

# Abschlussbericht Fraktionierung und Mobilität des Phosphors in Grünlandböden





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Fractionation and mobility of phosphorus in grassland soils

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## Phosphorus in permanent grassland soils in a mountainous region of Austria

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### Abstract

According to the current Austrian fertiliser recommendation system for phosphorus (P), many grassland soils in Austria are depleted in P, but the data basis for such an assumption is insufficient. Therefore, the aim of this study was to obtain data on concentrations of total P ( $P_t$ ) and of various P forms in typical Austrian terrestrial permanent grassland soils. Moreover, the P sorption capacity (PSC) and degree of P saturation (DPS), based on oxalate extraction, were assessed. Topsoil samples were collected from 106 different montane grassland sites covering a wide range of soil types, parent materials, grassland plant communities and intensity levels of grassland management. The majority of grassland soils were characterised by high  $P_t$  concentrations in the layer 0-10 cm; the mean concentration exceeded 1000 mg  $P_t$  kg<sup>-1</sup> soil. The topsoils frequently contained large amounts of organic P. On average, 71 % of the  $P_t$  was present in organic forms. Most topsoils exhibited low C:P ratios, high concentrations of oxalate-extractable P and high PSC values. Consequently, they possess the capacity to release and to retain large amounts of P. Management intensity had a major influence on the soil P status. Long-term annual manure applications and continued large P inputs from cattle excreta increased both the inorganic and organic P concentration as well as the DPS value in the soil layer 0-10 cm. Above a critical DPS value of about 30 %, water-soluble P content increased substantially. Soil N rather than soil P seems to be the most growth-limiting mineral element in intensively managed mountain grassland. A revision of the current Austrian fertiliser P recommendation system for grasslands is advisable.

**Keywords:** mountain grasslands, soil P forms, P sorption capacity, degree of P saturation, manuring, intensity of utilisation

### 1. Introduction

Soil phosphorus (P) status influences both soil fertility and nature conservation value of grasslands. In grassland soils, P is mainly adsorbed on the surfaces of sesquioxides, clay minerals and carbonate particles, occluded in Fe and Mn oxides or associated with soil organic matter. Plant roots can only take up P as orthophosphate anions ( $H_2PO_4^-$  and  $HPO_4^{2-}$ ) from the soil solution (Richardson et al., 2009). The reactions controlling P solubility in soil and, thus, P availability to the plants include dissolution/precipitation of P-containing minerals, adsorption/desorption of P on soil surfaces, microbial immobilisation of P/remineralisation of immobilised P and mineralisation of non-microbial organic P (Frossard et al., 2000).

P is the macronutrient with the lowest solubility and mobility in soil (Gerke, 2015). Therefore, plant growth in terrestrial ecosystems is frequently limited by the supply of N and/or P in soil (Vitousek and Howarth, 1991). The P supply to plants depends on the amounts of different inorganic and organic P forms present in the root zone of the soil, several other soil and environmental conditions affecting the P solubility in soil, and on various plant traits. In particular, root morphology (e.g., root length and diameter) and root characteristics (e.g., rate of root growth) are important for the P acquisition by plants (Hill et al., 2006). Plant roots can increase soil P solubility by acidification of the rhizosphere, exudation of organic acid anions (especially citrate and oxalate) and secretion of extracellular phosphatases (Vance et al., 2003; Gerke, 2015), leading to a superior P acquisition by plants in soils with low P solubility. Citrate is particularly effective at mobilising P from Al-P and Fe-P complexes in acid soils and Ca-P in calcareous soils (Richardson et al., 2009). However, plant species differ considerably both in their P requirement and in their ability to acquire soil P. Thus, the accurate estimation of plant available P content in grassland soils by routine soil analysis is difficult, because plant available P content is both soil- and species-specific.

Provided that other essential plant nutrients, such as N or K, are not limiting, P uptake by the vegetation, forage yield and quality in grasslands are usually positively related to the plant available P content in soil. Surface soil P content is primarily responsible for the delimitation and distribution of several grassland plant communities and

affects plant species richness (Critchley et al., 2002). A high concentration of plant available P in topsoil is frequently connected with a low diversity of vascular plant species (Janssens et al., 1998). In European grassland soils, P enrichment is a more important driver of species loss from semi-natural grasslands than N enrichment (Ceulemans et al., 2011). Many endangered plant species benefit from a low soil P supply (Wassen et al., 2005). Thus, low soil P phytoavailability appears to be a general edaphic characteristic of species-rich semi-natural grasslands with high nature conservation value (Gough and Marrs, 1990). Restoration of species-rich semi-natural grasslands is potentially limited by high P availability in soil (Gilbert et al., 2009). Vegetation structure and species composition of the grassland vegetation are influenced by the soil P level (Hejcman et al., 2010); especially legume growth is stimulated by soil and fertiliser P (Niklaus et al., 1998). Moreover, the rate of symbiotic N<sub>2</sub> fixation by legumes is also influenced by the soil P supply; P additions to P-poor soils usually favour N<sub>2</sub> fixation by forage legumes (Niklaus et al., 1998). Furthermore, P may also influence N mineralisation in soil; a low concentration of labile P can limit heterotrophic N mineralisation (Parfitt et al., 2005).

