Phosphorus and carbon in soil particle size fractions: A synthesis

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Abstract Despite the importance of phosphorus (P) as a macronutrient, the factors controlling the pool sizes of organic and inorganic P (OP and IP) in soils are not yet well understood. Therefore, the aim of this study was to gain insights into the pools sizes of OP, IP and organic carbon (OC) in soils and soil particle size fractions. For this purpose, I analyzed the distribution of OP, IP, and OC among particle size fractions depending on geographical location, climate, soil depth, and land use, based on published data. The clay size fraction contained on average 8.8 times more OP than the sand size fraction and 3.9 and 3.2 times more IP and OC, respectively. The OP concentrations of the silt and clay size fraction were both negatively correlated with mean annual temperature ($R^2 = 0.30$ and 0.31, respectively, $p < 0.001$). The OC:OP ratios of the silt and clay size fraction were negatively correlated with latitude ($R^2 = 0.49$ and 0.34, respectively, $p < 0.001$). Yet, the OC:OP ratio of the clay size fraction changed less markedly with latitude than the OC:OP ratio of the silt and the sand size fraction. The OC concentrations of all three particle size fractions were significantly ($p < 0.05$) lower in soils converted to cropland than in adjacent soils under natural vegetation. In contrast, the OP concentration was only significantly ($p < 0.05$) decreased in the sand size fraction but not in the other two particle size fractions due to land-use change. Thus, the findings suggest that OP is more persistent in soil than OC, which is most likely due to strong sorptive stabilization of OP compounds to mineral surfaces.

Keywords Ecological stoichiometry · Soil nutrients · Organo-mineral interactions · Land-use change · Soil organic matter stabilization · Persistence · Soil particle size fractions · Element ratios · Organic phosphorus

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Introduction

Phosphorus (P) is an essential macronutrient necessary to all living organisms that controls primary production in many ecosystems (Aerts and Chapin 1999; Reich and Oleksyn 2004; Goll et al. 2012). Rock P suitable for fertilizer production is a finite resource (Cooper et al. 2011; Cordell and White 2015). Therefore, it is important to better understand the dynamics of organic P (OP) and inorganic P (IP) in

soils to be able to manage soil P more sustainably (George et al. 2018). Due to the high affinity of organic phosphorylated compounds to mineral surfaces, OP might also play an important role in the sorptive stabilization of organic matter (OM) in soils (Kleber et al. 2007; Newcomb et al. 2017). However, little is currently known about the contribution of P to the stabilization of OM in soils (Tipping et al. 2016; Newcomb et al. 2017).

Phosphorus is present in soils in organic and inorganic forms that strongly interact with mineral surfaces and metal cations. Organic P comprises phosphomonoesters (PME), such as inositol phosphates, adenosine phosphates, and phospholipids, as well as phosphodiesters (PDE), such as deoxyribonucleic acid (DNA) and ribonucleic acid (RNA) (Stewart and Tiessen 1987; Darch et al. 2014). Inorganic P is mostly found in soil in the form of orthophosphate, which has a high affinity to precipitate with cations such as Ca^{2+}, Fe^{3+} and Al^{3+}, and to a lesser extent as polyphosphate (Hinsinger 2001; Darch et al. 2014). Being anions, phosphates sorb to positively charged surfaces in soil such as Fe and Al oxides and hydroxides as well as to positively charged binding sites on OM and at the edges of phyllosilicates (Hinsinger 2001; Celi and Barberis 2005; Gérard 2016). Further, they can be bound to mineral surfaces through ligand exchange (specific sorption). In addition, phosphates can also sorb to negatively charged surfaces through polyvalent metal cations (Kleber et al. 2007).

Organic phosphorylated compounds differ in their affinity to sorb to charged surfaces in soil. Phosphomonoesters with multiple phosphate groups such as inositol-hexa-, -penta-, -tetra-, and -tri-phosphate have a very high affinity to sorb to charged surfaces of amorphous Al and Fe oxides and mineral edges (McKercher and Anderson 1989; Martin et al. 2004; Celi and Barberis 2005; Berg and Joern 2006; Ruttenberg and Sulak 2011). Phosphodiesters have a lower charge density than orthophosphate and PMEs and their phosphate groups are considerably shielded, resulting in a lower capacity of PDEs to compete for sorption sites in soils (Stewart and Tiessen 1987; Darch et al. 2014). Sorption of OP compounds in soil also depends on soil pH since the pH affects protonation of OM and (hydr-)oxides as well as of phosphates. For instance, DNA sorbs very strongly when the soil pH is lower than 5 due to protonation of

adenine, guanine and cytosine in the DNA (Cai et al. 2007).

Many phosphorylated organic compounds are more effective in competing for binding sites than non-phosphorylated organic compounds (Afif et al. 1995; Fransson and Jones 2007; Celi and Barberis 2005; Schneider et al. 2010; Chassé and Ohno 2016). Thus, the phosphate moiety of OP compounds may contribute to the sorptive stabilization of organic matter (Kleber et al. 2007). Yet, the importance of OP for the formation of organo-mineral complexes is only poorly understood so far (Newcomb et al. 2017) despite the fact that organo-mineral complexes are increasingly believed to play an important role in the stabilization of OM against microbial decomposition in soil (von Lützow et al. 2006; Kleber et al. 2007; Kögel-Knabner et al. 2008; Schmidt et al. 2011).

Organo-mineral complexes have been intensively studied using particle size fractionation, which consists of mechanical disruption and dispersion of the soil sample followed by separation of particle size fractions through sieving and gravitational separation (Christensen 1992, 2001; von Lützow et al. 2007). Particle size fractionation is based on the concept that OM associated with particles of different size, and therefore also of different mineralogical composition, differs in structure (Christensen 1992, 2001). While quartz particles that dominate the sand size fraction exhibit only weak bonding affinities to OM, phyllosilicates and iron and aluminum (hydr-)oxides, that are abundant in the clay size fraction, provide a large specific surface area and numerous reactive sites to which OM can sorb (Sposito et al. 1999; Christensen 1992, 2001; von Lützow et al. 2006; Gérard 2016). Since sorption is an important stabilization mechanism of OM in soils, OM in the sand size fraction is considered the active pool, OM in the silt size fraction the intermediate pool, and OM in the clay size fraction is considered the passive pool (von Lützow et al. 2006). Support for this concept comes from the observation that OM in the clay size fraction is older and has a longer turnover time than OM in the sand and in the silt size fraction (Anderson and Paul 1984; Tiessen et al. 1994; Ludwig et al. 2003; Bol et al. 2009).

Soil OC and OP contents are not only affected by sorptive stabilization of OM but also by inputs to soil such as plant litter and amendments such as manure and inorganic fertilizer. The P concentration of plant

leaf litter depends on climate, latitude and biome. For forest biomes, it has been shown in a meta-analysis that the molar C:P ratio of leaf litter decreases in the order tropical forest > temperate coniferous forest > temperate broadleaf forest, and reaches a global mean of 1334 (McGroddy et al. 2004). In a second large synthesis study on senesced plant leaves in different biomes, it was found that the average molar C:P ratio across different plant functional types amounted to 1183, and increased with mean annual temperature (MAT) and mean annual precipitation (MAP) (Yuan and Chen 2009). While the global patterns of P in plant biomass and plant litter have been studied quite intensively (McGroddy et al. 2004; Reich and Oleksyn 2004; Yuan and Chen 2009), much less is known about the global patterns of OC and OP in soils (Kirkby et al. 2011; Tipping et al. 2016).

