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What is the P value of Siberian soils? Soil phosphorus status in south-western Siberia and comparison with a global dataset

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MINOR REVISIONS APPLIED

Dear editor, dear reviewers,

Here is the new version of our manuscript where we applied all the corrections we suggested in our point-by-point response closing the Discussion process. Besides these suggestions, no substantial modification was applied to the content of our manuscript.

Essentially, we applied all the corrections required, or suggested, by two anonymous reviewers. In particular, the title was completed and the entire manuscript passed an English check. Also, as we proposed in our response to the reviews, an additional figure was incorporated in the Supplementary material in order to improve the comparison of our study soils with those in the global data compilation.

We hope these modifications satisfy your expectations and are looking forward to your feedback.

Sincerely,

The authors

POINT-BY-POINT RESPONSE TO REVIEWS

Anonymous Referee #1

The reviewed manuscript present data on P stocks and bio-availability in soils of Siberia. Since this area is going through rapid climate change, and since little is known about the P availability in these soils, this is an important contribution. The authors also made a literature search and compiled data on P status (measured in similar methods) in soils around the world. This enabled them to put the Siberia data in context. Overall this study seems sound, and I recommended publishing it after some minor revisions, detailed below.

1) *The manuscript will benefit from English language editing. Especially the introduction and the discussion in which some of the sentence structure, and some of the words use, make it hard to read.*

RESPONSE: The modified manuscript was corrected by a qualified native English speaker.

2) *The title is confusing. P-value is usually used for statistics. 'P status' will be much better description for this work.*

RESPONSE: We modified the title as following: “What is the P value of Siberian soils? Soil phosphorus status in south-western Siberia and comparison with a global dataset”

3) *Page 19823, line 23, remove humus which is not well defined and replace by organic matter. Same throughout the text. See: Lehmann, Johannes, and Markus Kleber. The contentious nature of soil organic matter. "Nature 528.7580 (2015): 60-68.*

RESPONSE: We fully agree, we changed “humus” by “organic matter”.

4) *Since a lot of effort was put into compilation of global data, it might be a good idea to present this data by maps with colors representing P concentrations (and insets of areas of interest). This is of course if there is some spatial pattern. Another option is to present this global data by plotting it against variables it is correlated with, like pH etc., together with the soils from the current study.*

RESPONSE:

a) We are pleased to see that such a global data compilation provokes your interest. However, we believe the presentation of the global distribution of P pool concentrations is out of the scope of the article we propose to *Biogeosciences*, which focuses on our Siberian soils. A thorough analysis of global datasets, notably with maps of the global distribution of P pools, is in preparation by Augusto *et al.* for *Global Ecology and Biogeography*.

b) About your second proposition, we again think it is not the really in the scope of this article to seek for correlations between P pools and soil properties at the global scale. The study of the environmental controls on P availability is a program in itself. A recent publication reports global relations between the availability of inorganic P and soil properties (Achat *et al.*, 2016).

c) However, we think that better characterizing Siberian soils is a good idea. In practice, we extended the comparison of our Siberian soils with the soils of our global data compilation by adding details on commonly measured soil properties. This was done by adding the Figure S4 (see at the end of this document) to the supplementary material. As a consequence, some comments on this Fig. were added in the Results section of our manuscript. This enabled us to better situate the Siberian soils among the other soils of the data compilation. Most of the soil properties presented in this new Fig. do not have a strong impact on inorganic P availability (Achat *et al.*, 2016) and are not likely to improve the Discussion section. Nevertheless, and still to describe better Siberian soils in

contrast to other soils, improved the paragraph of discussion about Al and Fe oxides (subsection 4.3) with explicit reference to Achat *et al.* (2016), and comparison with their results. Also, the soil C:P and N:P ratios, presented in the new Fig., were rapidly discussed in regard to the global ranges provided by Cleveland & Liptzin (2007) and Xu *et al.* (2013).

References cited in this response:

- Achat D L, Pousse N, Nicolas M, Brédoire F & Augusto L. Soil properties controlling inorganic phosphorus availability: general results from a national forest network and a global compilation of the literature. *Biogeochemistry*, 127, 255-272, doi:10.1007/s10533-015-0178-0, 2016
- Cleveland C C & Liptzin D. C:N:P stoichiometry in soil: is there a “Redfield ratio” for the microbial biomass? *Biogeochemistry*, 85, 235-252, doi:10.1007/s10533-007-9132-0, 2007
- Xu X, Thornton P E & Post W M. A global analysis of soil microbial biomass carbon, nitrogen and phosphorus in terrestrial ecosystems. *Global Ecology and Biogeography*, 22, 737-749, doi:10.1111/geb.12029, 2013

Anonymous Referee #3

General comments:

This is a very interesting study on the different forms, stocks and bio-availability of P in Siberian soils. An interesting effort was also made to compare P values obtained on Siberian soils to P values obtained on soils around the world. The question of P availability for plants and microorganisms is a key issue for our understanding of the functioning and evolution of eco- and agro-systems in a context of climate change. I thank the authors for incorporating the comments of the “quick review” in this new version of the manuscript. I consider this article acceptable to be published in Biogeosciences, but with minor revisions.

Specific comments:

Title:

It is a cool name but it is a little bit confusing (reference to statistical analysis) and it does not mention the availability of P for the plants which is, in my view, an important result of your study.

RESPONSE: see our response to reviewer #1. We appended a subtitle which should avoid the confusion that both reviewers pointed out.

Introduction:

The vocabulary used and the structure of some sentences make some ideas hard to understand. Two examples:

1- 19821, line 13-15: “These altered physical conditions are expected to modify the composition of the plant communities and the bioclimatic zones of Siberia have been predicted to shift northward and their relative size to change.”

RESPONSE: We changed for: “Due to these altered physical conditions, vegetation communities may be modified. Projections indicate a shift of the Siberian bioclimatic zones northwards and a variation of their relative sizes”

2- 19822, line 9: “Also, P fertilization in agriculture is barely, if not at all, practised in Siberia”.

RESPONSE: We changes “Also” by “In addition”

Materials and methods:

- 19825, line 15: “Such soil preparation was reported to affect biogeochemical processes only at a

low magnitude (Cernohlávková et al., 2009; Chapman et al., 1997).” I do not understand the meaning of this sentence. Drying largely affects biogeochemical processes (for example: mineralization). You should correct or precise this idea.

RESPONSE: Indeed, microbial processes are impacted by drying and our phrase on “biogeochemical” processes is not correct. We replaced “biogeochemical” by “physico-chemical” which fits better with what we measured (we quantified only physico-chemical processes, not mineralization). These physico-chemical processes were found to be lowly impacted by sieving.

- What is the influence of the air drying-rewetting and grinding on: (i) the concentration of phosphate ions in solution, (ii) the diffusive phosphate ions at the solid-solution interface, (iii) soils textures (I think that this variable has been evaluated before grinding, am I wrong?).

RESPONSE:

First, we precise that soil is not ground for isotopic dilution (only dried and sieved at 2 mm). This should be more explicit in the revised version. Also, to answer your last question, texture was evaluated before grinding.

Achat et al (2012) showed that soil drying at 60 °C for 48 h alters the microbial biomass (cell lysis), and induce a release of inorganic P (as water soluble compounds such as phosphate ions). Therefore, total inorganic P and possibly diffusive phosphate ions are likely to be over-estimated, and organic P to be under-estimated, when measured on samples which have been dried. However, soil drying is part of a standard procedure in isotopic dilution and is usually performed at air temperature, which is lower than 60 °C and minimize impacts of drying. By using the standard procedure, we were able to compare our results with literature and to include them in the global data compilation.

Thus we added the following precisions in the text of the MM: “However, it also permits the prevention of microbial processes between sampling and analysis. We were careful to limit drying effects {Achat_2012} using a "soft method" (air drying to a constant weight instead of oven-drying at 60 °C, for example). In addition, air drying is a part of the usual protocol of the 32P isotopic dilution method (along with sieving at 2 mm, the use of a biocide such as toluene and measurements at 20 °C, see below). This allows the replication of measurements and comparison of the results with those in the literature.”

Reference cited in this response:

Achat D L, Augusto L, Gallet-Budynek A & Bakker M R. Drying-induced changes in phosphorus status of soils with contrasting soil organic matter contents – Implications for laboratory approaches Geoderma, 187-188, 41-48, doi:10.1016/j.geoderma.2012.04.014, 2012

- 19827, line 9: You should give the concentration of toluene not the volume.

RESPONSE: We changed to "10 µL toluene mL⁻¹ soil solution"

- 19827, line 11: “This biocide does not affect P biochemical processes (Bünemann et al., 2007)”. If you suppress/reduce life from your samples you should inevitably influence P biochemical processes. This information contradicts the idea p19830 line 1: “Since a biocide was added in the suspension, mineralization was stopped and we only measured physico-chemical processes”. You should correct or precise this idea.

RESPONSE: Indeed, there is a contradiction in what we wrote. We changed the term “biochemical processes” by “physico-chemical processes”. Those are the processes we were interested in with the isotopic dilution and they were found to not be influenced by biocide (Bünemann et al., 2007).

- 19829, line 1: “In this study, we computed the values of Pr for 1 day, 1 week, 1 month and 3 months.” In the manuscript you did not give the results for 1 month, is that important to precise this

point in the “material and methods” part?

RESPONSE: indeed, we did not show the values for 1 month to limit the amount of data presented in tables/Figures. We removed all mentions of Pr (1 month) in the text (MM).

Discussion:

The vocabulary used and the structure of some sentences make some ideas/paragraphs hard to understand.

Two examples:

1- 19837, line 8-11: “Soil formation processes and soil physico-chemical properties also explain that we observed such “outliers”. Despite overall slight effects only, soil content in Al and Fe oxides had some visible influence on soil P at the scale of some soil profiles.”

RESPONSE: We changed to: “... These “outliers” can be understood by considering the impact of soil forming processes on soil physico-chemical properties. At TOM...”

2- 19837 line 22 – 19838 line 2: “The restricted number of significant correlations – between P pools or isotopic dilution parameters (m and n) and soil physico-chemical properties – we identified in our study is not necessarily indicative of an absence of control on the P status. It may simply reflect that the values of the tested soil variables and P pools stand within a restricted range (same order of magnitude or difference of only one order; Table 2 and S4). Soils of the SW part of Siberia are indeed relatively homogeneous. They have developed on loess material deposited during the Quaternary era, mainly during the two last glaciation periods (Chlachula, 2003; Muhs, 2007) and despite some contrasted climate conditions, they have not been sufficiently impacted by diverging pedogenetic processes.” This part can be simplified.