On the other hand, P is potentially a serious environmental pollutant, especially in high-rainfall areas such as mountainous regions. P losses from grasslands via surface runoff, leaching and drainage systems may lead to eutrophication of surface waters, ground water and adjacent terrestrial ecosystems. Since P is strongly adsorbed by most soils, a continual high application rate of farm manure or mineral P fertiliser, exceeding annual P removal with the harvest, inevitably must result in a P accumulation in topsoil (Schellberg et al., 1999). However, the P retention capacity of soils is limited and subject to saturation. Consequently, P-saturated grassland soils are critical source areas for elevated P losses by surface runoff and leaching, whereas grassland soils with low P saturation represent low-risk sites.

For a resource-conserving and environmentally sound grassland management, knowledge of the amounts and proportions of various P forms in different grassland soils as well as information about their P sorption capacity (PSC) and degree of P saturation (DPS) are important. In many mountainous regions of Central Europe, however, very little detailed work has been done on the P status of permanent grassland soils; especially information about the PSC and DPS values is lacking in spite of their importance to mobility and plant availability of applied P and native soil P. In Austria, most studies have been concerned only with CAL-extractable P, as measured by routine soil analysis. Heinzlmaier et al. (2005), for example, reported that many Austrian grassland soils have low CAL-extractable P concentrations and P deficiency is a widespread phenomenon in Austrian grassland. Therefore, application of mineral P fertiliser is usually recommended. However, forage yield, P concentration and P content in the harvested biomass can range from low to high even at low level of CAL-P in topsoil (Weißensteiner et al., 2014). It seems that CAL-P does not represent adequately the plant available P content in grassland soils. There is, thus, considerable confusion amongst advisers and farmers about the suitability of the CAL method for making P fertiliser recommendations. Furthermore, the CAL method has not been developed to evaluate the risk of P losses from grassland soils. Therefore, more detailed information on the current P status of Austrian permanent grassland soils is needed for making environmentally sound P fertiliser recommendations. Moreover, knowledge of the influence of management practices on soil P status is essential for a more efficient use of farm manure and mineral P fertilisers. This is also of considerable agronomic and economic significance, because rock phosphate is a finite, non-renewable resource (Frossard et al., 2000) and the price of mineral P fertilisers will thus further increase in the future.

The four main objectives of this study are:

- (1) to determine for a typical mountain grassland region in Austria the concentrations of total P and of various P forms in different permanent grassland soils in the layer 0-10 cm,
- (2) to assess their PSC and DPS in topsoil in order to get information on P loss risk,
- (3) to analyse the relationships between various soil P forms, PSC or DPS and related soil properties,
- (4) to evaluate the influence of management intensity on the P status in topsoil.

## **2. Materials and methods**

### *2.1. Study area*

The study was conducted in a typical mountain grassland region in the northern part of Styria, Austria (47°N, 13-14°E). Geologically, the study area is located in the Northern Calcareous Alps and in the Greywacke zone. In the glacially formed landscape, climate is relatively cool and humid, with a mean annual air temperature of 6.7°C and a mean annual precipitation of 1227 mm. Mean monthly air temperature varies from -3.5°C in January to 16.3°C in July. Precipitation is evenly distributed throughout the year. From April to October (growing season) 66 % of the annual precipitation occurs. Length of the snow cover is 105 days a year on average, leading to a short vegetation period (ZAMG, 2002). The rural landscape is dominated by permanent grassland, which is in Austria at least 10 years old. Montane grassland vegetation on terrestrial soils belongs mainly to the alliances