The OC contents in soils are known to be strongly affected by land-use change from native or semi-native vegetation to cropland (Post and Kwon 2000; Guo and Gifford 2002), however, less is known about the effects of land-use conversion on OP and IP contents (Negassa and Leinweber 2009; MacDonald et al. 2011; Spohn et al. 2016). It has been shown in a study in the UK that arable soils were dominated by orthophosphate, while extensively-grazed grassland soils were dominated by OP compounds (Stutter et al. 2015). Further, it was reported that cropland soils in Canada contained decreased OC and OP and increased easily available IP contents compared to grassland soils (Cade-Menun et al. 2017). However, the loss of OP relative to OC caused by land-use conversion and the role of minerals for the stabilization of OP is not yet well understood.

The objective of this study was to gain insights into pool sizes of OP and OC in mineral soils and soil particle size fractions. For this purpose, I analyzed the distribution of OP, OC, and IP among particle size fractions depending on geographical location of the soils, climate, land use, and soil depth, based on data from published studies. Latitude, MAP, and MAT were chosen as independent variables in the analyses of the OC:OP ratios in the particle size fractions because they have been shown to control the C:P ratio of plant leaves and leaf litter (Reich and Oleksyn 2004; Yuan and Chen 2009). I tested the hypotheses that (i) OP is more strongly enriched in the clay size fraction with respect to the sand size fraction than OC and IP, (ii) the OC:OP ratio changes less in the clay than in the sand size fraction with latitude (iii) the OP content of the clay size fraction is less affected by land-use change than the OP content of the sand and silt size fraction, and (iv) the OP content of the clay size fraction is less affected by land-use change than the OC content of the same fraction due to preferential sorptive stabilization of OP.

Materials and methods

Dataset

I searched for peer-reviewed studies that report OP concentrations of particle size fractions of soils via Google Scholar and ScienceDirect, using the terms "particle size fractions", "soil organic phosphorus", "organic matter fractionation", "soil phosphorus", and "organic matter" in all possible combinations. All particle size fractions had to be gained by mechanical destruction and dispersion of the soil sample followed by separation of the particle size fractions through sieving and gravitational separation, in order to be included in the dataset. Studies reporting OP concentrations of water-stable aggregates or density fractions, etc. or combined particle size fractionation with other physical fractionation techniques were excluded. All studies had to report OP concentrations determined either by an ignition method according to Saunders and Williams (1955) or as the sum of at least two organic Hedley fractions (Hedley et al. 1982). The Hedley fractions had to be extracted according to Tiessen and Moir (1993), and organic P in the fractions had to be determined as the difference of total P determined by ICP and inorganic P measured photometrically. All, except for four studies, included in this analysis determined OP by the ignition method according to Saunders and Williams (1955). Of the four studies that used Hedley fractionation, two calculated OP as the sum of three Hedley fractions, and the other two calculated OP as the sum of two Hedley fractions (see Supplementary Table S1). Studies reporting OP in less than two Hedley fractions were excluded. All studies were required to report OP concentrations of the three particle size fractions: sand size, silt size, and clay size. Studies that reported OP concentrations of only one or two particle size fractions were not included in the synthesis in order to keep the data set balanced. If studies reported OP

concentrations for more than three fractions (for example, separately for coarse silt and fine silt or coarse sand and fine sand), a weighted mean based on the masses of the two sand or two silt size fractions, respectively, was calculated. Only in a few cases, in which the masses of the fractions were not reported, arithmetic means were calculated.

Besides OP concentrations of the particle size fractions, the following soil chemical properties were extracted from the publications; TOC, total inorganic phosphorus (TIP), and total organic phosphorus (TOP) of the bulk soil as well as OC and inorganic phosphorus (IP) concentrations of each particle size fraction. TIP was calculated as the difference between TP and TOP. For the sake of clarity, the terms TOC, TOP, TIP, and total P (TP) will be used only when referring to the bulk soil in the following, and OC, OP, IP and P when referring to the concentrations of OC, OP, IP, and P (sum of OP and IP) of the particle size fractions.

Furthermore, the following variables were extracted from the studies; latitude, MAP and MAT of the study site, the country where the study site was located, the soil order, the land use type, the name, the depth, and the bulk density of the soil horizon or depth increment. In addition, data on the mass of each particle size fraction (in percentage of total) was extracted from the publications. If the latitude was not reported, it was retrieved from digital maps based on site name or other descriptors. In case data were reported in graphs, data were acquired directly from the authors or were extracted from the graphs using the open-source software DataThief (Tummers 2006).

In total, I found 118 observations (data on 118 soil horizons) reported in 13 different publications that met the criteria of the literature search (Table 1 and data in Supplement). The studied soils are located in 12 different countries at latitudes ranging from 3° to 57° across both hemispheres (Table 1). Of the 118 soil horizons, 80 were topsoil horizons and 43 horizons formed part of soil profiles, for which data on three or more horizons was provided. In addition, 10 land-use type comparisons for topsoils were found, each consisting of a soil at a (semi-)natural site and a soil at an adjacent cropland site with comparable soil properties (Table 1). In all studies on land-use type comparisons, the cropland had been established for a minimum of 40 years. The weighted mean of the

sampling depth of all topsoil horizons amounted to 15.0 cm (Supplementary Table S1).

Data analysis

Molar C:P ratios (in mol per mol, as opposed to g per g) were calculated based on the molecular weight of C and P, and only molar ratios are reported throughout the manuscript, in order to allow comparison with previous studies. Arithmetic means were calculated for all stocks and concentrations. In addition, I calculated geometric means of the element ratios. In order to avoid autocorrelation and dependence of data, only topsoil horizons were included in the analyses, except for the analysis of the vertical distribution of OP in the particle size fractions (see below). I calculated linear regression models for total element concentrations and element ratios in the particle size fractions of the topsoils as a function of latitude, MAT, MAP, and the MAT:MAP ratio. In addition, I calculated multiple regression models with both MAT and MAP as independent variables. For all analyses including latitude, only the degree of latitude was considered, but no differentiation between southern and northern hemisphere was made. Before calculating linear regressions of TOC and TOP as well as of OC and OP in each of the three particle size fractions, the data were log transformed in order to achieve normal distribution. For all other regression analyses, no data transformation was required.

To analyze the effect of land-use conversion from natural or semi-natural vegetation to cropland on the distribution of OC and OP in the particle size fractions, only studies that reported the OC and OP concentrations of the particle size fractions of two comparable soils from the same area under different forms of land use were considered. If a study compared a native site and several cropland sites, only the arable site with the longest duration of arable land use was included in the analysis. Stocks of TOP, TOC, TIP, and TP in the top 10.0 cm of the soils were calculated based on the bulk densities of the soils. The change in stocks and concentrations of TOP, TOC, TIP, and TP as well as the change in concentrations of OP, OC, and IP in the particle size fractions due to land-use conversion from (semi-)native vegetation to cropland was calculated separately for each pair of sites. Arithmetic means and standard deviations of changes in element contents of all 10 comparisons were calculated. Concentrations

Table 1 References included in the meta-analysis together with the country where the study sites are located, the latitude, the mean annual precipitation (MAP) and the mean annual temperature (MAT) of the study sites as well as the total number of horizons for which data on particle size fractions is provided, number of topsoil horizons, number of soil profiles, land-use types, number of soil profiles, number of land-use comparisons and the type of land-use comparison