RESPONSE: We propose: “The restricted number of significant correlations identified - between P pools or isotopic dilution parameters (m and n) and soil physico-chemical properties - is not necessarily indicative of an absence of control of the P status. It may simply reflect that the soil variables tested and P pool fall within a restricted range (with differences only up to one order of magnitude; Tables and S4). In fact, Al and Fe oxides, but also C, have noticeable effects when studying data compilations with wider ranges of values {Achat_2016}. This restricted range of variation in SW Siberia, despite the contrasting soil processes, probably has to be related to the relatively young age of the soils, which have developed on loess deposited during the two last glaciations in the Quaternary era{Chlachula_2003, Muhs_2007}.”

- Paragraph 4.3: You differentiate levels, concentrations and pH by qualifiers such as “high” and “very high”. Please be more precise.

RESPONSE: We added mentions to figures/quartiles

- 19838, line 20-22: “Contrarily to the other measured P pools in the studied SW Siberian soils, the concentrations of diffusive phosphate ions in the topsoil were not so high, in comparison to global levels (although not being very low; Fig. 4).” This is a very interesting result which deserved to be better discussed in this part.

RESPONSE: We developed 3 hypotheses that are likely, in our opinion, to explain such a result:

- these Siberian soils are young and have probably experienced only a low mineral alteration. Total P stock is high but it is possible that a great part is in primary mineral forms, which are not available on short time scales
- harsh Siberian climate conditions (cold winter but also water deficit in summer for the southernmost sites) may also induce slow kinetics of soil organic matter decomposition. This may contribute to the high organic P concentrations (relatively to the global values, see the Fig. 4 of the BGD manuscript), and organic P would not be a source of available P as important as in other ecosystems
- the relatively low sum of Al and Fe oxides may also limit Pr, by contrast to other soils at the global scale

Also, as part of these ideas were already present in the previous MS, some paragraphs were reorganized.

- 19838, line 25-27: *“In comparison, our SW Siberian soils have a low sum of Al and Fe oxides (68.44–184.08 mmol kg⁻¹) – and the narrow range of values explains why we found only a few correlations between P pools and oxides – and a very high pH (5.37–7.16, Table S4)”. You should divide this sentence in two sentences.*

RESPONSE: this sentence was modified during the reorganization of the paragraph and after English check.

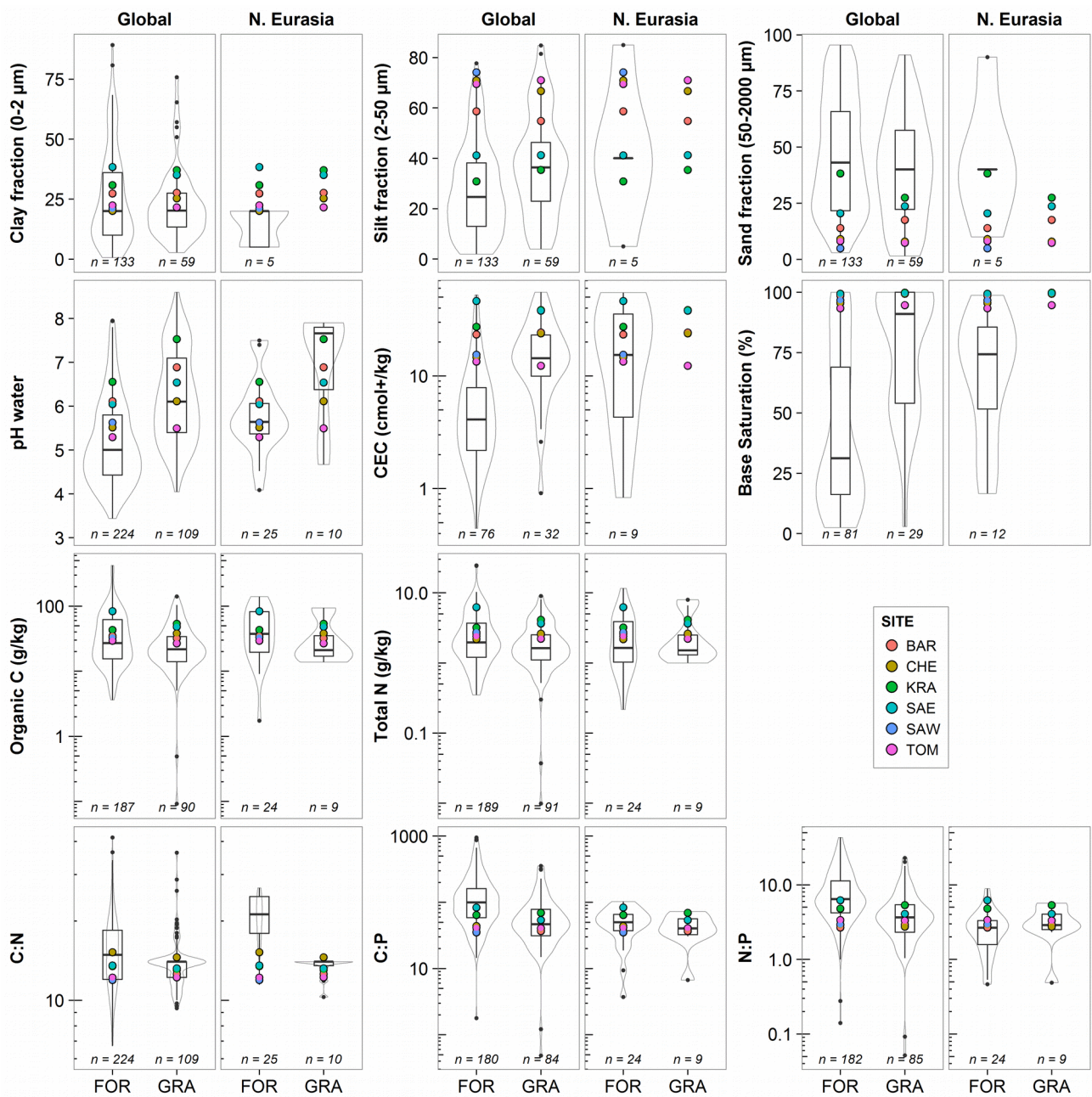


Figure S4: Comparison of selected soil properties in topsoils (about 0 to -20 cm) of SW Siberia (coloured dots) and different vegetation types (FOR: forests; GRA: grasslands -- box- and violin-plots) at the global scale and in Northern Eurasia (N. Eurasia), along broad gradients of soil and geology contexts. Parameters with less than 5 values available in our compilation dataset are not displayed. The ``n`` provided indicates the number of individual points used to build the box- and the violin-plots.

This figure was added to the supplementary material.

What is the P value of Siberian soils? Soil phosphorus status in south-western Siberia and comparison with a global dataset

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Abstract. Climate change is particularly strong in Northern Eurasia and substantial ecological changes are expected in this extensive region. The reshaping and migration northwards of bioclimatic zones may offer opportunities for agricultural development in western and central Siberia. However, the bioclimatic vegetation models currently employed for projections still do not consider soil fertility, in spite of being highly critical for plant growth. In the present study, we surveyed the phosphorus (P) status in the south-west of Siberia where soils are developed on loess parent material. We selected six sites differing in pedoclimatic conditions and the soil was sampled at different depths down to one metre in aspen (*Populus tremula* L.) forest as well as in grassland areas. The P status was assessed by conventional methods and by isotope dilution kinetics. We found that P concentrations and stocks, as well as their distribution through the soil profile, were fairly homogeneous at the regional scale studied, although there were some differences between sites (particularly in organic P). The young age of the soils, together with slow kinetics of soil formation processes have probably not yet resulted in a sufficiently wide range of soil physico-chemical conditions to observe more diverging P status. The comparison of our dataset with similar vegetation contexts on the global scale revealed that the soils of south-western Siberia and more generally of Northern Eurasia, often have (very) high levels of total, organic and inorganic P. The amount of plant-available P in topsoils, estimated by the isotopically exchangeable phosphate ions, was not particularly high, but was intermediate at the global scale. However, large stocks of plant-available P are stored in subsurface layers which currently have low fine-root exploration intensities. These results suggest that the P resource is unlikely to constrain vegetation growth and agricultural development under the present conditions or in the near future.

1 Introduction

Occupying about 10 million km⁻² (6.7% of global terrestrial land), Siberia has a paramount influence because ecological processes occurring here can have an impact at the global scale. Ranging from latitudes 45 to 75° N, it covers several bioclimatic zones, from south to north: steppe, forest-steppe, sub-taiga, southern taiga, middle taiga, northern taiga, forest tundra and

tundra. As the global climate change signal is particularly strong in Northern Eurasia (IPCC, 2013), substantial reshaping of ecosystems is ongoing in the region. The expected increase in average air temperatures will be responsible for longer vegetation growing seasons and frost-free periods, for the melt of permafrost in northern areas and for the modification of soil freeze-thaw cycles in southern areas (Groisman et al., 2012). The intensity and distribution of precipitation may change, resulting in differences in fire and hydrological regimes (Shiklomanov and Lammers, 2009; Shkolnik et al., 2010; Soja et al., 2007).
5 **Due to these altered physical conditions, vegetation communities may be modified. Projections indicate a shift of the Siberian bioclimatic zones northwards and a variation of their relative sizes** (Jiang et al., 2012; Shuman et al., 2015; Soja et al., 2007; Tchebakova et al., 2009, 2010). In particular, the area occupied by steppe and forest-steppe would increase at the expense of taiga zones. These modifications of ecosystem features may result in alternative land uses (Bergen et al., 2012; Kicklighter et al., 2014). Notably, under future climatic conditions, cropping of new species will be possible, or existing species may be used on vaster zones than at present in the southern parts of Western and Central Siberia (Kicklighter et al., 2014; Tchebakova et al., 2011). Primary productivity may be enhanced due to a “fertilization” effect induced by higher CO₂ levels in the air (Mooney et al., 1991; Norby et al., 2005; Schimel, 1995) along with longer periods sustaining plant growth. However, such projections lack the consideration of other important drivers of plant productivity such as the availability of resources like
10 nutrients and water in soils (Fernández-Martínez et al., 2014; He and Dijkstra, 2014; Oren et al., 2001; Reich et al., 2006a, b, 2014; van Groenigen et al., 2006). Even though there is an increasing interest in the study of Siberian ecosystems, functional ecological data remain sparse in the international literature (Gordov and Vaganov, 2010; Groisman and Soja, 2009).