*Mesobromion*, *Arrhenatherion*, *Polygono-Trisetion* and *Cynosurion* (Bohner and Sobotik, 2000). Forage yield usually varies from 2 to 10 t dry matter ha<sup>-1</sup>yr<sup>-1</sup> and the amount of P removed by the harvested biomass is in the range of 5 to 35 kg P ha<sup>-1</sup>yr<sup>-1</sup> (Pötsch et al., 2013), depending primarily on the vegetation type. Because of unfavourable climatic and topographical conditions, management intensity on permanent grassland is relatively low. The more intensively used meadows are cut three to four times each year, often followed by cattle grazing in autumn. The more intensively used pastures are grazed by dairy cows four to five times per grazing season, lasting from mid-April to the end of October. Stocking rate during the grazing season is approximately 2.5 to 3.0 livestock units (LU) ha<sup>-1</sup>. Average annual stocking rate of the farms is 1.2 to 1.5 LU per hectare grassland. The manured grassland receives farm manure (mainly cattle manure and/or cattle slurry), whereas mineral P fertilisers are applied sparingly. According to current Austrian fertiliser recommendations (BMLFUW, 2006), P applications in farm manures and mineral fertilisers to mountain grasslands with an adequate soil P status should be in the order of 4 to 39 kg P ha<sup>-1</sup>yr<sup>-1</sup>, depending primarily on the yield potential of the site.

## 2.2. Sampling sites

Sampling sites were carefully selected from field surveys, farmer interviews and soil maps in order to include the major soil types, grassland plant communities and intensity levels of grassland management in the study area. Only permanent grassland soils of known management history were investigated, whereas soils of temporary grasslands (leys) were excluded from the study. At the sampling sites, a long-term (> 10 years) constant grassland management was an important prerequisite. To obtain information about the current and previous management, farmers were interviewed. Altitude of the sampling sites ranged from 600 to 1180 m a.s.l. and topography varied from flat areas to moderately steep slopes. Only those terrestrial soil types, which frequently occur in mountainous regions of Central Europe (Rendzinas, Para-rendzinas, Rankers, Brown Earths and calcareous Brown Loams), were selected for this study. Soil parent materials ranged from different types of consolidated rocks (mainly phyllite, schist, limestone, marl) to various unconsolidated glacio-fluvial sediments. Soil thickness varied from shallow (< 30 cm) to deep (> 70 cm). Soil texture ranged from loamy or silty sand to sandy or silty loam. Grassland was separated into two groups based on their intensity of utilisation. Meadows with one or two cuts each year and cattle pastures with a stocking rate less than or equal to 1.5 LU ha<sup>-1</sup>yr<sup>-1</sup> were assigned to the extensively used grassland. Meadows and mowing pastures with more than two utilisations per year and cattle pastures with a stocking rate greater than 1.5 LU ha<sup>-1</sup>yr<sup>-1</sup> were classified as intensively used grassland. Since we got sometimes no precise information about the long-term annual farm manure and P fertiliser application rates, the grassland soils were only separated into two groups: regularly manured or never manured (unmanured and unfertilised). Vegetation differences support this distinction between the selected groups.

## 2.3. Soil sampling

Topsoil samples (0-10 cm depth) were collected from the A horizon at 106 montane grassland sites randomly distributed over the entire study area between 2007 and 2013. None of the sampled soils had received farm manure or P fertiliser during the sampling period in September. In order to minimize spatial site heterogeneity, at each site 10 individual samples were taken by spade from a representative and homogenous sampling area (50m<sup>2</sup>) within a meadow, mowing pasture or pasture (and not from the whole area) and were mixed to obtain one composite soil sample per site. We only sampled the uppermost 10 cm of the soil, because this soil layer responds most sensitively to management practices and soil samples for routine soil analysis are also collected from this soil layer.

## 2.4. Soil analyses

Soil samples were air-dried and passed through a 2-mm sieve. Basic physical and chemical soil properties were analysed by standard procedures according to the Austrian Standards Institute. Particle-size distribution was carried out by the pipette method of Köhn. Total carbon (C<sub>t</sub>), nitrogen (N<sub>t</sub>) and sulphur (S<sub>t</sub>) were determined by dry combustion and measured with an CNS elemental analyser (VarioMAX CNS, Elementar Analysensysteme GmbH, Hanau, Germany). Organic carbon (C<sub>org</sub>) was calculated as the difference between C<sub>t</sub> and carbonate C, which had been determined gas volumetrically with a Scheibler-apparatus. Soil pH (pH CaCl<sub>2</sub>) was measured in 0.01 M CaCl<sub>2</sub> solution. CAL-soluble P (CAL-P) was extracted by a calcium-acetate-lactate solution. Water-soluble total P (H<sub>2</sub>O-P) was measured at a soil:water ratio of 1:20 and determined by ICP. H<sub>2</sub>O-P represents the readily soluble and highly mobile P in soil. CAL-P is used as an index of plant available P in soil and serves as basis for P fertiliser recommendations in Austria. It is also a commonly used routine soil P test method in Germany. Oxalate-extractable Al, Fe, Mn and P (Al<sub>ox</sub>, Fe<sub>ox</sub>, Mn<sub>ox</sub>, P<sub>ox</sub>) were determined by the method of Schwertmann (1964). Al<sub>ox</sub>, Fe<sub>ox</sub> and Mn<sub>ox</sub> represent mainly the amorphous and poorly crystalline oxides and hydrous oxides of Al, Fe and Mn in soil. According to Gerke (2015), the oxalate solution also extracts some Al and Fe associated with humic substances. P<sub>ox</sub> is used as an estimate of the amount of P already sorbed by the soil (Maguire et al., 2001). However, it should be noted that oxalate also extracts some Ca-bound P and thus overestimates sorbed P especially in calcareous soils (Börling et al., 2004). Total Al, Fe, Mn and P (Al<sub>t</sub>, Fe<sub>t</sub>, Mn<sub>t</sub>, P<sub>t</sub>) were determined by digestion of