References	Country	Latitude (°)	MAT (°C)	MAP (mm)	Total number of horizons	Number of topsoil horizons	Number of soil profiles, with number of horizons	Land-use type*	Number of land-use comparisons	Type of land-use comparison
Agbenin and Tiessen (1995)	Brazil	8	25.2	750	12	5	2, with 4–5 horizons	n	0	
Guzel and Ibrikci (1994)	Turkey	40	17.5	704	16	3	3, with 5–6 horizons	n, c	0	
Lobe et al. (2001), von Sperber et al. (2017)	South Africa	28, 27, 29	13.8, 16.6 16.0	625, 563, 516	27	27	0	n, c	3	Native grassland vs. cropland
Makarov et al. (2004)	Russia	43	6.3–1.2	700–1400	15	7	3, with 3 horizons	n	0	
Rubæk et al. (1999)	Germany, Denmark	44, 55	6.5, 7.7	1500, 862	7	7	0	n, c	1	Spruce forest vs. cropland
Solomon et al. (2000), Solomon and Lehman (2000)	Tanzania	4	20.0	550	5	5	0	n, c	1	Native grassland vs. cropland
Solomon et al. (2002)	Ethiopia	7	18.0, 19.9	1800, 1250	6	6	0	n, c	2	Native woodland vs. cropland
Syers et al. (1969)	New Zealand	43	10.0	650	6	2	2, with 3 horizons	n	0	
Tiessen and Stewart (1983)	Canada	52	2.0	354	8	8	0	n, c	3	Native grassland vs. cropland
Uriyo et al. (1977)	Tanzania	3	26.0	1070	3	3	0	n	0	
Williams and Saunders (1956)	United Kingdom	57	8.6	1777	13	7	1, with 4 horizons	n	0	
Sum					118	80	11		10	

*(Semi-)natural vegetation (n), cropland (c)

and stocks of TOC, TOP, TIP, and TP as well as concentrations of OC, OP, IP, and P in the particle size fractions of the (semi-)native soils were compared to the concentrations and stocks in the cropland soils by ANOVA followed by Tukey HSD test. In addition, changes in concentrations and stocks of TOC, TOP, TIP, and TP in response to land-use conversion were compared by ANOVA followed by Tukey HSD test. For this purpose, normality of data was examined visually by QQ-plots and analytically by the Shapiro–Wilk test. Homogeneity of variances were checked by Levene's test. In all analyses $\alpha = 0.05$ was considered the threshold for significance.

In order to examine the vertical distribution of OP and IP in particle size fractions, an analysis of the profile data was conducted. For this analysis, I considered only data on soil horizons that were reported together with data on at least two soil horizons of the same soil in order to keep the depth distribution balanced. The mean depth was calculated for all soil horizons. Monoexponential models of the OP concentrations of the particle size fractions as a function of soil depth were fitted to the data. In addition, linear regression models of the IP:OP ratio of each of the particle size fractions as a function of soil depth were fitted to the data. All data analyses were conducted in R 3.4.0 (R Core Team 2013).

Results

Distribution of C and P in particle size fractions in topsoils

In the topsoils, the mean concentrations of OP, IP, OC and P in the clay size fraction were higher than in the sand size fraction (Fig. 1a–d). The clay size fraction contained on average 8.8 times more OP than the sand size fraction and 3.9, 3.1 and 5.1 times more IP, OC, and P, respectively (Fig. 1a–d). The molar OC:OP ratios amounted on average to 771, 424, and 204, in the sand, silt and clay size fraction, respectively (Fig. 1e). The IP:OP ratios of the sand, silt and clay size fraction amounted on average to 10.2, 2.9 and 2.0 (Fig. 1f). The TOP concentration of the bulk soil was strongly correlated with the TOC concentration ($R^2 = 0.80$, $p < 0.001$), and the mean molar TOC:TOP ratio of the bulk soil amounted to 250. Similarly, the OP concentration of the sand, silt and clay size

fraction was significantly correlated to the OC concentration of the same fraction ($R^2 = 0.49$, 0.70, 0.61, respectively, all $p < 0.001$).

Global distribution of C and P in particle size fractions

TOP was most strongly correlated with MAT ($R^2 = 0.47$, $p < 0.001$), whereas TOC was most strongly correlated with MAP ($R^2 = 0.42$, $p < 0.001$; Table 2, Supplementary Table S2). Both TOP and TOC were correlated with the combination of MAT and MAP (adjusted $R^2 = 0.63$ and 0.54, respectively, both $p < 0.001$). TIP was also significantly correlated with MAP ($R^2 = 0.25$, $p < 0.001$) but not with latitude or MAT ($p > 0.05$). Furthermore, TP was not significantly ($p > 0.05$) correlated with latitude or MAT, and only weakly with MAP (Table 2).

The OP concentrations of the silt and clay size fraction were both most strongly correlated with MAT ($R^2 = 0.30$ and 0.31, respectively, both $p < 0.001$; Fig. 2b, a), similar to the TOP concentrations. The OC concentration of the clay size fraction was most strongly correlated with MAT ($R^2 = 0.48$ $p < 0.001$; Fig. 2c), while the OC concentrations of the sand and the silt size fraction were more strongly correlated with MAP ($R^2 = 0.45$ and 0.31, respectively, both $p < 0.001$), similar to TOC (Table 2). Much of the variability of the OC concentration of the clay size fraction was explained by the combination of MAT and MAP (adjusted $R^2 = 0.68$, $p < 0.001$; Table 2). In contrast to OP, the IP concentrations of the clay size and silt size fraction were not significantly ($p > 0.05$) correlated with MAP, and less strongly than OP with MAT and latitude (Table 2). The P concentrations (sum of OP and IP) of the particle size fractions showed no correlation with latitude, MAT or MAP (Table 2).