In the domain of biogeochemistry, knowledge about the status of the major nutrients is lacking and potentially misleading assumptions could be made for Siberia. Together with nitrogen (N), phosphorus (P) is frequently a limiting resource for primary
20 production at the ecosystem scale (Elser et al., 2007; Harpole et al., 2011), but it is often considered that P is not the main limiting factor in northern ecosystems (Hedin, 2004; Reich and Oleksyn, 2004). **In addition,** P fertilization in agriculture is barely practised in Siberia, or not at all. However, a reconsideration of such a paradigm might be necessary in the context of global change. In fact, the increase of atmospheric CO₂ concentrations and N deposition, which are in general stronger and faster than any P input, are modifying the CNP stoichiometry of ecosystems (Peñuelas et al., 2013). As a consequence,
25 a progressive shift from N limitation to P limitation or N-P co-limitation can occur (Ågren et al., 2012; Peñuelas et al., 2012; Vitousek et al., 2010). These modifications of biogeochemical cycling at global and regional scales will participate in the way ecosystem reshaping is driven, for example through the modification of plant communities as they adapt to new stoichiometric constraints (Güsewell, 2004). It may also have consequences on agricultural potential at these scales.

In addition, the global resources of P that are used for mineral fertilizer production are limited (Cooper et al., 2011; Cordell et al., 2009). Therefore, enhancing our understanding of P cycles and managing them appropriately at the global scale is highly
30 relevant (Cordell et al., 2011; MacDonald et al., 2011) since modern terrestrial P cycling is dominated by human activities (Filippelli, 2008). One solution which would help to restrict the use of primary P resources, would be the development of cropping systems in areas where the soils contains sufficient plant-available P to prevent the (massive) use of P fertilizers. In this perspective, parts of Siberia are expected to become climatically more suitable for agriculture. Assessing the P status of
35 these Siberian regions is thus of relevance, and this was the main goal of our study.

In the present study, we aimed to identify the P status of the soils of SW Siberia, a region characterized by different types of soil along a North–South climatic gradient. We addressed the following questions: (1) how is the P stock structured in terms of pools and with depth, in the soils of SW Siberia? (2) Which environmental factors control this P status? (3) How can we qualify this P status in comparison with a panel of contrasting pedo-climatic conditions at the global scale? To do this, we selected six sites with contrasting pedo-climatic conditions in SW Siberia and presenting two characteristic vegetation covers, aspen (*Populus tremula*) forests and grasslands. We quantified total P, organic P, phosphate ions in solution and diffusive phosphate ions as a function of time in the soils from these sites. Classical soil analysis methods were combined with an isotopic dilution kinetics method. The sizes of P pools assessed at Siberian sites were compared with a global dataset compiled from 236 references.

2 Materials and methods

2.1 Site description

Many soils of south-western (SW) Siberia have developed on loess deposits – the Eurasian loess belt covers a broad latitudinal zone between 40 and 60° N – and present favourable texture and mineralogy for plant growth (Chlachula, 2003; Muhs, 2007). Soil formation depends on climatic conditions, vegetation cover and can be further shaped by anthropogenic actions. All of these – climatic conditions, vegetation cover and human activities – differ in intensity essentially along a gradient from south to north. Consequently, from the common origin of loess deposits, the soils in SW Siberia have undergone different types of development and are classified in the main groups of Chernozems, Phaeozems, and Luvisols. Water-table movements, leaching of carbonates and organic matter accumulation or distribution throughout the profile are the most striking features in these soils. The soil forming processes related to soil moisture levels and dynamics as well as the stability of organic matter (mineralization rates in relation to temperature and moisture regimes) and the type of vegetation are known to influence the soil P status (Giesler et al., 2002; Miller et al., 2001; Sundqvist et al., 2014; Vincent et al., 2014). We selected six sites in SW Siberia covering a transition including forest-steppe and sub-taiga zones. The main site characteristics are given in Table 1 (see also Tables S1–S3 in the Supplement and in Brédoire et al., 2016).

All the soil profiles studied were developed on a loess parent material and vegetation cover had comparable features in terms of dominant species composition, stand age and low human impact (i.e. no active management for the last few decades; Tables S2 and S3 in the Supplement). The main characteristics of the initial loess material are the predominance of coarse-silt particles and clay and the presence of CaCO₃; the latter having had different fates related to the different soil development processes. In Barnaul (BAR), Chebula (CHE), Krasnozerskoye (KRA) and Salair East (SAE), the main soil forming processes are the formation and accumulation of organic matter, leaching of carbonates in the topsoil and formation of secondary carbonates in deep soil layers. Soils belong to the Chernozems and Phaeozems soil groups. In Salair West (SAW) and Tomsk (TOM) soils experience watertable movements, with periodical saturation. Consequently, clays are washed from the topsoil and accumulate in the deeper layers and carbonates have disappeared from the first metre of the soil profile. In addition, the

litter decomposes faster than in forest-steppe and the accumulation of **organic matter** is very low at the soil surface. At these two sites, soils belong to the Luvisols group.

Five of the sites were almost pure aspen (*Populus tremula* L.; Table S2) forest stands together with nearby grassland areas. One site (SAW) only had forest cover with aspen. So there were six forest sites and five with grassland in our dataset for SW
5 Siberia. All aspen stands had closed canopies.

2.2 Sampling and preparation of the samples

For each type of vegetation cover at each site, we delimited three study plots (about 300 m²) about 200–2000 m apart. Those three plots were considered as replicates. One sampling campaign permitted sampling at all sites within three weeks in July 2013. At each plot, we dug a soil pit (with a surface area of about 2 by 1 m) down to 120 cm, except in SAE grasslands where
10 we reached a dense schist material around 80 cm which prevented us from going any deeper than 100 cm. In each soil pit, about 1 kg of soil was sampled horizontally with hand tools, at depths of 5, 15, 30, 60 and 100 cm ±5 cm. Another sample was taken with a cylinder (97 cm⁻³) to assess soil density.

Litter was sampled over an area of 30 cm by 40 cm in the vicinity of each soil pit. In this study we defined all the dead plant material deposited on the soil surface as “litter” (senescing leaf litterfall, small branches and senescing understorey vegetation
15 in forests; senescing herbaceous vegetation in grasslands). Consequently, the material collected in July, 2013 resulted mostly from the dead material from the previous vegetation season (2012) and the residues of older seasons, i.e. mainly OL and OF horizons, and possibly OH (at BAR, CHE, KRA and SAE).

Bulk soil samples were air dried to constant weight. After drying, soil samples coming from the same site and the same vegetation cover (i.e. 3 samples per site and per vegetation cover) were pooled and sieved at 2 mm to remove stones and coarse
20 roots. Soil density samples were not pooled. They were oven dried at 105 °C for 48 h and stones were removed when present (i.e. only in deep horizons of SAE).

Bulk litter samples were oven dried at 60 °C to constant weight. They were then pooled by site and by vegetation cover and the composite samples (3 per site and per vegetation cover) were ground before chemical analyses, except for the isotopic dilution.

25 Such soil preparation (sieving and drying) has been reported to affect **physico-chemical** processes only at a low magnitude (Černohlávková et al., 2009; Chapman et al., 1997). **However, it also permits the prevention of microbial processes between sampling and analysis. We were careful to limit drying effects (Achat et al., 2012) using a “soft method” (air drying to a constant weight instead of oven-drying at 60 °C, for example). In addition, air drying is a part of the usual protocol of the ³²P isotopic dilution method (along with sieving at 2 mm, the use of a biocide such as toluene and measurements at 20 °C, see
30 below).** This allows the replication of measurements and comparison of the results with those in the literature.

2.3 Physico-chemical analyses

2.3.1 Main soil properties

The French standard methods (Association Française de NORmalisation; AFNOR, 1999) were used for most of the physico-chemical soil analyses. For soil texture, the five size-fractions for clay ($< 2 \mu\text{m}$ diameter), fine loam ($2\text{--}20 \mu\text{m}$), coarse loam
5 ($20\text{--}50 \mu\text{m}$), fine sand ($50\text{--}200 \mu\text{m}$), and coarse sand ($200\text{--}2000 \mu\text{m}$) were assessed after decarbonation (NF X 31–107). Soil pH-H₂O was determined in a water/soil suspension with a mass-to volume ratio of 1 g : 2.5 mL (NF ISO 10390). Total organic C and N contents were determined by dry combustion with oxygen (NF ISO 10694 and NF ISO 13878, respectively). Total calcium carbonate contents were assessed using a volumetric method (NF X 31–105). Poorly crystalline aluminium (Al) and iron (Fe) oxides were extracted with an ammonium oxalate solution (McKeague and Day, 1966).

10 2.3.2 Total, organic and inorganic P

Total P concentrations (P_{tot} , in $\mu\text{g g}^{-1}$ soil) were determined, after grinding, by ICP following wet digestion with concentrated fluoric (HF) and perchloric acids after calcination at 450°C based on a standardized procedure (AFNOR NF X 31–147; AFNOR, 1999). Total soil organic P concentrations (P_{org} , in $\mu\text{g g}^{-1}$ soil) were determined as the difference between P extracted with H₂SO₄ in ignited and non-ignited soil samples (2 g of dry soil for 70 mL of 0.2 N H₂SO₄; Saunders and Williams, 1955),
15 concentrations were determined with a green malachite colourimetric method (van Veldhoven and Mannaerts, 1987). Total inorganic P concentrations (P_{inorg} , in $\mu\text{g g}^{-1}$ soil) were subsequently calculated as the difference between P_{tot} and P_{org} .

2.3.3 Plant-available phosphate ions

Plants take up P as ions from the soil solution. Thus, a good way of estimating a realistic plant-available P pool in the soil is to quantify both the concentration of phosphate ions in solution and the capacity of the solid phase to maintain this concentration.
20 To do this, we quantified the phosphate ions in the soil solution (C_p in $\mu\text{g mL}^{-1}$ soil solution or Q_w in $\mu\text{g g}^{-1}$ soil) and the diffusive phosphate ions at the solid–solution interface (P_r in $\mu\text{g g}^{-1}$ soil). P_r is the quantity of phosphate ions that can be exchanged between solid constituents (ions are adsorbed on soil particles) on a concentration gradient. P_r results from molecular agitation; it can be considered as a “P buffering capacity”. The sum of P_r and Q_w is the isotopically exchangeable phosphate ions (E) and is considered as a good proxy for the gross amount of plant-available P (Fardeau, 1996; Morel and
25 Plenchette, 1994). C_p and P_r were determined by an isotopic dilution kinetics method (Fardeau, 1996; Frossard and Sinaj, 1997; Frossard et al., 2011) as described below.

