.

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Table 1. Phosphorus removal and surplus, soil Total P (TP), Olsen P, organic P (P_{org}), soil organic matter (SOM) and TOC/TN ratio in the Ap horizon of soils cultivated with maize for grain (MG) and maize for silage (MS) and treated with mineral (NPK and PK) or organic (slurry, S, and manure, M) fertilizers in a long term platform (NW Italy).

Cropping system	Fertiliser	P removal	P surplus	Total P	Olsen P	P _{org}	SOM	TOC/TN
		kg ha	¹ y ¹		mg kg ⁻¹	g kg ⁻¹		
	NPK	35	30	1015	22	101	19	10
MC	PK	27	37	1031	11	87	20	10
WG	S	36	85	1087	24	117	24	11
	М	35	109	1167	52	172	23	11
	NPK	49	16	827	20	n.d.	17	10
MS	PK	43	22	882	5.0	n.d.	18	11
IVIS	S	55	66	909	26	n.d.	23	11
	М	58	87	1047	43	n.d.	20	11
Statistical analysis								
	Mean							
Cropping	MG	33	65	1074	27	119	22	10
system	MS	51	48	926	24	nd	19	11
Significativity		0.00	0.00	ns	ns	ns	ns	ns
	Mean		-					
	NPK	42 b	23 d	921 b	21 b	87	19 b	10
Fortilisors	PK	35 b	29 c	956 b	8.2 c	101	18 b	10
i ertinsers	S	45 a	75 b	998 b	25 b	117	22 a	11
	Μ	46 a	98 a	1107 a	48 a	172	24 a	11
Significativity		0.00	0.00	0.03	0.00	ns	0.05	ns

Cropping systems X fertiliser and block effect not significant

Table 2. Total suspended solids (TSS) and total P (TP), total dissolved P (TDP), reactive P (RP), particulate P (PP) un-reactive P (UP) in the suspensions obtained using the DESPRAL test from the Ap horizon of soils cultivated with maize for grain (MG) and maize for silage (MS) and treated with mineral (NPK and PK) or organic (slurry, S, and manure, M) fertilisers in a long term platform (NW Italy).

Cropping systems	Fertilisers	TSS	TP	TDP	RP	PP	UP	PP/TP	PP/TSS
		g L⁻¹			$mg L^{-1}$			%	$mg g^{-1}$
	NPK	1.15	1.89	0.11	0.10	1.78	0.02	94	1.57
MG	PK	1.07	1.69	0.05	0.03	1.65	0.01	97	1.53
MG	S	0.89	1.58	0.13	0.10	1.46	0.03	92	1.65
	М	0.83	2.01	0.29	0.25	1.72	P OP 78 0.02 65 0.01 46 0.03 72 0.05 59 0.03 76 0.02 49 0.03 77 0.03 65 0.03 65 0.03 65 0.03 65 0.03 18 ns 68 0.01 b 70 0.02 b 47 0.03 ab 74 0.04 a 115 0.00	86	1.84
	NPK	1.41	1.68	0.09	0.06	1.59	0.03	95	1.74
MS	PK	0.91	1.79	0.03	0.01	1.76	0.02	98	1.41
IVIS	S	0.86	1.59	0.10	0.07	1.49	0.03	94	1.74
	М	0.85	1.98	0.20	0.17	1.77	0.03	90	1.81
Statistical analysis									
	Mean								
Cropping system	MG	1.00	1.79	0.14	0.12	1.65	0.03	92	1.65
	MS	0.98	1.76	0.11	0.08	1.65	0.03	94	1.68
Significativity		ns	ns	ns	ns	ns	ns	ns	ns
	Mean								
	NPK	1.28 ab	1.79 ab	0.10 b	0.08 b	1.68	0.01 b	94 b	1.66 ab
Fortilisors	PK	0.99 b	1.74 ab	0.04 b	0.02 b	1.70	0.02 b	98 b	1.47 b
T ertilisers	S	0.87 a	1.59 b	0.11 b	0.09 b	1.47	0.03 ab	93 b	1.69 ab
	М	0.84 a	1.99 a	0.25 a	0.21 a	1.74	0.04 a	88 a	1.83 a
Significativity		0.01	0.05	0.00	0.00	ns	0.00	0.00	0.01