The TOC:TOP ratio was most strongly correlated with latitude ($R^2 = 0.20$, $p < 0.001$; Table 3, Supplementary Table S3). The OC:OP ratios of the sand, silt and clay size fraction were also mainly correlated with latitude ($R^2 = 0.22$, 0.49 and 0.34, respectively, all $p < 0.001$; Fig. 2e, f, Table 3). The OC:OP ratio of the clay size fraction changed less strongly with latitude than the OC:OP ratio of the silt and the sand size fraction, as indicated by the slopes of the linear regression models, which amounted to $- 40.8$,
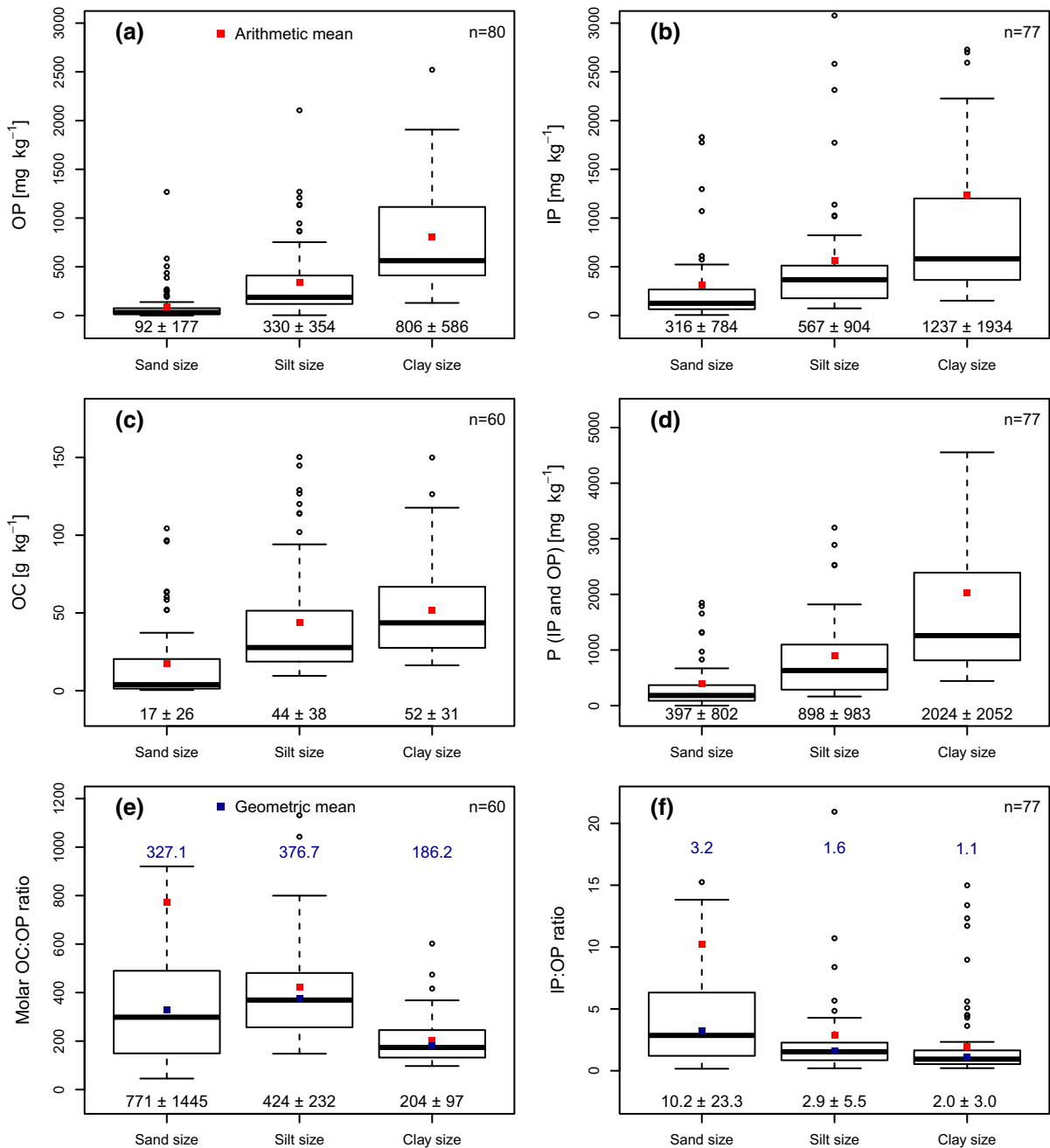
Fig. 1 Organic phosphorus (**a**), inorganic phosphorus (**b**), organic carbon (**c**), and phosphorus (sum of organic and inorganic phosphorus) concentrations (**d**) together with the ratio of organic carbon-to-organic phosphorus (**e**), and the ratio of inorganic phosphorus-to-organic phosphorus (**f**) of the three particle size fractions in the topsoil. Numbers at the bottom of each boxplot depict arithmetic means ± the standard deviations, and the arithmetic mean of each fraction is also indicated by a red square. For the element ratios (**e**, **f**), the geometric mean of each fraction is indicated by a blue square and a blue number. The number of observations (n) is depicted in the top right corner of each plot
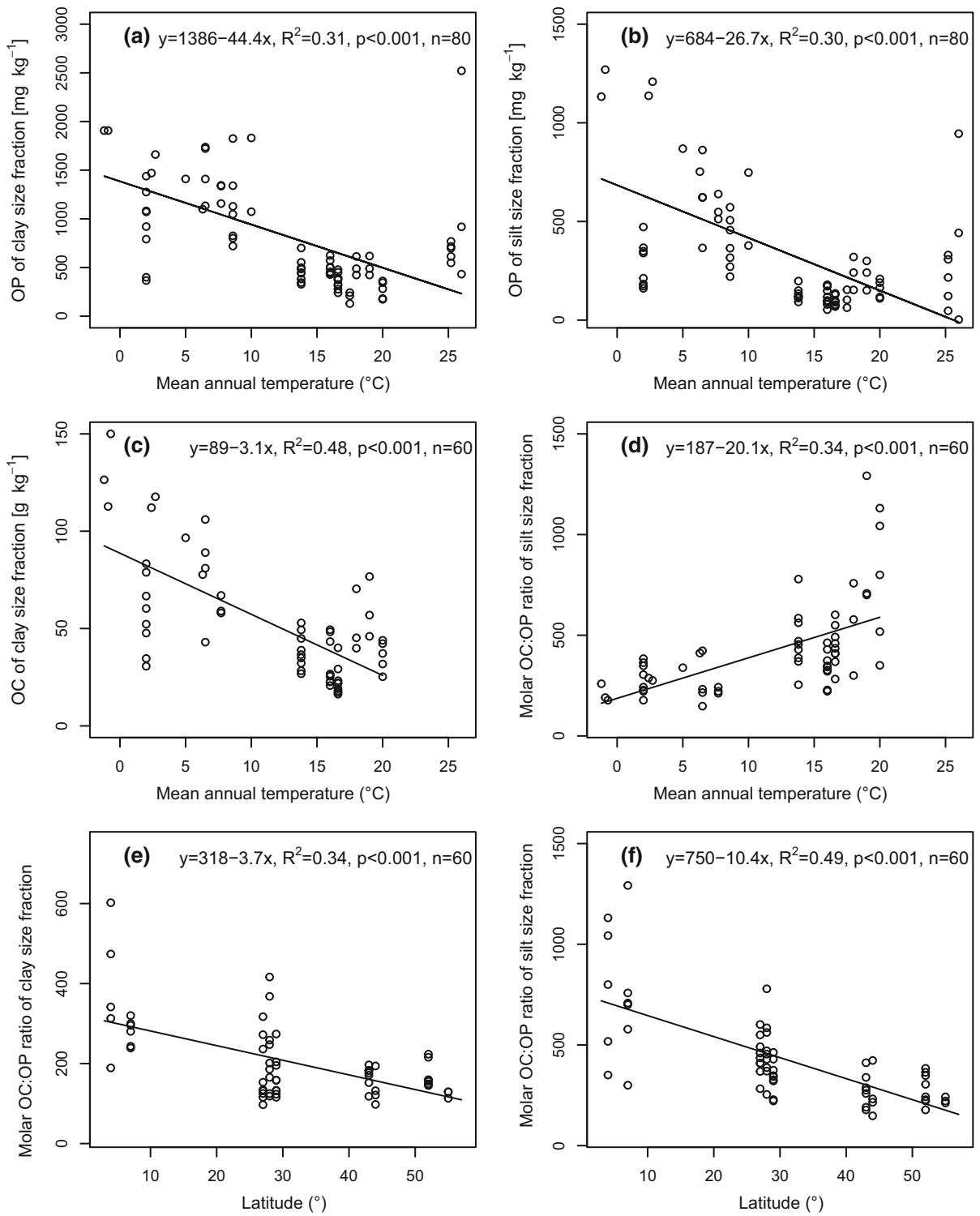
− 10.4, and − 3.7, in the sand, silt and clay size fraction, respectively (Fig. 2e, f, Table 3, Supplementary Table S3). The TIP:TOP ratio and the IP:OP ratio of the clay size fraction were both correlated with MAT ($R^2 = 0.32$ and 0.34, respectively, both $p < 0.001$; Table 3).