For each litter or mineral soil sample, five suspensions (1 g of litter or soil, sieved at 2 mm, with 10 mL of deionized water) were equilibrated for 16 h on a roller ($40 \text{ cycles min}^{-1}$) at 20°C (this temperature is commonly reported in the literature and is close to the average temperature of the soil at 20 cm in our study sites in the summer, Table S1). Toluene ($10 \mu\text{L}$
30 toluene mL^{-1} soil solution; M. Lineres, unpublished results) was added to the suspension at the beginning in order to stop microbial activity. This biocide does not affect P physico-chemical processes (Bünemann et al., 2007). The phosphate ions in

solution of the pre-equilibrated suspensions were labelled by introducing carrier-free ^{32}P ions in negligible concentrations but with known amounts of the introduced radioactivity (R). Suspensions were then sampled with a plastic syringe after 4, 10, 40, 100 and 400 min and filtered on a membrane at 0.2 μm . Then, both C_p and radioactivity remaining in the filtered solution at the time of sampling ($r(t)$) were quantified. C_p was determined using a green malachite colourimetric method (van Veldhoven and Mannaerts, 1987) and Q_w was calculated using the volume of water (V in mL) and the mass of litter or soil (m_s in g):

$$Q_w = C_p \times \frac{V}{m_s} \quad (1)$$

For each sample, C_p was not impacted by the sampling time of the isotopic dilution method (Fig. S1 in the Supplement). The radioactivity remaining in the filtered solution ($r(t)$) was determined in a counter (Packard TR 1100) using a liquid scintillation cocktail. In the steady state conditions of the suspension (C_p constant), the gross transfer of phosphate ions from the solid constituents to the solution is equal to the gross transfer of phosphate ions from the solution onto the solid constituents. We assumed that no isotopic discrimination occurs between the two P isotopes (^{31}P ions and ^{32}P ions) during the transfers between the liquid and the solid phases. The amount of unlabelled phosphate ions newly transferred from the solid constituents to the solution ($Pr(t)$) was then calculated from Q_w and $r(t)$ values following the principle of isotopic dilution (R is diluted in E).

$$\frac{R}{E} = \frac{r(t)}{Q_w} = \frac{R - r(t)}{Pr(t)} \quad (2)$$

Rearranging Eq. (2) gives:

$$Pr(t) = \frac{Q_w \times (R - r(t))}{r(t)} = Q_w \left(\frac{1}{r(t)/R} - 1 \right) \quad (3)$$

where: $\frac{r(t)}{R}$ (dimensionless) is the isotopic dilution ratio.

The theoretical Eq. (4), adapted from Fardeau (1993, 1996) was used to fit the experimental values of $\frac{r(t)}{R}$ closely, as a function of isotopic dilution time:

$$\frac{r(t)}{R} = m \left(t + m^{\frac{1}{n}} \right)^{-n} \quad \text{for} \quad \frac{r(t)}{R} \geq \frac{r(\infty)}{R} \quad (4)$$

where: m and n are fitting parameters and $\frac{r(\infty)}{R}$ corresponds to the maximum possible dilution of the isotope, considering that all inorganic P can take part in the isotopic dilution. The value of $\frac{r(\infty)}{R}$ tends towards $\frac{Q_w}{P_{\text{inorg}}}$ (Fardeau, 1993; Frossard et al., 2011). The parameter m , which is the fraction of radioactivity remaining in solution after 1 min ($\frac{r(1 \text{ min})}{R}$), accounts for the immediate physico-chemical reactions, while the parameter n accounts for the slow ones (Fardeau et al., 1991; Fardeau, 1993). The quality of the fit for Eq. (4) is shown in Fig. S2 in the Supplement and the values of m and n are provided in Table S5 in the Supplement.

Combining Eqs. (3) and (4), we can derive the value of Pr over time, each value corresponding to a pool of P more or less rapidly available to plants. The number and the size of such pools can be defined considering plant functioning (Fardeau, 1993). In this study, we computed the values of Pr for 1 day, 1 week, and 3 months. While 1 day is the mean duration for active root uptake, 3 months is approximately the duration of the vegetation season in south-western Siberia and we might expect this to fit with intense root activity.

2.4 Data handling and statistics

Five soil layers were defined between 0 and 120 cm according to the soil horizon description of each soil pit (horizons were merged or divided in order to have 5 layers corresponding to the 5 sample depths, the profiles studied presented between 4 and 7 horizons, the mean number of horizons of the 33 profiles studied is 5). Assuming that elemental concentrations and soil densities measured in each of the five defined horizons were representative of the entire horizon, we computed the stock (in Mg ha⁻¹) of each P pool using mean soil densities and horizon thicknesses:

$$\text{stock} = \frac{1}{10000} \times [P] \times d \times h \quad (5)$$

where: $[P]$ is the concentration of the P pool (in $\mu\text{g g}^{-1}$), d the soil density (in g cm^{-3}) and h the thickness of the soil horizon in cm. In litter, the P stocks were computed (in Mg ha⁻¹) using the mass and the surface area sampled:

$$10 \quad \text{stock} = \frac{1}{10000} \times [P] \times m_{\text{litter}} \quad (6)$$

where: $[P]$ is the concentration of the P pool (in $\mu\text{g g}^{-1}$) and m_{litter} the mass of litter (in g m^{-2}). We used the limit of -20 cm to distinguish between top- and subsoil to fit with most agronomic studies, but also with the zone where most of the fine root exploration occurs in SW Siberia (Brédoire et al., 2016).

In order to gain an idea of the structure of the P stocks in the soils studied, we computed the relative proportions of the different P pools measured, as a fraction of P_{tot} . P_{tot} is the sum of P_{org} and P_{inorg} . Since a biocide was added to the suspension, mineralization was stopped and we only measured physico-chemical processes. Thus, all exchangeable P (the sum of Q_w and Pr) is part of P_{inorg} . Pr being calculated as a function of time and the maximum time considered in this study being 3 months, the potential remaining fraction of P_{inorg} is considered as non-diffusive, or diffusive in more than 3 months. We note that when considering two values of Pr computed at different times, the pool of exchangeable P computed at the longer time includes the one computed at a shorter time.

Relations between P parameters and soil physico-chemical properties were investigated by computing Spearman's rank correlation coefficients, scatter plots and (non-)linear regressions. Soil physico-chemical properties varied with soil depth (Table S4 in the Supplement) as well as the P parameters investigated (Table 2). Thus, we looked for correlations in each soil layer separately in order to avoid covariation and interdependence issues (Table S6 in the Supplement). We also analyzed correlations with fine root (diameter < 0.8 mm) length density (FRLD) and fine root mass density (FRMD) measured in the same soil pits and at the same soil depths as for the soil physico-chemical properties (Brédoire et al., 2016).

Since analyses were made on composite samples we did not quantify the variability of our measurements at the site level for given vegetation cover and soil depth. Thus, differences between sites were not tested through formal statistical tests. However, we calculated the coefficient of variation (ratio of the standard deviation to the mean) for each layer and vegetation cover.

All data management, (non-)linear regressions and statistical analyses (correlation coefficients and their significance), were performed with R 3.2.1 (R Core Team, 2015).

2.5 Comparison at the global scale

To compare the phosphorus status of our study sites with other grassland or forest ecosystems and with croplands, we compiled data on different P fractions in soils. In practice, we used different requests involving keywords such as “soil”, “phosph*”, “total content”, “isotopic dilution”, “isotopically exchangeable P”, “grassland”, “forest”, “woodland”, etc. These requests were carried out both in Web of Science and Google Scholar. To derive the pools of diffusive and isotopically exchangeable phosphate ions, we selected all publications using the same isotopic dilution procedures as in the present study (i.e. Fardeau’s procedure; Fardeau, 1993, 1996). Additional publications were selected in order to improve the geographical coverage for total and organic P. In particular, we examined all the tables of contents of the *Soviet Soil Science* and the *Eurasian Soil Science* journals to provide a better cover of Northern Eurasian ecosystems. Based on all the selected references, we compiled a dataset of different P fractions (total P, organic P, phosphate ions in soil solution, diffusive phosphate ions and isotopically exchangeable phosphate ions) in soils of grasslands, forests, or croplands. This database contained P values for up to 373 distinct sites depending on the P fraction, the geographical scale and the vegetation type studied, which were collected from 236 references. This database was representative of soils throughout the world as shown by the geographical distribution of compiled sites (Fig. 1), even though the studies using the isotopic dilution kinetics method in forest were sparse. In particular, out of the 116 forest study sites present in the compilation – with values for inorganic P, organic P, phosphate ions in solution, diffusive phosphate ions and isotopically exchangeable phosphate ions –, 106 are located in France. Nevertheless, France does have very diverse soils and geology. The most represented soil types are Podzols, Cambisols and Luvisols, but Planosols, Leptosols, Calcisols, Arenosols, Regosols and Andosols are also present in some sites (IUSS Working Group WRB, 2014). The main parent materials are calcareous formations, eruptive and metamorphic rocks, sandstone, detritic and weathered formations. Of these 106 French sites, 50 are hardwood forests (2 species) and 56 are coniferous forests (5 species). Therefore, our dataset was representative of forests at the global scale for total soil P, and representative of very diverse temperate forests for isotopic P data. In addition to the concentrations in different P pools, we also collected data on other soil properties such as texture, pH-water, cation exchange capacity (CEC), base saturation, organic C, and total N. The references of the data compilation are provided in the Supplement.

3 Results

3.1 Quantification of P pools

The concentrations of total P (P_{tot} ; 694–1095 $\mu\text{g g}^{-1}$ at –5 cm, 319–694 $\mu\text{g g}^{-1}$ at –100 cm), organic P (P_{org} ; 389–774 $\mu\text{g g}^{-1}$ at –5 cm, 37–79 $\mu\text{g g}^{-1}$ at –100 cm) and phosphate ions in solution (Q_w ; 2–22 $\mu\text{g g}^{-1}$ at –5 cm, 0.1–0.4 $\mu\text{g g}^{-1}$ at –100 cm) decreased with depth in the 1 m profiles at all the studied sites for both forest and grassland (Table 2). The litter layer presented the highest concentrations for these pools; Q_w being one to two order(s) of magnitude more concentrated in the litter (223–638 $\mu\text{g g}^{-1}$) than in the upper soil layer (2–22 $\mu\text{g g}^{-1}$ at –5 cm). No systematic variation with depth was found throughout the profile for inorganic P (P_{inorg} ; 296–626 $\mu\text{g g}^{-1}$ at –5 cm, 282–616 $\mu\text{g g}^{-1}$ at –100 cm) and diffusive phosphate ions (e.g.

Pr (1 day); 16–56 $\mu\text{g g}^{-1}$ at –5 cm, 2–67 $\mu\text{g g}^{-1}$ at –100 cm; Table 2). However, Pr (1 day) decreased in the three first mineral soil layers, except for the grassland in SAE.