the soil with aqua regia. Elemental concentrations in the extracts were determined by inductively coupled plasma spectroscopy (OES-ICP, Jobin Yvon 238 Ultrace, Instruments S.A. GmbH, Grasbrunn, Germany) at 214.914 nm (P), 396.153 nm (Al), 238.204 nm (Fe) and 257.610 nm (Mn). Inorganic P ( $P_i$ ) was determined by extraction with 0.1 M sulphuric acid. The difference between  $P_t$  and  $P_i$  was assumed to represent organic P ( $P_{org}$ ). P sorption capacity (PSC) and degree of P saturation (DPS) were calculated as follows:

$$PSC \text{ (mmol kg}^{-1}\text{)} = 0.5 \times (Al_{ox} + Fe_{ox})$$

$$DPS \text{ (\%)} = 100 \times P_{ox} \times PSC^{-1}.$$

PSC is a measure of the ability of soil to adsorb P and DPS indicates the potential desorbability of soil P (Beauchemin and Simard, 1999). Many studies (e.g., Leinweber et al., 1999) have reported that the DPS can be used to estimate P leaching losses from soils. DPS should not exceed 30 % as an upper environmental threshold (Leinweber et al., 1997). The PSC and DPS, based on oxalate extraction, were developed for carbonate-free, acidic, sandy soils (Van der Zee and Van Riemsdijk, 1988). According to Beauchemin and Simard (1999), however, both soil parameters can be used even for calcareous soils. Zhang et al. (2005) emphasise that the P sorption in soils can be assessed using the more economical and time-saving oxalate extraction instead of time-consuming adsorption isotherms.

### 2.5. Statistical analyses

The normality of data and the homogeneity of variances were tested using the Shapiro-Wilk test and the Levene test. The Mann-Whitney test was chosen to evaluate the effects of manuring and intensification of utilisation on selected soil chemical properties. Spearman's rank correlation was used for correlation analysis. All results were stated as statistically significant if  $p < 0.01$  and highly significant if  $p < 0.001$ . Statistical data analyses were performed with SPSS Statistics 21.

## 3. Results

Basic physical and chemical properties, P forms, PSC and DPS values of the investigated terrestrial permanent grassland soils are shown in Tables 1 to 3. The topsoils (0-10 cm) ranged widely in physico-chemical soil parameters. The pH values (pH  $CaCl_2$ ) varied from 4.4 to 7.4. The mean concentrations of  $C_{org}$ ,  $N_t$  and  $S_t$  were found to be 43, 5.1 and 0.5 g  $kg^{-1}$ , respectively. The mean ratios of  $C_{org}:N_t$ ,  $C_{org}:S_t$ ,  $N_t:S_t$ ,  $C_{org}:P_t$ ,  $C_{org}:P_{org}$  and  $N_t:P_t$  were 10, 96, 14, 51, 66 and 5, respectively. The mean  $C_{org}:N_t:S_t:P_t$  ratio amounted to 36:4:0.4:1. The clay content varied from 30 to 380 g  $kg^{-1}$  with a mean value of 140 g  $kg^{-1}$ . The mean concentrations of  $Al_{ox}$ ,  $Fe_{ox}$  and  $Mn_{ox}$  were found to be 78, 104 and 12 mmol  $kg^{-1}$ , respectively. The mean ratio of  $Al_{ox}:Fe_{ox}:Mn_{ox}$  amounted to 1:3:0.3. The mean ratios of  $Al_t:Al_{ox}$ ,  $Fe_t:Fe_{ox}$  and  $Mn_t:Mn_{ox}$  were 9, 5 and 2, respectively. The mean concentrations of  $P_t$ ,  $P_i$ ,  $P_{ox}$  and  $P_{org}$  were found to be 1198, 388, 599 and 811 mg  $kg^{-1}$ , respectively. On average, 71 % of the  $P_t$  content was present in organic forms. The mean concentrations of CAL-P and H<sub>2</sub>O-P were found to be 27 and 9 mg  $kg^{-1}$ , respectively. CAL-P represented on average 2.3 % of  $P_t$ , while H<sub>2</sub>O-P accounted for 0.8 %. The mean PSC and DPS values were 91 mmol  $kg^{-1}$  and 22 %, respectively. Of the 106 grassland soils evaluated, 20 (19 %) had DPS values greater than the 30 % threshold, as recommended by Leinweber et al. (1997). The maximum of 57 % was found in an intensively grazed pasture soil which had received much dung and urine from dairy cows for a long time period. At this overgrazed site, also the highest concentration of CAL-P,  $P_i$ ,  $P_{ox}$  and  $P_t$  (204, 1624, 1881, 2600 mg  $kg^{-1}$  soil, respectively) was measured.