Cropping systems X fertiliser and block effect not significant

Table 3. Fe, AI and P, extracted in oxalate (Fe_{ox}, AI_{ox} and P_{ox}), degree of P saturation (DPS) and P sorption index (PSI) of bulk soils from the maize for grain system (MG) treated with mineral (NPK and PK) or organic (manure, M, and slurry, S) fertilisers in a long term platform (NW Italy).

Management	Fertiliser	Fe _{ox}	Al _{ox}	Pox	DPS	PSI
		g kgʻʻ		mg kg⁻¹	%	
Mineral	NPK	2.17	0.59	268b	29b	0.17b
	PK	2.21	0.62	316b	33b	0.22b
Organic	S	2.15	0.61	292b	31b	0.11b
	М	2.16	0.56	420a	46a	0.07a
Sig		ns	ns	0.00	0.00	0.00

Table 4. Some chemical characteristics of the dispersed solids from the maize for grain system (MG) treated with mineral (NPK and PK) or organic (manure, M, and slurry, S) fertilisers in a long term platform (NW Italy).

	aTC	aTN	^a Ca	aTP	^b Pox	^b Fe _{ox}	^b Al _{ox}	^c DPS _{solid}	°TOC/TN	°PER	°CER	ďζ
	g ł	kg ⁻¹		mg kg ⁻¹		g	kg⁻¹	%				mV
NPK	15b	21	1299b	1.6b	996	6.4a	1.80a	36	7.3	1.6	1.3	-27
РК	16b	20	1052c	1.7b	1048	5.3b	1.62b	44	8.0	1.6	1.4	-20
S	18b	23	2224b	1.8b	979	4.2b	1.44b	49	7.9	1.7	1.4	-18
Μ	20a	27	1326a	2.2a	990	3.9c	1.48c	52	7.5	1.8	1.5	-16
Sig.	0.00	ns	0.00	0.04	ns	0.00	0.00	ns	ns	ns	ns	ns

^a Total amount of carbon (TC), nitrogen (TN), calcium (Ca) and phosphorus (TP)
 ^b Phosphorus, iron and aluminium extracted in oxalate
 ^c Degree of phosphorus saturation (DPS_{solid}), total organic carbon/total nitrogen ratio (TOC/TN), phosphorus enrichment ratio (PER) and carbon enrichment ratio (CER)
 ^d Zeta potential that show the electrophoretic mobility of the solid suspension (*ζ*)

Table 5. Estimation of P surplus and P unaccounted in the Ap horizon of soils cultivated with maize for grain (MG) and maize for silage (MS) and treated with mineral (NPK and PK) or organic (slurry, S, and manure, M) fertilisers in a long term platform (NW Italy) with a value of 1.4 kg dm⁻³ of bulk density.

System	Management	Fertiliser	Р	ΔΡ	TPsoil	ΔTPsoil	P unaccounted
			surplus	surplus			(ΔTPsoil /Psurplus * 15 yr)%
			kg ha ⁻¹ y ⁻¹		kg ha ⁻¹		%
MG	Min	NPK	30	0	4263	0	0
		PK	37	7	4330	67	7
	Org	S	85	55	4565	302	41
		М	109	79	4901	638	33
MS	Min	NPK	16	0	3473	0	0
		PK	22	0	3704	0	0
	Org	S	66	50	3818	345	41
		М	87	71	4397	924	11

 ΔP is the difference in P surplus with respect to that in NPK ΔTP soil is the difference in soil total P with respect to that in NPK



Figure 1. Relationship between (a) reactive P (RP), (b) particulate P (PP) and Olsen P in the Ap horizon of soils cultivated with maize for grain (MG) and maize for silage (MS) in a middle term field experiment (NW Italy).