We computed stocks (Mg ha^{-1}) for the different P pools (Table 3). With the exception of Q_w , the subsoil contributed the most to the total stocks (72–85 % of P_{tot} , 64–73 % of P_{org} excluding SAE, 82–90 % of P_{inorg} and 67–94 % of Pr (1 day)). The three layers considered (litter, topsoil and subsoil) contributed almost equally to the total stock of Q_w (respectively, 10–56, 26–65 and 7–49 %). All sites presented values in the same order of magnitude for a given P pool and a given layer. The values for forest and grassland were also close. One notable difference occurred at the site SAE, where soil P pools were lower in forest than in grassland and where the pools in forest were lower than in the other sites. KRA presented the highest stocks in litter for all P pools, however, its stocks in the topsoil were the lowest (except for Q_w and Pr (1 day) in grassland) and they were also relatively low in the subsoil.

For each layer, we calculated the relative contribution of each P pool to total P (Fig. 2). With the exception of one grassland site (TOM), P_{org} accounted for more than 50 % of P_{tot} in the litter layer. The concentration of phosphate ions in solution (Q_w) represented 20–38 % of P_{tot} in the litter layer with similar values for forest and grassland at each site. One site (TOM) presented much higher values of Q_w in litter, reaching 45 and 67 % of P_{tot} in forest and grassland respectively. All the sites studied, and whatever the vegetation cover, exhibited the same pattern along the mineral soil profile. The relative proportion of P_{org} decreased, while the relative proportion of P_{inorg} increased with depth. In the two upper soil layers the distribution of P pools was very comparable. P_{org} accounted for 34–71 % of P_{tot} and Pr (3 months) for 3–13 %. Q_w represented up to 2 % of P_{tot} at –5 cm, dropped below 0.1 % at –30 cm and was about 0.01 % at –100 cm. The proportions of Pr tended to be higher in forest than in grassland. Below –15 cm, the proportion of P_{org} decreased to 6–19 % at –100 cm. In the deepest layers, the proportions of Pr tended to be higher than in the first two, with notable exceptions: extremely low values at –100 cm in SAE, and Pr (3 months) representing 100 % of P_{inorg} at –60 cm in TOM grassland.

3.2 Relations between P pools and environmental parameters

We tested the correlations between P parameters and the main soil physico-chemical properties (Table S6 and Fig. S3 in the Supplement). P_{inorg} was significantly correlated with P_{tot} (Spearman's rank correlation coefficients ranging between 0.627 and 0.989). This was also observed between n and pH at most depths except at –15 and –100 cm (–0.636 to –0.793). In the three top layers, P_{org} was significantly correlated with organic C (0.682 to 0.843) and m with Q_w (0.609 to 0.855). In the two deepest layers, Pr and isotopically exchangeable phosphate ions (E) were significantly correlated with the clay fraction (0.782 and 0.852). They were also negatively correlated with CaCO_3 (–0.649) at –60 cm (Table S6) but this was driven by one point which was very depleted in CaCO_3 and with very high Pr and E (Fig. S3). A few correlations were found with Al and Fe oxides: with P_{org} at –30 cm (–0.636) and with n at –60 cm (0.718).

A few relationships between fine root densities and P pools were significant (Table S6 and Fig. S3). At –15 cm, fine root length density (FRLD) was significantly and negatively correlated with Q_w (–0.636), m (–0.764), Pr (1 day) (–0.691) and E (1 day) (–0.736). At –30 cm, FRLD was significantly and negatively correlated with n (–0.773) and fine root mass density (FRMD) with n (–0.655), Pr (0.636) and E (0.618).

No relationship was found between the different variables of the P status and any of the climatic parameters presented in Table S1 (data not shown).

3.3 Comparison at the global scale

Total P concentrations in topsoil (the first 20 cm of the soil) ranged at the global scale between 62 and 2480 $\mu\text{g g}^{-1}$ in croplands, 5 between 19 and 3090 $\mu\text{g g}^{-1}$ in forests and between 32 and 3548 $\mu\text{g g}^{-1}$ in grasslands (Fig. 3). Our measurements in SW Siberia ranged between 345 and 770 $\mu\text{g g}^{-1}$ in forests and between 481 and 741 $\mu\text{g g}^{-1}$ in grasslands; these values were close to and above the global upper quartile for forests and between the global median and the upper quartile for grasslands. Compared with global cropland values, these Siberian concentrations were mostly above the upper quartile. Restricting the domain of comparison to Northern Eurasia, SW Siberian soils ranged between the lower and the upper quartiles for forests and between 10 the median and the upper quartile for grasslands, indicating that our sites are representative of Northern Eurasia. In the subsoil (-20 to -100 cm), less points were available at the global and Northern Eurasian scales for comparison. However, our SW Siberian forest and grassland soils occupied wider ranges in comparison to the corresponding vegetation types: from below the median to above the upper quartile at the global scale and a similar range of values to Northern Eurasia.

The concentrations of P_{org} , P_{inorg} and phosphate ions in solution (C_p) in the topsoil of the SW Siberian forests studied were 15 generally above the upper quartile, in comparison essentially with French forests having contrasting species, soil and geology (Fig. 4). In grassland, the SW Siberian values were mostly comprised between the global median and upper quartile. Compared with global cropland ranges, our measurements were around and above the upper quartile for P_{tot} and P_{org} , mainly below the upper quartile for P_{inorg} and from the median to above the upper quartile for C_p . Interestingly, the proportion of measured P_{org} (% of P_{tot}) varied quite a lot in the range reported at the comparative scales, particularly in forests where SW Siberian values 20 varied from below the lower quartile to above the upper quartile. In contrast with the other P pools, the concentrations of Pr (1 day) and E (1 day) were more moderate: they ranged between the median and the upper quartile in forests and between the lower quartile and the median in grasslands, these values being lower than the global cropland median.

Relative to the soils included in the comparison dataset, the SW Siberian topsoils studied presented high contents (often above the third quartile of the global distribution ranges for both forest and grassland) of the silt fraction ($2\text{--}50\ \mu\text{m}$) and 25 low contents (below the first quartile) of the sand fraction ($50\text{--}2000\ \mu\text{m}$) (Fig. S4). Their pH-water ($5.3\text{--}7.5$) tended to be higher when compared with the global levels ($4.7\text{--}6.3$, first–third quartiles), particularly in forests, but the ranges of the SW Siberian soils were similar to those of Northern Eurasia. Our study soils also had particularly high CEC ($12\text{--}46\ \text{cmol} + \text{kg}^{-1}$ as compared to the global first–third quartiles $3\text{--}15\ \text{cmol} + \text{kg}^{-1}$) and extremely high base saturation ($93\text{--}99\%$ versus $21\text{--}87\%$). Their concentrations in organic C were medium to very high ($27\text{--}83\ \text{g kg}^{-1}$ versus $15\text{--}52\ \text{g kg}^{-1}$ for the first–third 30 global quartiles), as were their concentrations in total N ($2\text{--}6\ \text{g kg}^{-1}$ versus $1\text{--}4\ \text{g kg}^{-1}$). Finally, the studied Siberian forest soils presented lower C : N, C : P, and N : P mass ratios than the global levels (C : N ranged between 12 and 15 versus 12–19 for the first–third global quartiles; C : P was 35–83 versus 50–153; and N : P was 3–6 versus 4–10) while the SW Siberian grasslands presented ratios in the same ranges as our global data compilation (Fig. S4).

4 Discussion

4.1 A relatively homogeneous P status

All the sites, for both aspen forest and grassland, presented a similar distribution of the P pools throughout the soil profile. Total P concentrations decreased with depth, mainly in relation to the decrease in the concentration of organic P (Table 2). The stock variation was of the same order of magnitude between and within sites, and between contrasting vegetation cover types. The concentrations and the stocks we computed were close to those reported by Achat et al. (2013a). These authors reported standard errors of 1–27 % for the concentrations of total P, organic P, inorganic P, phosphate ions in soil solution and diffusive phosphate ions, with three replicates per condition in two sites of the same region. Assuming a similar spatial variability, the concentrations and stocks we measured or computed for given soil layers appeared relatively homogeneous (values in the same order of magnitude without notable outliers) at the regional scale.

Despite lower concentrations of the P pools in the subsoil, this contributed the most to the total stocks computed over 1 m (Table 3) because of its greater thickness. For the same reason, at the soil profile scale, inorganic P represented far more than 50 % of the total P stock (Table 3), while organic P concentrations represented a high proportion of total P in the litter and in the first three soil layers (Table 2). For the whole profile, the P stock in the soils studied can be qualified as predominantly mineral down to 1 m.

4.2 Environmental factors controlling the regional P status

In spite of small variations in the current P status of the soils investigated, we found that this status was impacted by a set of variables. At first, we observed that the amount of P was highly dependent on the amount of inorganic P, particularly in the subsurface layers of the sites studied (Fig. 2 and Table 3). Biogeochemical cycling and soil development processes explain the P status with depth. In the topsoil, organic P represented a large part of total P (Fig. 2) and was related to organic C (Table S6 and Fig. S3). This is a direct consequence of P uptake, immobilization in plant tissues, followed by litterfall and subsequent accumulation in the top horizons (Barber, 1995). Clay minerals (on their edges), carbonates and organic matter have surfaces presenting positive charges that are reactive with phosphate ions (Gérard, 2016; Hinsinger, 2001; Parfitt, 1978). In the topsoil, the preponderance of organic P suggests that microbial processes may play an important role in the plant-availability of P through the release of phosphate ions by mineralization. Conversely, in deep horizons P plant-availability is principally explained by mineral phases such as the clay fraction (Table S6 and Fig. S3). Contrary to other case studies (Achat et al., 2011; do Carmo Horta and Torrent, 2007; Tran et al., 1988; Walbridge et al., 1991), we found only a few relationships with Al and Fe oxide concentrations. These oxides also present positive charges that are known to be reactive with phosphate ions (Achat et al., 2011; Regelink et al., 2015).

The inspection of the correlations involving parameters m and n provides further insights into the drivers of phosphate ions exchange at the solid–solution interface. Correlations with m , which is the fraction of radioactivity remaining after one minute in the isotopic dilution, give information about rapid processes, while correlations with n are considered to be indicative of processes driving slow exchange reactions. Both parameters were related to the phosphate concentration in solution (Q_w).