Table 2 Results of (multiple) linear regression analyses for total organic C (TOC), total organic P (TOP), and total inorganic P (TIP) as well as organic carbon (OC), organic phosphorus (OP) and inorganic phosphorus (IP) concentrations of the three particle size fractions as a function of latitude (Lat) as well as mean annual temperature (MAT) and mean annual precipitation (MAP), their ratio (MAT:MAP), and the two of them (MAT + MAP; multiple regression)

	TOC	TOP	TIP	TP	OC of sand size fraction	OC of silt size fraction	OC of clay size fraction	OP of sand size fraction	OP of silt size fraction	OP of clay size fraction	IP of sand size fraction	IP of silt size fraction	IP of clay size fraction	P of sand size fraction	P of silt size fraction	P of clay size fraction
Lat	> 0.05	< 0.01 0.10	> 0.05	> 0.05	> 0.05	> 0.05	< 0.01 0.16	> 0.05	< 0.01 0.11	< 0.001 0.19	> 0.05	< 0.05 0.06	< 0.05 0.07	> 0.05	> 0.05	> 0.05
MAT	< 0.001 0.27	< 0.001 **0.47**	> 0.05	> 0.05	< 0.05 0.10	< 0.001 0.17	< 0.001 **0.48**	< 0.001 0.19	< 0.001 **0.30**	< 0.001 **0.31**	< 0.05 0.07	< 0.01 0.11	< 0.001 0.16	> 0.05	> 0.05	> 0.05
MAP	< 0.001 **0.42**	< 0.01 0.14	< 0.001 0.25	< 0.05 0.06	< 0.001 **0.45**	< 0.001 **0.31**	< 0.001 0.27	> 0.05	< 0.001 0.15	< 0.001 0.17	> 0.05	> 0.05	> 0.05	> 0.05	> 0.05	> 0.05
MAT:MAP	< 0.001 **0.51**	< 0.001 **0.51**	< 0.01 0.13	> 0.05	< 0.001 **0.35**	< 0.001 **0.33**	< 0.001 **0.57**	< 0.001 **0.19**	< 0.001 **0.38**	< 0.001 **0.43**	> 0.05	> 0.05	> 0.05	> 0.05	> 0.05	> 0.05
MAT + MAP	< 0.001 **0.63**	< 0.001 **0.54**	< 0.001 0.23	< 0.01 0.11	< 0.001 **0.50**	< 0.001 **0.43**	< 0.001 **0.68**	< 0.001 0.19	< 0.001 **0.39**	< 0.001 **0.41**	< 0.05 0.06	< 0.01 0.11	< 0.001 0.17	> 0.05	> 0.05	< 0.05 0.08

The first number depicts the p value, the second one the R^2 for all significant ($p < 0.05$) regressions. For the multiple linear regressions, the adjusted R^2 is shown. All $R^2 \geq 0.30$ are given with bold letters

(a) $y = 1386 - 44.4x$, $R^2 = 0.31$, $p < 0.001$, $n = 80$

(b) $y = 684 - 26.7x$, $R^2 = 0.30$, $p < 0.001$, $n = 80$

(c) $y = 89 - 3.1x$, $R^2 = 0.48$, $p < 0.001$, $n = 60$

(d) $y = 187 - 20.1x$, $R^2 = 0.34$, $p < 0.001$, $n = 60$

(e) $y = 318 - 3.7x$, $R^2 = 0.34$, $p < 0.001$, $n = 60$

(f) $y = 750 - 10.4x$, $R^2 = 0.49$, $p < 0.001$, $n = 60$

◄ **Fig. 2** Organic phosphorus (OP) concentrations of the clay size fraction (**a**) and silt size fraction (**b**), organic carbon concentrations of the clay size fraction (**c**), and the molar organic carbon-to-organic phosphorus (OC:OP) ratio of the silt size fraction as a function of the mean annual temperature (**d**), together with the molar organic carbon-to-organic phosphorus (OC:OP) ratio of the clay size fraction (**e**) and of the silt size fraction (**f**) as a function of latitude. The R^2 is depicted in the top right corner of each plot together with the p value and the number of observations (n)

Effects of land-use change on C and P

Due to land-use conversion from (semi-)natural vegetation to cropland, only the TOC ($p < 0.05$), but not the TOP, TIP or TP concentration (all $p > 0.05$) changed significantly in the topsoils (Fig. 3a). The TOC concentration decreased on average by 58% compared to the soil under (semi-)natural vegetation (Fig. 3a). The changes in TOP, TIP, and TP concentrations amounted to -35%, $+23\%$ and -11% with respect to the soils under (semi-)natural vegetation, but the changes were not statistically significant (Fig. 3a). The changes in TOC, TOP, TIP, and TP stocks showed a similar pattern (Fig. 3b) as observed for the concentrations, and only the change in the TOC stock was marginally significant ($p < 0.1$). The TIP

stock increased by 45% due to land-use change (with respect to the native soil), but the change was not statistically significant (Fig. 3b).

The OC concentrations of all three particle size fractions were significantly ($p < 0.05$) lower in the croplands than in the soils under (semi-)natural vegetation (Fig. 3c). The change in OC concentration due to land-use conversion decreased in the order sand (-71%) > silt (-47%) > clay (-35%) size fraction (Fig. 3c). In contrast to OC, the OP concentration was only significantly ($p < 0.05$) decreased in the sand, but not in the silt or in the clay size fraction in response to land-use conversion (Fig. 3d). In contrast to OC and OP, the concentrations of IP in the particle size fractions tended to increase, albeit not significantly (Fig. 3e). The changes in the P concentrations in the particle-size fractions were not statistically significant (Fig. 3f).

Vertical distribution of C and P

The OP concentrations of the silt and the sand size fraction were much larger than the OP concentration of the clay size fraction in the upper 35 cm of the soils (Fig. 4a). The OP concentration in the depth segment 0–10 cm amounted on average to 110, 474, and

Table 3 Results of (multiple) linear regression analyses of the ratio of total organic C-to-total organic P of the bulk soil (TOC:TOP), the ratio of total inorganic P-to-total organic P of the bulk soil (TIP:TOP), and the ratio of inorganic P-to-organic P (IO:OP) and organic C-to-organic P (IP:OP) of the particle

size fractions as a function of latitude (Lat) as well as mean annual temperature (MAT) and mean annual precipitation (MAP), their ratio (MAT:MAP), and the two of them (MAT + MAP; multiple regression)

	TOC:TOP ratio	TIP:TOP ratio	TOC:TP ratio	OC:OP ratio of sand size fraction	OC:OP ratio of silt size fraction	OC:OP ratio of clay size fraction	IP:OP ratio of sand size fraction	IP:OP ratio of silt size fraction	IP:OP ratio of clay size fraction
Lat	< 0.001	< 0.001	> 0.05	< 0.001	< 0.001	< 0.001	< 0.05	< 0.001	< 0.001
	0.20	0.27		0.22	**0.49**	**0.34**	0.09	0.15	0.24
MAT	< 0.05	< 0.001	< 0.001	< 0.05	< 0.001	< 0.001	> 0.05	< 0.001	< 0.001
	0.07	**0.32**	0.22	0.09	**0.34**	0.18		0.24	**0.34**
MAP	< 0.01	> 0.05	< 0.05	> 0.05	> 0.05	> 0.05	> 0.05	> 0.05	> 0.05
	0.17		0.10						
MAT:MAP	> 0.05	< 0.001	< 0.001	> 0.05	< 0.05	> 0.05	< 0.01	< 0.01	< 0.001
		0.25	0.20		0.15		0.11	0.13	0.18
MAT + MAP	< 0.001	< 0.001	< 0.001	< 0.001	< 0.001	< 0.01	< 0.001	< 0.001	< 0.001
	0.21	**0.31**	0.22	**0.47**	**0.33**	0.15	0.18	0.22	**0.33**