Generally m increased with Q_w while n decreased (Table S6 and Fig. S3), in agreement with previous studies (Achat et al., 2009, 2013a; Fardeau, 1993; Morel et al., 2000). The dynamics of phosphate ions (slow reactions in the present study) were also dependent on pH, which modifies the charge of reactive solid surfaces and the speciation of phosphate ions (Barrow, 1983; Hinsinger, 2001; Strauss et al., 1997a, b; Ziadi et al., 2013). In addition, we found slight secondary effects of Al and Fe oxides on slow phosphate ion exchange reactions: residual values of the parameter n increased with the increase in oxide contents (data not shown). This is in accordance with a preliminary study in SW Siberia (see more details on the effects of Al and Fe oxides on parameter n in Achat et al., 2013a).

Nevertheless, at some sites, a few layers did not exhibit the general features of the P status described above. These “outliers” can be understood by considering the impact of soil forming processes on soil physico-chemical properties. At TOM, the periodical water-table movements may be responsible for the relatively stronger accumulation of clays and oxides in deeper soil layers (Table S4). Since these elements are reactive with phosphate ions, they may contribute to the higher concentrations and proportions of diffusive phosphate ions in these soil layers (especially at -60 cm in grassland; Table S4). At KRA, the accumulation of CaCO_3 (Table S4) could be responsible for high levels of diffusive phosphate ions in the subsoil. In fact, in alkaline soils such as in KRA, phosphate ions tend to precipitate with Ca cations which have an increasing solubility at pHs above 8 (Hinsinger, 2001; Kuo and Lotse, 1972). At SAE, the schist material underlying the loess deposit (below -80 cm) is probably responsible for low P pool concentrations (particularly in forests) and extremely low proportions of diffusive phosphate ions in the deep layers compared with the other sites.

The restricted number of significant correlations identified – between P pools or isotopic dilution parameters (m and n) and soil physico-chemical properties – is not necessarily indicative of an absence of control of the P status. It may simply reflect that the soil variables tested and P pool fall within a restricted range (with differences only up to one order of magnitude; Tables 2 and S4). In fact, Al and Fe oxides, but also C, have noticeable effects when studying data compilations with wider ranges of values (Achat et al., 2016). This restricted range of variation in SW Siberia, despite the contrasting soil processes, probably has to be related to the relatively young age of the soils, which have developed on loess deposited during the two last glaciations in the Quaternary era (Chlachula, 2003; Muhs, 2007). Additionally, soil forming processes are expected to be relatively slow in such a dry and cold region (Jenny, 1941).

4.3 High levels of total P fractions but moderate ones for plant-available P

In general, the SW Siberian soils studied presented very high concentrations (above the third quartile) for total P, organic P, inorganic P and phosphate ions in soil solutions in forest and high concentrations (close to the third quartile) in grassland, when compared with our compilation of data at the global scale (or diverse soil and geological contexts mainly in France, for all P pools except total P, in forests) (Figs. 3 and 4). In addition, it might be possible to generalize the high level of total P stocks to Northern Eurasia, at least for the soils developed in the loess belt (Fig. 3). Of course, more field measurements are required to verify this statement, particularly in the vast zone currently covered by taiga and which is not in the loess belt. This result, if confirmed, would be of primary importance in the context of global change and of tensions related to resources of P for agriculture.

However, we noted that these relatively high concentrations of total P in SW Siberian soils did not automatically indicate a high P availability for plant nutrition. In fact, an important parameter is the ability of the soil to refill a depleted soil solution (e.g. due to root uptake) with phosphate ions. This “P buffering capacity” assimilates the quantity of diffusive phosphate ions between the solid and the liquid phases of soil. Contrary to the other measured P pools in the SW Siberian soils studied, the concentrations of diffusive phosphate ions in the topsoil were not that high in comparison with global levels (although not being very low; Fig. 4). Several hypotheses may explain such a phenomenon, notably: the early development stage of the soils studied, the relatively slow kinetics of the processes producing phosphate ions, and the relatively low contents in metal oxides coupled with high pH. These three hypotheses are developed in the next two paragraphs.

Following the conceptual model of Walker and Syers (1976), which describes the changes in the forms and amounts of P pools with time, together with the comments we made in the sections above about the regional homogeneity of the P status, we concluded that these SW Siberian soils are probably in the early stages of soil development. This stage is characterized by the build-up of an appreciable organic P stock, but also by a stock of primary inorganic P, which remains large and is made available by weathering. Thus, there may still be a high potential of primary mineral weathering in these soils. Moreover, the mineralization of organic matter is another source of phosphate ions available to refill the soil “P buffering capacity” (Achat et al., 2013b; Büneemann, 2015). The kinetics of both mineral weathering and mineralization might be relatively slow in SW Siberia due to the relatively cold and dry climate conditions (Jenny, 1941). The study of the kinetics of these mechanisms is relatively difficult and was not carried out within the scope of this study. However, they could be of importance, as they are likely to be impacted by global change. Organic matter mineralization would mainly depend on temperature and moisture (Bengtson et al., 2005; Paul et al., 2002). Mineral alteration would mainly depend on temperature and pH (Augusto et al., 2000; Drever, 1994).

In French forests, the sums of Al and Fe oxides range from 4.5 to 1157.7 mmol kg⁻¹ and pHs from 3.6 to 8.3 (data compilation of 106 sites; Achat et al. (2016)). In comparison, our SW Siberian soils have low sums of Al and Fe oxides (68.44–184.08 mmol kg⁻¹) and very high pHs (5.37–7.16, Table S4). When compared with our global data compilation, SW Siberian pH values can be qualified as high to very high (around and above the third quartile) in forests, but remain in the global range (first–third quartile) for grasslands, which generally exhibit higher pH values than forests in our data compilation (Fig. S4). The narrow ranges of values measured in our study sites may explain why we found only a few significant correlations between P pools and oxides. Furthermore, the (very) high pHs of these Siberian soils are probably partly responsible for the low reactivity of phosphate ions, notably because the number of positive charges decreases with increasing pH (Barrow, 1983; Hinsinger, 2001; Ziadi et al., 2013). Coupled with a low quantity of oxides (i.e. fixation sites), this might explain, at least partly, the average values of diffusive (*Pr*) and isotopically exchangeable (*E*) phosphate ions in the SW Siberian soils studied, while total pools were (very) high.

The absence of correlation between fine root densities and P pools (Table S6) suggests that root exploration is not related to a search for P. In addition, the richness of total P in the soils studied also impacted elemental stoichiometry, particularly in forests where the C:P (35–83) and the N:P (3–6) ratios were relatively low compared with global levels (Fig. S4). These findings – low C:P and N:P ratios in SW Siberian soils – are in accordance with the global mean values reported for forests (212

and 14.6 for C : P and N : P, respectively) but also for grasslands (166 and 12.3 for C : P and N : P, respectively) by Cleveland and Liptzin (2007). The ranges reported by Xu et al. (2013) for boreal forests, temperate broadleaf forests and grasslands also confirm that the Siberian soils studied have high amounts of P in comparison with other elements such as C and N. The relatively low N : P ratios measured in the litter layers (9–14; Table S4), in the soil (at least in forest, Fig. S4) as well as in green aspen leaves (9–12, data not shown) suggest that P is unlikely to be the primary limiting nutrient for plant nutrition and litter decomposition, and that it could be N which might be the limiting factor (Aerts and Chapin, 1999; Reich and Oleksyn, 2004; Güsewell and Gessner, 2009). However, compared with our global data compilation, the C : N ratios of the Siberian soils studied were relatively low, particularly in forests (Fig. S4), indicating that these soils may have high amounts of total N. In that case, N would only be limiting if mineralization processes – on which most of plants are dependant for N resources – were not sufficient to respond to plant requirements, at least during the period of maximum requirements (for example in spring).

In general, the availability of P probably does not constrain plant growth in the ecosystems studied to any great extent. This conclusion is in line with the review made by Smurygin (1974) about fertilization experiments in the former USSR.

Will this P status be sufficient to fulfil future plant requirements in the context of global change? In the speculative situation where topsoils are depleted by intense biomass exports, our results suggest that the large P stocks in deeper soil layers could sustain the demand (Table 3). This would imply a deepening of plant fine root systems, which has already been observed with ongoing global change, related to the increase in atmospheric CO₂ concentrations (Iversen, 2010) or with the lengthening of vegetation growing seasons (Lempereur et al., 2015; Majdi and Öhrvik, 2004). In SW Siberia, we suggest that deeper fine root systems would be more likely to be driven by other resources, in particular water, in the steppe and forest-steppe zones (Brédoire et al., 2016).

20 5 Conclusions

This study revealed that the concentrations, the stocks of the different P pools measured and their distribution in the soil profile were relatively homogeneous at the scale of SW Siberia, although there were some differences between sites (mainly organic P) possibly due to varying microbial activity and slight differences in physico-chemical soil properties. In this region, we argue that the young age of the soils, developed on loess parent material, coupled with slow kinetics of pedogenesis have probably not yet resulted in a sufficiently wide range of soil physico-chemical conditions to observe more diverging P status. The comparison of these Siberian P levels with similar types of vegetation on the global scale revealed high to very high levels of total, organic and inorganic P in the topsoils. It would seem to be possible to generalize these results to Northern Eurasia, but additional measurements are required to verify this statement. The amount of plant-available P in topsoils, evaluated as isotopically exchangeable phosphate ions, was intermediate on the global scale. However, large stocks of isotopically exchangeable phosphate ions are stored in the subsurface layers where fine root exploration is currently low. These results suggest that the P resource is unlikely to constrain vegetation growth and agricultural development under present conditions and in the near future.

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Table 1. Main characteristics of the study sites. Additional information are provided in Tables S1–S3.

Site ID	BAR	CHE	KRA	SAE	SAW	TOM
Geographical characteristics						
Name ^a	Barnaul	Chebula	Krasnozerskoye	Salair East	Salair West	Tomsk
Ecological zone	Forest-steppe (southern part)	Forest-steppe (northern part)	Steppe to Forest-steppe	Sub-taiga to Forest-steppe	“Blackish taiga”	Sub-taiga
Latitude (° N)	53.41	55.55	53.59	54.39	54.18	56.30
Longitude (° E)	83.47	84.00	79.14	85.75	85.17	85.43
Elevation (m a.s.l.)	221	186	141	305	358	232
Climate characteristics (annual mean 1981–2010)						
Air temperature (°C)	2.7	1.3	2.9	2.3	1.2	0.9
Precipitation (mm)	431.5	509.8	324.5	432.3	453.0	566.5
Soil classification						
Soil in forest	Haplic Phaeozem	Haplic Phaeozem	Phaeozem	Leptic Phaeozem	Haplic Luvisol	Albic Luvisol
Soil in grassland	Calcic Chernozem	Haplic Phaeozem	Calcic Hortic Chernozem	Leptic Phaeozem		Albic Luvisol
Forest stand characteristics (mean values)						
Density (tree ha ⁻¹)	1664	387	767	1883	1144	1139
DBH ^b (cm)	14.9	33.9	26.3	13.7	22.8	21.4
Height (m)	11.2	28.0	18.7	15.7	24.8	18.2
Age (years)	27	62	51	21	47	56

^a Name of the closest city or name of the local area. ^b Diameter at breast height (1.3 m).

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Table 2. Phosphorus concentrations of different pools measured in litter and soil layers of south-western Siberia. Concentrations are expressed in $\mu\text{g P g}^{-1}$ soil (or litter), depth is in cm. “Litter” means all the dead plant material deposited on the soil surface (senescing leaf litterfall, small branches and senescing understorey vegetation in forests; senescing herbaceous vegetation in grasslands) i.e. mainly OL and OF horizons, and possibly OH (at BAR, CHE, KRA and SAE) at the date of sampling.

P pool	Depth (cm)	Forest							Grassland					
		BAR	CHE	KRA	SAE	SAW	TOM	CV	BAR	CHE	KRA	SAE	TOM	CV
Total P	Litter	1235.6	1174.5	1318.6	1231.3	1515.1	1011.8	13	1165.8	1340.4	1122.1	1318.6	953.1	13
	–5	1017.3	851.4	729.2	1095.9	1039.2	759.7	17	877.6	956.2	847.0	921.3	694.2	12
	–15	951.8	663.7	615.6	908.2	864.5	676.8	19	864.5	938.7	698.6	873.2	624.4	17
	–30	960.6	628.7	541.4	416.1	768.5	558.9	30	755.4	899.4	628.7	563.2	528.3	23
	–60	764.1	676.8	394.7	323.5	585.1	489.0	31	593.8	689.9	515.2	611.3	493.4	14
	–100	637.5	659.3	408.2	319.2	646.2	528.3	27	593.8	694.2	414.4	593.8	537.0	18
Organic P	Litter	817.3	760.1	839.5	896.2	910.8	758.9	8	800.5	690.4	640.7	855.5	660.0	13
	–5	391.6	405.6	418.5	773.7	470.0	436.1	30	388.8	539.2	539.5	521.8	398.7	16
	–15	319.6	286.8	335.1	614.6	379.4	375.7	31	358.3	472.2	413.7	495.6	333.6	17
	–30	332.1	208.7	286.4	202.6	284.3	217.5	21	276.9	422.0	343.6	100.3	206.1	46
	–60	156.8	133.5	96.9	58.2	114.7	137.8	30	108.1	90.1	201.4	123.4	89.7	38
	–100	50.3	58.8	79.5	37.1	68.5	63.5	25	48.6	78.7	45.7	37.0	64.5	30
Inorganic P	Litter	418.3	414.4	479.1	335.1	604.3	253.0	29	365.3	650.0	481.4	463.1	293.1	30
	–5	625.7	445.8	310.7	322.2	569.2	323.7	32	488.8	417.0	307.6	399.4	295.5	21
	–15	632.2	376.9	280.5	293.6	485.1	301.1	35	506.3	466.5	284.9	377.7	290.8	26
	–30	628.5	420.1	255.1	213.5	484.2	341.4	39	478.5	477.4	285.2	462.9	322.2	23
	–60	607.3	543.3	297.8	265.3	470.4	351.2	33	485.7	599.7	313.9	487.9	403.7	23
	–100	587.1	600.5	328.8	282.1	577.7	464.8	29	545.2	615.5	368.7	556.8	472.6	19
Phosphate ions in soil solution	Litter	353.2	397.6	406.1	343.8	500.4	457.1	15	393.7	520.7	223.2	271.2	637.8	42
	–5	10.3	15.8	11.2	22.1	17.9	1.5	55	6.4	2.9	13.7	1.9	1.7	95
	–15	5.3	2.3	1.5	6.0	3.3	1.6	57	1.0	1.3	1.1	1.0	0.7	23
	–30	3.6	0.8	0.7	0.4	0.9	0.2	114	0.4	0.8	0.8	0.5	0.1	56
	–60	1.1	0.3	0.5	0.1	0.2	0.2	89	0.2	0.3	0.7	0.7	0.2	62
	–100	0.2	0.2	0.2	0.1	0.4	0.3	44	0.2	0.2	0.4	0.1	0.1	50
Diffusive phosphate ions in 1 day	Litter	88.8	84.2	72.9	80.0	103.9	37.3	29	36.6	23.5	59.9	85.8	3.0	77
	–5	42.5	56.1	34.9	53.4	48.1	26.3	26	31.6	20.3	36.1	21.1	16.2	33
	–15	33.1	25.0	17.1	26.7	35.4	26.2	24	21.5	15.8	27.3	22.8	18.7	20
	–30	29.2	15.3	26.6	15.6	24.6	11.9	35	16.6	13.5	17.7	40.8	13.7	56
	–60	39.6	38.4	30.5	14.7	25.4	29.9	31	20.0	48.5	20.4	13.4	89.4	82
	–100	24.3	40.4	32.3	2.2	66.7	57.4	62	17.5	35.3	47.4	2.5	36.3	64

CV: coefficient of variation (ratio of the standard deviation to the mean, in %).

Table 2. Continued.

P pool	Depth (cm)	Forest							Grassland					
		BAR	CHE	KRA	SAE	SAW	TOM	CV	BAR	CHE	KRA	SAE	TOM	CV
Diffusive phosphate ions in 1 week	Litter	88.8	84.2	72.9	80.0	103.9	37.3	29	36.6	23.7	74.3	109.8	3.0	86
	–5	64.7	92.7	52.0	79.8	74.5	57.3	22	47.8	33.1	53.8	33.7	29.4	27
	–15	52.9	45.9	29.8	43.5	70.0	51.0	27	34.2	26.8	51.3	42.7	39.3	24
	–30	46.4	28.8	57.2	29.4	51.5	26.6	33	28.4	24.3	30.9	71.0	31.7	51
	–60	70.1	73.9	51.1	31.9	53.9	64.4	27	35.2	95.9	37.1	20.2	178.7	89
–100	47.0	73.1	61.7	4.0	137.6	91.8	65	30.4	65.1	94.3	4.6	64.5	67	
Diffusive phosphate ions in 3 months	Litter	88.8	84.2	72.9	80.0	103.9	37.3	29	36.6	24.0	94.3	143.7	3.0	96
	–5	108.7	170.4	84.5	129.2	125.8	155.5	24	80.1	61.0	87.1	61.6	62.4	17
	–15	95.3	99.1	60.4	79.1	166.4	119.5	36	62.4	52.4	116.4	96.2	102.6	32
	–30	83.4	65.0	154.6	66.7	133.8	75.6	39	57.1	51.5	63.5	146.2	94.5	48
	–60	147.4	174.1	100.3	87.9	144.2	175.4	27	73.9	234.2	80.4	34.1	403.4	93
–100	111.5	159.3	144.1	8.5	355.3	169.6	71	62.4	145.0	231.7	10.2	136.9	72	

CV: coefficient of variation (ratio of the standard deviation to the mean, in %).

Table 3. Stocks of the different P pools computed in Mg ha^{-1} for the litter, the topsoil (about 0 to -20 cm), the subsoil (about -20 to -120 cm) and for the whole profile for the different sites. “Litter” means all the dead plant material deposited on the soil surface (senescing leaf litterfall, small branches and senescing understorey vegetation in forests; senescing herbaceous vegetation in grasslands) i.e. mainly OL and OF horizons, and possibly OH (at BAR, CHE, KRA and SAE) at the date of sampling.

P pool	Layer	Forest							Grassland					
		BAR	CHE	KRA	SAE	SAW	TOM	CV	BAR	CHE	KRA	SAE	TOM	CV
Total P	Litter	0.037	0.028	0.057	0.024	0.014	0.012	58	0.008	0.003	0.026	0.012	0.002	95
	Topsoil	2.549	1.749	1.121	1.462	1.729	1.433	29	2.338	2.030	1.464	2.089	1.432	22
	Subsoil	9.728	8.865	6.247	3.887	10.190	7.287	31	9.541	9.682	6.848	7.740	7.366	16
	Total	12.313	10.642	7.424	5.374	11.934	8.732	29	11.888	11.714	8.338	9.840	8.800	16
Organic P	Litter	0.024	0.018	0.036	0.018	0.009	0.009	55	0.006	0.001	0.015	0.008	0.001	89
	Topsoil	0.894	0.782	0.622	1.003	0.764	0.805	16	0.995	1.079	0.896	1.185	0.791	16
	Subsoil	2.010	1.520	1.787	0.958	2.075	1.705	24	1.809	2.002	1.964	1.043	1.604	23
	Total	2.928	2.320	2.445	1.978	2.848	2.518	14	2.809	3.082	2.875	2.235	2.396	13
Inorganic P	Litter	0.012	0.010	0.021	0.007	0.006	0.003	65	0.003	0.001	0.011	0.004	0.001	107
	Topsoil	1.655	0.967	0.498	0.459	0.965	0.628	52	1.344	0.951	0.568	0.904	0.641	35
	Subsoil	7.718	7.345	4.460	2.929	8.116	5.582	34	7.732	7.680	4.883	6.696	5.762	19
	Total	9.385	8.322	4.979	3.395	9.086	6.214	35	9.078	8.631	5.462	7.605	6.404	20
Phosphate ions in soil solution	Litter	0.010	0.010	0.017	0.007	0.005	0.005	52	0.003	0.001	0.005	0.002	0.001	63
	Topsoil	0.018	0.015	0.008	0.016	0.012	0.003	45	0.008	0.004	0.012	0.003	0.002	67
	Subsoil	0.017	0.004	0.006	0.002	0.008	0.003	83	0.003	0.005	0.008	0.005	0.002	44
	Total	0.045	0.029	0.031	0.024	0.025	0.012	40	0.014	0.010	0.025	0.011	0.006	54

CV: coefficient of variation (ratio of the standard deviation to the mean, in %).

Table 3. Continued.