The first number depicts the p value, the second one the R^2 for all significant ($p < 0.05$) regressions. For the multiple linear regressions, the adjusted R^2 is shown. All $R^2 \geq 0.30$ are given with bold letters
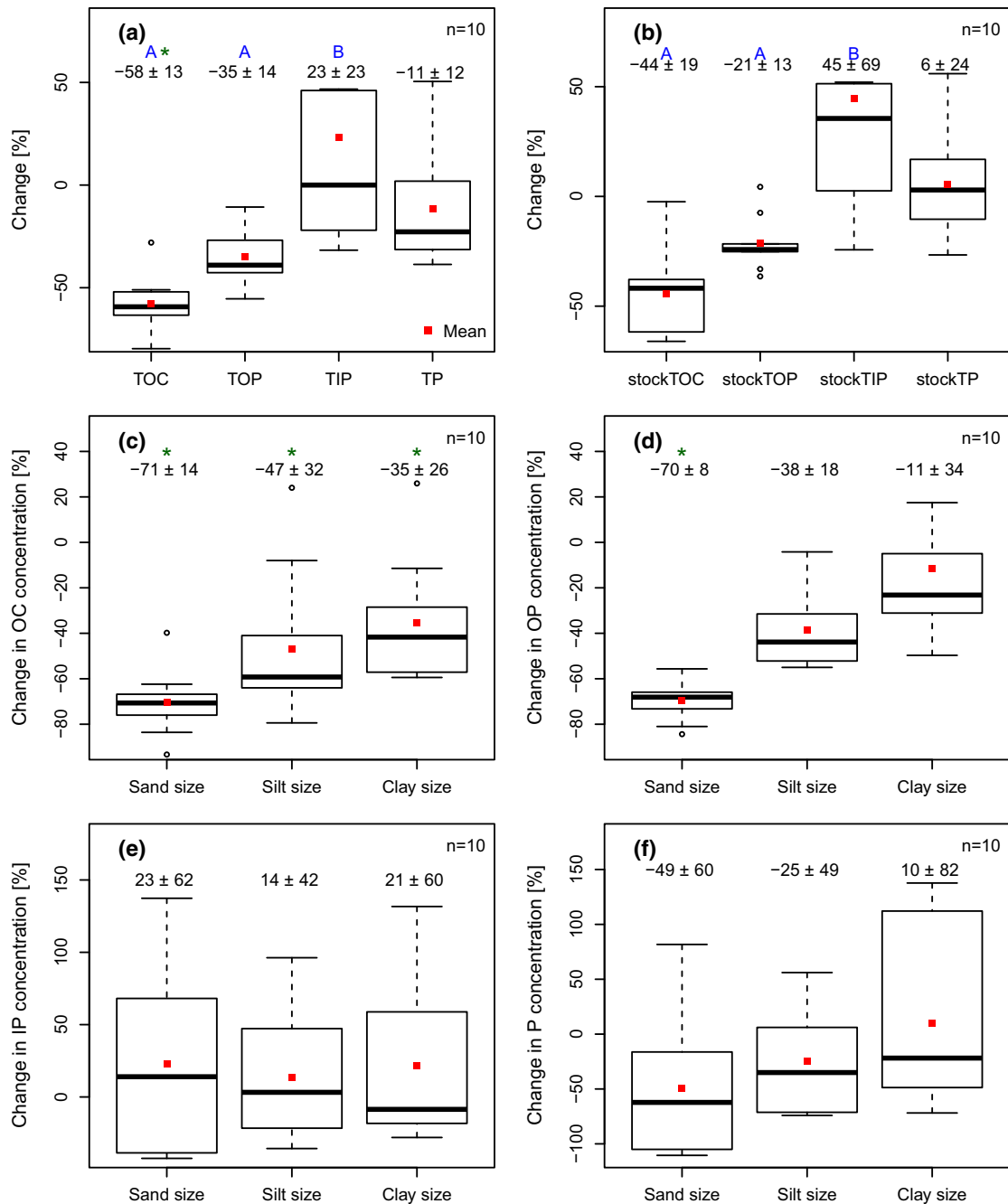
Fig. 3 Changes in the concentrations of total organic carbon (TOC), total organic phosphorus (TOP), total inorganic phosphorus (TIP), and total phosphorus (TP) (**a**), and changes in the stocks of TOC, TOP, TIP and TP in the bulk soil (**b**), together with changes in organic carbon (OC; **c**), organic phosphorus (OP; **d**), inorganic phosphorus (IP; **e**), and total phosphorus (P; **f**) of the particle size fractions due to land-use change from (semi-) native vegetation to cropland. Changes were calculated relative to the native site for each of the 10 pairs of sites, consisting of a (semi-)native site and an adjacent cropland site. Numbers above each boxplot depict the arithmetic mean ± the standard deviation. The arithmetic mean is also indicated by a red square. A significant (p < 0.05) difference between the native soil and the cropped soil is indicated by a dark green star (*). Different capital letters indicate significant differences between changes in TOC, TOP and TIP in the bulk soil. The number of observations (n; i.e., number of pairs of sites) is depicted in the top right corner of each plot

Fig. 4 Organic phosphorus (OP) concentrations (**a**), inorganic phosphorus (IP) concentrations (**b**) and the ratio of inorganic phosphorus-to-organic phosphorus (IP:OP; c) in the three particle size fractions as a function of soil depth. The exponential models fitted to the OP concentrations of the particle size fractions and the corresponding p values are given for all three particle size fractions. The liner models fitted to the IP:OP ratios of the particle size fractions and the corresponding p values and R^2s are given for the clay and the silt size fraction. The number of observations (n) is indicated in the top right corner of each plot

1030 mg kg^{-1} in the sand, silt and clay size fraction, respectively. The OP concentrations in the depth segment 10–20 cm were very similar and amounted to 66, 454, and 1041 mg kg^{-1} in the sand, silt and clay

size fraction, respectively. Below 35 cm, the OP concentrations of the silt and the clay size fraction decreased strongly (Fig. 4a). In contrast to OP, IP had the highest topsoil concentrations in the silt size fraction (Fig. 4b). The ratio of IP:OP was much higher in the sand than in the silt and clay size fraction in the upper 50 cm of the soils (Fig. 4c). With increasing depth, the IP:OP ratio increased in the clay and especially in the silt size fraction as indicated by the slopes of the liner models that amounted to 0.19 and 0.56, respectively (Fig. 4c).

Discussion

Methodological considerations

Based on the criteria of the literature search, data on OP in particle size fractions of 118 soil horizons were found. Thus, the size of the synthesis study is comparable to other meta-analyses on P in soils. The synthesis study by Cross and Schlesinger (1995) on soil Hedley P fractions, for example, is based on 88 soil horizons, and the synthesis study by Yang and Post (2011) added 90 observations to the data set. More recently, a synthesis study by Darch et al. (2014) analyzed NMR data on OP species in 18 soil horizons, and Deiss et al. (2018) analyzed data on P compounds in 100 soils that were extracted from a total of 13 references.

As in any synthesis study in soils science, the sampling depth differs between studies. Therefore, the vertical distribution of OP and IP in soils was studied here (Fig. 4), and it was found that the content of OP in the particle size fractions in the top 10 cm hardly differed from the depth segment ranging from 10-20 cm. Thus, the error derived from the difference in sampling depths is likely to be small.

OC and OP in particle size fractions

The molar TOC:TOP ratio in the topsoils amounted on average to 250, which is in agreement with data presented in Kirkby et al. (2011). The mean molar TOC:TOP ratio was much lower than the C:P ratios of senesced plant leaves and leaf litter, which, on a global average, amount to 1183 and 1334, respectively (McGroddy et al. 2004; Yuan and Chen, 2009). Thus, OP is largely enriched in soil compared to plant

detritus. The reason for this is likely that OP compounds sorb on average more vigorously to the soil mineral phase than non-phosphorylated organic compounds (Afif et al. 1995; Fransson and Jones 2007; Celi and Barberis 2005; Schneider et al. 2010; Chassé and Ohno 2016). Sorption protects OP against microbial decomposition, and thus against conversion to IP (Kleber et al. 2007; Giaveno et al. 2010; Newcomb et al. 2017). In addition, some P-rich OP compounds, such as inositol-hexaphosphate are very recalcitrant, in the sense that microbes decompose them only slowly because of their molecular structure (Stewart and Tiessen 1987; Darch et al. 2014). Thus, the strong sorption of OP and the recalcitrance of some phosphorylated compounds likely make OP more persistent in soil than non-phosphorylated organic compounds, which decreases the mineralization of OP, and thus leads to relatively low TOC:TOP ratios in soil compared to leaf litter.

The increase in OP content with decreasing particle fraction size (Figs. 1a, 4a) can probably be explained by differences in mineralogy among the fractions. The silt, and especially the clay size fraction is highly enriched in Fe and Al (hydr-)oxides and phyllosilicates, while the sand size fraction is dominated by quartz. Thus, the size of the specific surface area and the amount of binding sites increases in the order sand < silt < clay size fraction (Sposito et al. 1999; Christensen 2001; von Lützow et al. 2006). Due to the large reactive surface areas of Fe and Al (hydr-)oxides and clays, the silt and particularly the clay size fraction strongly adsorb OP (Celi and Barberis 2005; Gérard 2016).

Organic P was more strongly enriched in the clay size fraction (compared to the sand size fraction) than OC (Fig. 1). This can be attributed to the fact that OP compounds have on average a higher capacity to compete for sorption sites in soil than non-phosphorylated organic compounds (Afif et al. 1995; Fransson and Jones 2007; Schneider et al. 2010; Chassé and Ohno 2016). The strong sorption of OP to mineral surfaces in the clay size fraction likely leads to a preferential stabilization of OP compounds in soil. This explanation is in accordance with a recent study on TOP in temperate forest (Zederer and Talkner 2018). Furthermore, the results are also in accordance with a conceptual model that states that OP is preferentially stabilized in soil through sorption to charged surfaces (McGill and Cole 1981).

Organic P was more strongly enriched in the clay size fraction (compared to the sand size fraction) than IP (Fig. 1). However, only some organic phosphorylated compounds compete more successfully for sorption sites in soil than IP (McKercher and Anderson 1989; Celi and Barberis 2005; Chassé and Ohno 2016; Spohn and Schleuss 2019), of which the most abundant one is inositol-hexa-phosphate (Celi and Barberis 2005). Thus, the larger enrichment of OP than of IP in the clay size fraction (compared to the sand size fraction) suggests that the OP pool of the clay size fraction is dominated by organic compounds with multiple phosphate groups such as inositol-hexa-phosphate. This is in agreement with the high abundance of inositol-hexa-phosphate in most soils (Turner et al. 2002).

Taken together, the capacity of OP to strongly compete for sorption sites stabilizes OP compounds against decomposition and leads to enrichment of OP in soil, in particular in the clay size fraction. In addition, higher recalcitrance of some OP compounds compared to non-phosphorylated compounds (Stewart and Tiessen 1987; Turner et al. 2002) likely also contributes to the enrichment of OP in soil, relative to OC.

Global distribution of OC and OP in particle size fractions

Here I found that the OP concentrations of the particle size fractions were negatively correlated with MAT, and that the OC:OP ratios of the particle size fractions were negatively correlated with latitude (Fig. 2, Tables 2, 3). These results are in agreement with other studies on soil OP. The negative correlation of OP of the particle size fractions and MAT is in accordance with a negative correlation between soil TOP and MAT found recently in a global synthesis of data on soil P fractionations (Hou et al. 2018). The findings are also in accordance with the results of a meta-analysis on the stoichiometry of soil OM, reporting that the OC:OP ratio is much wider in tropical than in temperate soils (Tipping et al. 2016). The reasons for the correlations might be latitude- and MAT-dependent differences in the OP inputs to soil as well as latitude- and MAT-dependent differences in the decomposition of OC and OP compounds.

The negative correlation of OP and MAT is in accordance with a negative correlation between MAT

and the P concentration of plant leaf litter (McGroddy et al. 2004; Yuan and Chen 2009). In addition, the negative correlation between the OC:OP ratio and latitude is in accordance with the negative correlation of foliage C:P ratio and latitude (McGroddy et al. 2004; Reich and Oleksyn 2004; Vitousek and Sanford 1986). This coincidence suggests that the reasons for the relationships observed in soil are latitude- and MAT-dependent differences in the plant litter inputs to soil. However, it might also be that P limitation, which tends to increase with decreasing latitude (at least at low altitudes, where the degree of weathering tends to increase with decreasing latitude) leads to preferential mineralization of OP close to the equator, causing the negative correlation between the OC:OP ratio and latitude. The latter interpretation is supported by the often observed increase in soil phosphatase activity with decreasing P availability (for a review see Marklein and Houlton (2012)). Furthermore, this interpretation is in accordance with a conceptual model by McGill and Cole (1981) stating that OP mineralization is independent of C mineralization.

The finding that the OC:OP ratio changed less with latitude in the clay than in the silt and sand size fraction (Fig. 2e and f, Table 3, Supplementary Table S3) can be attributed to the high sorption capacity of the clay size fraction. Sorption of OP to mineral surfaces, which are abundant in the clay size fraction, likely stabilizes OP compounds against decomposition, and thus increases the turnover time of OP in soil and in ecosystems (Spohn and Sierra 2018). The reduced decomposition of OP compounds in the clay size fraction seems to partially compensate for low OP inputs at low latitudes, leading to smaller changes in the OC:OP ratio of the clay size fraction with latitude than in the two other particle size fractions.

The correlations found between latitude and the OC:OP ratios of the clay and the silt size fractions are stronger than the correlations found for latitude and the TOC:TOP ratio of the bulk soil (Table 3). This suggests that the relationships between latitude and soil stoichiometry are masked in the bulk soil due to the variability of the masses of the particle size fractions. Thus, the results suggest that particle size fractionation has a large potential to render relationships between climate and soil stoichiometry visible that are obscured in bulk soil by differences in soil texture. The TIP of the bulk soil and the IP

concentrations of the particle size fractions were less strongly correlated with latitude, MAT, and MAP than the concentrations of OP and OC (Table 2). The reason for this is likely that biomass production, and thus OP and OC inputs to soil, depend on climate, and thus on latitude, whereas IP and total P concentrations depend more firmly on the P content of the bedrock (Porder and Ramachandran 2013).