P pool	Layer	Forest							Grassland					CV
		BAR	CHE	KRA	SAE	SAW	TOM	CV	BAR	CHE	KRA	SAE	TOM	
Diffusive phosphate ions in 1 day	Litter	0.003	0.002	0.003	0.002	0.001	0.000	56	0.000	0.000	0.001	0.001	0.000	118
	Topsoil	0.094	0.083	0.039	0.052	0.073	0.054	32	0.068	0.038	0.059	0.052	0.039	25
	Subsoil	0.397	0.480	0.447	0.110	0.741	0.532	45	0.280	0.464	0.496	0.187	0.588	41
	Total	0.494	0.565	0.490	0.164	0.815	0.586	41	0.348	0.503	0.557	0.240	0.627	35
Diffusive phosphate ions in 1 week	Litter	0.003	0.002	0.003	0.002	0.001	0.000	56	0.000	0.000	0.002	0.001	0.000	122
	Topsoil	0.148	0.144	0.064	0.081	0.136	0.108	31	0.106	0.064	0.101	0.093	0.077	20
	Subsoil	0.707	0.898	0.843	0.223	1.535	0.937	49	0.487	0.882	0.961	0.313	1.142	46
	Total	0.858	1.044	0.910	0.306	1.673	1.045	45	0.593	0.945	1.064	0.407	1.219	40
Diffusive phosphate ions in 3 months	Litter	0.003	0.002	0.003	0.002	0.001	0.000	56	0.000	0.000	0.002	0.001	0.000	126
	Topsoil	0.260	0.291	0.117	0.141	0.304	0.267	35	0.186	0.121	0.202	0.199	0.187	19
	Subsoil	1.506	2.037	1.951	0.563	3.979	2.032	56	1.005	2.045	2.286	0.616	2.623	50
	Total	1.769	2.330	2.071	0.705	4.284	2.300	52	1.191	2.166	2.491	0.816	2.810	45

CV: coefficient of variation (ratio of the standard deviation to the mean, in %).

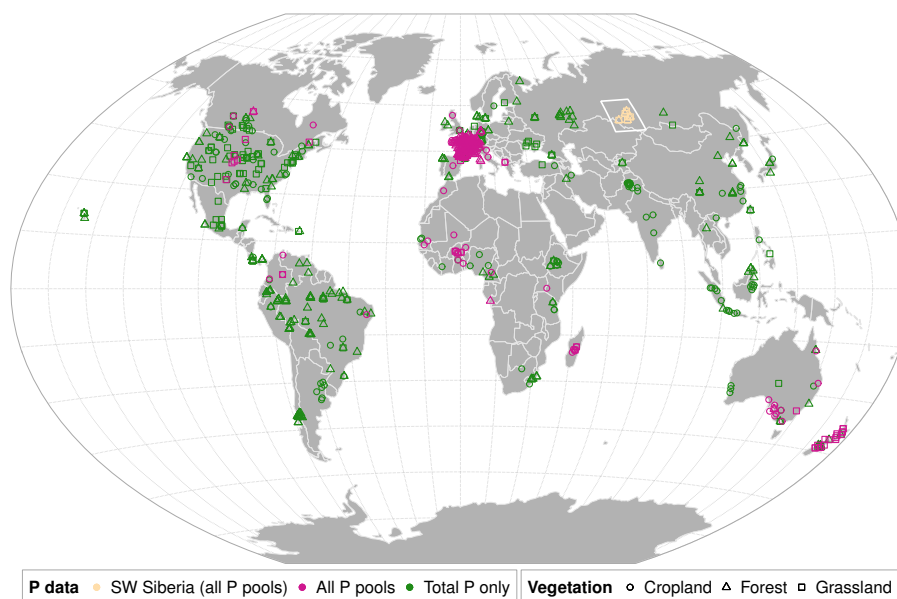


Figure 1. Location of the study sites (south-western Siberia is highlighted in white, data points in beige) and the data points from a literature compilation. Distinction is made between the quantity of information available for each point (colour) and between vegetation cover (shape). “All P pools” stands for: total P, organic P, inorganic P, phosphate ions in soil solution, diffusive phosphate ions and isotopically exchangeable phosphate ions. Winkel-Tripel projection, graticules 15°.

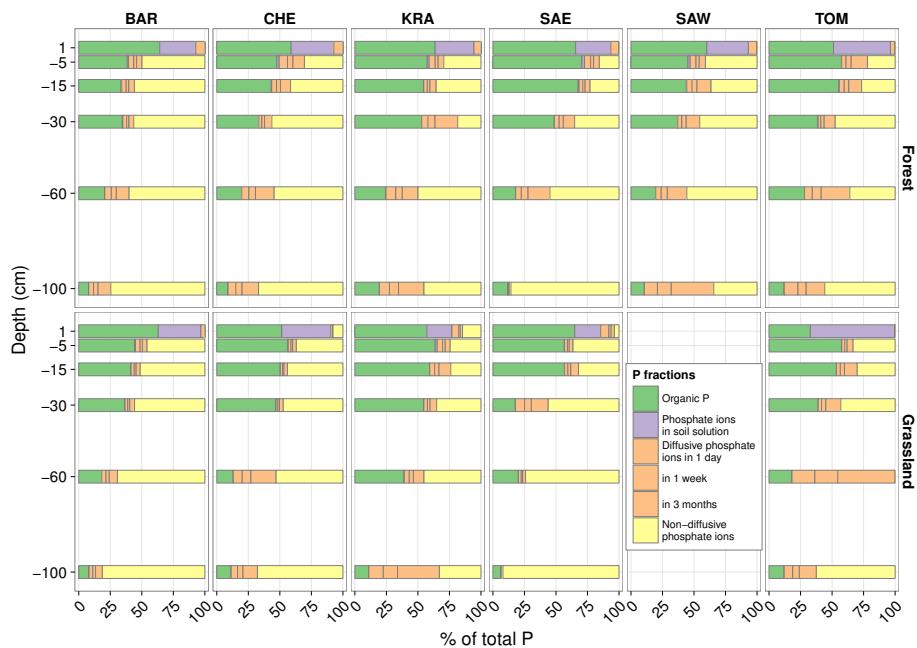


Figure 2. Structure of total P (P_{tot}) in terms of P ions in the soil solution (Q_w), diffusive P ions at different time scales (Pr) and non-diffusive, or diffusive in more than 3 months, P ions ($P_{\text{non-diff}}$). Each fraction of P is expressed as % of P_{tot} . Note that the diffusive fractions for the longer times are included in the diffusive fractions at longer time (e.g. $Pr(1 \text{ day})$ is included in $Pr(1 \text{ week})$ and they are both included in $Pr(3 \text{ months})$). Depth “1” is the litter. “Litter” means all the dead plant material deposited on the soil surface (senescing leaf litterfall, small branches and senescing understorey vegetation in forests; senescing herbaceous vegetation in grasslands) i.e. mainly OL and OF horizons, and possibly OH (at BAR, CHE, KRA and SAE) at the date of sampling.

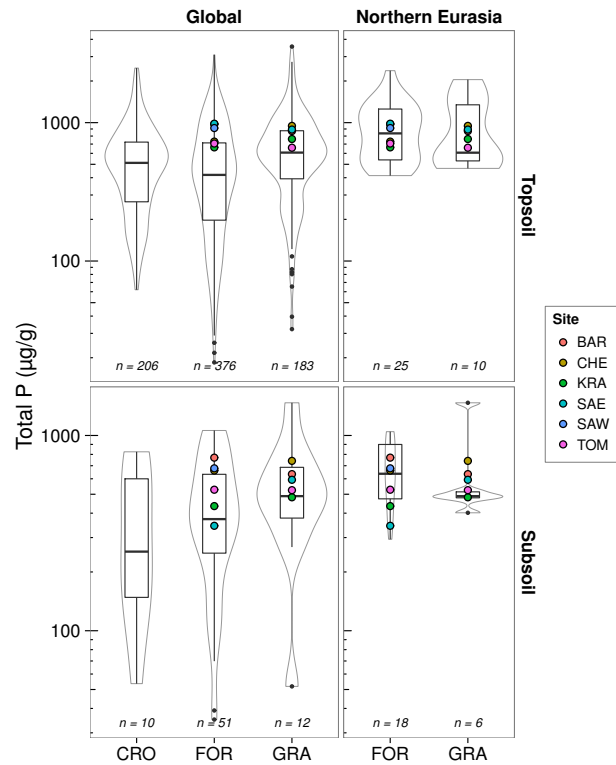


Figure 3. Comparison of total P concentrations in topsoils (about 0 to -20 cm) and subsoils (-20 to -100 cm depth) of south-western Siberia (coloured dots) with similar vegetation contexts (CRO: croplands; FOR: forests; GRA: grasslands) at the global scale and at the Northern Eurasian scale (box- and violin-plots). The “n” provided indicates the number of individual points used to build the box- and the violin-plots.

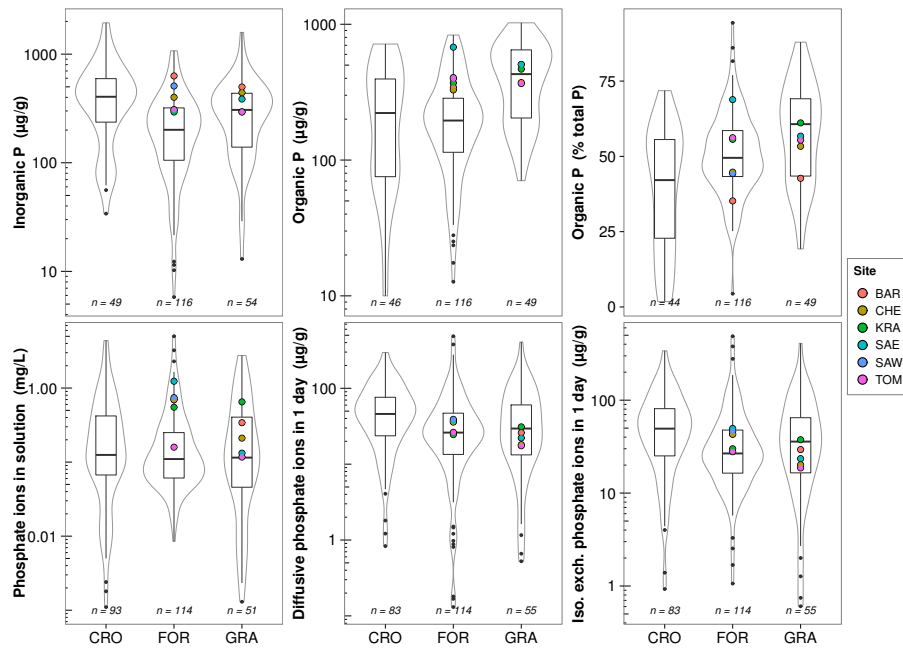


Figure 4. Comparison of the different components of the P status in topsoils (about 0 to –20 cm) of south-western Siberia (coloured dots) and different vegetation types (CRO: croplands; FOR: forests; GRA: grasslands – box- and violin-plots) at the global scale (croplands and grasslands) or at the country scale (forests mostly located in France, along broad gradients of soil and geology). “Iso. exchangeable” is an abbreviation for “isotopically exchangeable”. The “n” provided indicates the number of individual points used to build the box- and the violin-plots.