The TOC concentration of the bulk soil and the OC concentrations of the sand and silt size fraction were most strongly correlated with MAP (Table 2). This is in accordance with a synthesis study on soil TOC concentrations and can be attributed to the fact that vegetation type and plant productivity are strongly related to precipitation (Jobbágy and Jackson 2000).

Taken together, the results indicate that the relationships of the OC:OP ratios and the OP concentrations with latitude and MAT might be caused either by latitude- and MAT-dependent differences in the plant litter inputs to soil or in latitude-dependent differences in decomposition of OP compounds. In addition, the comparison of the different particle size fractions indicates that sorptive stabilization of OP compounds in the clay size fraction decreases mineralization of OP in this fraction, which compensates for latitude-dependent differences in the stoichiometry of plant litter inputs to soil.

Effect of land-use change on C and P

The paired-site analysis showed that the soil TOC stock decreased on average by 44% in the upper 10 cm of the soils due to land-use conversion from (semi-)native vegetation to cropland (Fig. 4b). This is in accordance with a global meta-analysis, reporting that the conversion of grassland to cropland leads to a loss of 59% and the conversion of forest to cropland leads to a loss of 42% of the initial TOC stock in the topsoil (Guo and Gifford 2002). This agreement indicates that the change in TOC found here is close to the global mean calculated based on a much larger number of observations. Thus, the present analysis seems to be representative despite the fact that only 10 pairs of sites were analyzed. The reason for the decrease in OC following land-use change from semi-native vegetation to arable land use is increased microbial mineralization of OC that is facilitated by the breakdown of aggregates and the aeration of the soil as well as the change in vegetation, leading to changed OC inputs,

and the inputs of nutrient-rich OM, such as manure (Post and Kwon 2000; Guo and Gifford 2002).

There might be two main reasons for the observation that the TOC but not the TOP concentration changed significantly due to land-use conversion from (semi-)native vegetation to cropland in the bulk soils (Fig. 3a). First, it might be that TOP is more persistent in soil than TOC, which could be due to either sorptive stabilization of OP compounds or higher recalcitrance of OP compounds. Second, OC that is mineralized (mostly) leaves the soil in the form of CO_2, while mineralized P usually remains in soil and can be taken up by biota which can convert it again into organic P. Third, it might be that the arable soils received OP-rich organic fertilizer and manure which has a low OC:OP ratio and compensates for losses of OP through mineralization more efficiently than for losses of OC. However, in the studies analyzed here, the dominant P input to the croplands was IP (Tiessen and Stewart 1983; Rubæk et al. 1999; Solomon and Lehman 2000; Solomon et al. 2002; von Sperber et al. 2017). Therefore, the first two explanations seem to be most likely although it cannot be completely excluded that OP-rich inputs to the cropland soils partially compensated for increased mineralization of OP caused by land-use change.

The differences in OC concentrations between the cropped soils and the native soils were significant for all three particle size fractions. Even in the clay size fraction, a relatively large share (35%) of the OC was lost due to land-use conversion (Fig. 3c). In contrast, the OP concentration changed only significantly in the sand size fraction due to land-use conversion (Fig. 3d), suggesting that OP in the silt and in the clay size fraction is more strongly protected against microbial decomposition than OC. This provides support for the concept that many OP compounds are more persistent than OC in soil either due to adsorption to mineral surfaces or due to a higher recalcitrance. In addition, the fact that mineralized P does not leave the soil as a gas but usually remains in soil, where it can be turned into organic P again, might also contribute to the apparent higher persistence of OP than of OC.

In contrast to TOP, TIP tended to increase due to land-use conversion (Fig. 3a, b), which can be attributed, first, to inputs of fertilizers containing IP, and second, to increased mineralization of OP. However, given that the dominant P input to the croplands

was IP in the studies considered here (Tiessen and Stewart, 1983; Rubæk et al. 1999; Solomon and Lehman 2000; Solomon et al. 2002; von Sperber et al. 2017), and that the loss of OP, and thus the net mineralization of OP was low, the first explanation is more plausible. The result that TIP tended to increase in response to land-use change is in accordance with Stutter et al. (2015) reporting that arable soils were dominated by IP whereas extensively grazed grasslands were dominated by OP.

The concentration of IP increased similarly in all three particle size fractions in response to land-use conversion (Fig. 3e), which is in contrast to the changes in OP that markedly differed between the particle size fractions. The reason for the difference in the responses of OP and IP in the particle size fractions to land-use conversion is likely that OP mostly remained in the clay size fraction where it was protected against microbial decomposition, whereas IP was enriched in all fractions due to anthropogenic P inputs after land-use conversion.

The TP concentration and stock hardly changed due to land-use conversion (Fig. 3a, b). However, these findings cannot be generalized. Whether TP in topsoils changes after land-use conversion largely depends on the amount and the form of P inputs to soil as well as on the P stocks of the native soils (Campbell et al. 1986; Motavalli and Miles 2002; Negassa and Leinweber 2009; Groppo et al. 2015).

It has to be taken into account that only changes in the topsoils were considered here. In the subsoil, changes in OC (Poeplau and Don 2013) and OP in response to land-use change are very likely smaller. Furthermore, the relationship between losses in OP and losses in IP in the particle size fractions might change with soil depth, since the IP:OP ratio of the silt and the clay size fraction increases with soils depth (Fig. 4c). In addition, it has to be considered that in two studies included in this meta-analysis, OP was quantified as the sum of OP in only two Hedley fractions. This approach likely leads to an underestimation of OP in soils due to an incomplete extraction. If the OP concentration or stock is underestimated, the relative change in OP (% change, see Fig. 3) is likely overestimated, and the real relative loss of OP would be even smaller. Thus, in case there is a methodological bias, I underestimate the persistence of OP here, and OP would be even more stable compared to OC after land-use change than described here.

Taken together, the findings indicate that land-use change from (semi-)natural vegetation to cropland leads to a larger loss of OC than of OP, especially in the clay and the silt size fraction. The reasons for this might be (i) a more efficient sorptive stabilization of OP than of OC, (ii) a higher recalcitrance of OP compounds than of P-free organic compounds, (iii) gaseous losses of C but not of P, and (iv) inputs of organic compounds with low C:P ratio such as manure to the croplands that compensate for mineralization of OP. While the paired size analysis provides valuable insights into the loss of OP in relation to OC caused by land-use change, it has to be considered that only 10 pairs of sites were analyzed here, which gives only limited insights into the effects of land-use change on OP in soil. More analyses are required to gain an in depth understanding of the effects of land-use change on OP in soil in different climate zones.

Conclusions

The four hypotheses are approved because it was found that (i) OP was more strongly enriched in the clay size fraction with respect to the sand size fraction than OC and IP, (ii) the OC:OP ratio changed less in the clay than in the sand size fraction with latitude, (iii) the OP content of the clay size fraction was less affected by land-use change than the OP content of the sand and silt size fraction, and (iv) the OP content of the clay size fraction was less affected by land-use change than the OC content of the same fraction. The strong adsorption of OP to mineral surfaces and the recalcitrance of some OP compounds likely protect OP against decomposition, which leads to selective preservation of OP compared to OC. The results indicate that interactions with minerals might be the most important mechanism that stabilizes OP in soil.

The results of this study have important implications as they indicate that OP might play an important role in the formation of organo-mineral complexes, which should be further investigated in the future. In addition, the study showed that particle size fractionation has a large potential to render relationships between climate and soil stoichiometry visible that are masked by differences in soil texture, and thus are not apparent from the analysis of bulk soil. Hence, more studies on soil stoichiometry should consider particle size fractions in the future.

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