The effects of grassland management on selected soil chemical properties in the layer 0-10 cm are presented in Table 4. In long-term (> 10 years) unmanured and unfertilised permanent grassland soils, the median concentrations of H<sub>2</sub>O-P, CAL-P,  $P_t$ ,  $P_{ox}$  and  $P_{org}$  were highly significantly lower compared with continuously annually manured soils. The median ratios of  $C_{org}:N_t$ ,  $C_{org}:S_t$ ,  $C_{org}:P_t$ ,  $C_{org}:P_{org}$  and  $N_t:P_t$  were highly significantly larger in unmanured and unfertilised soils than in regularly manured soils. The intensity of utilisation also had a strong effect on several soil parameters. The median concentrations of H<sub>2</sub>O-P, CAL-P,  $P_t$ ,  $P_i$ ,  $P_{ox}$ ,  $P_{org}$  and the DPS value were found to be significantly or highly significantly lower in long-term extensively than in continuously intensively used soils. The median ratios of  $C_{org}:N_t$ ,  $C_{org}:P_t$ ,  $C_{org}:P_{org}$  and  $N_t:P_t$  were significantly or highly significantly lower in intensively compared with extensively used soils.

Results of the correlation analysis are summarized in Table 5. Only correlation coefficients with  $p < 0.01$  are shown. The relationships between various soil P forms, PSC or DPS and related soil properties (pH, sand and clay content, concentrations of  $C_{org}$ ,  $Al_{ox}$ ,  $Fe_{ox}$ ,  $Mn_{ox}$ ) are discussed below.

#### 4. Discussion

Topsoil samples (0-10 cm depth) were collected from 106 different montane permanent grassland sites. The topsoils were mostly moderately acid and rather rich in organic matter. The clay content averaged  $140 \text{ g kg}^{-1}$  soil. As expected, the concentrations and ratios of some soil parameters varied considerably among sites primarily as a result of different soil types, parent materials and intensity levels of grassland management. The soil P forms showed differing degrees of variation. In general,  $\text{H}_2\text{O-P}$  and  $\text{CAL-P}$  were more variable than  $\text{P}_t$  and  $\text{P}_{\text{org}}$ . The  $\text{C}_{\text{org}}:\text{P}_t$  and  $\text{C}_{\text{org}}:\text{P}_{\text{org}}$  ratios showed much higher variation than the  $\text{C}_{\text{org}}:\text{N}_t$  and  $\text{C}_{\text{org}}:\text{S}_t$  ratios, indicating that N and S are more closely related to the soil organic matter than P in the A horizon of permanent grassland soils.

In the studied topsoils, the concentrations of  $\text{Al}_{\text{ox}}$  and  $\text{Fe}_{\text{ox}}$  were generally relatively high. The mean concentrations were  $78$  and  $104 \text{ mmol kg}^{-1}$ , respectively. Leinweber et al. (1997) found much lower mean values for grassland soils in two regions in northwest Germany ( $25$  and  $30 \text{ mmol kg}^{-1} \text{ Al}_{\text{ox}}$ ,  $31$  and  $45 \text{ mmol kg}^{-1} \text{ Fe}_{\text{ox}}$  in the layer 0-30 cm). The concentrations of  $\text{Al}_{\text{ox}}$ ,  $\text{Fe}_{\text{ox}}$  and  $\text{Mn}_{\text{ox}}$  were negatively correlated with soil pH (Table 5), indicating that soil acidification promotes the formation of oxalate-extractable sesquioxides in mountain grassland soils. Humus-rich, acid soils are usually enriched in amorphous Al and Fe due to the continuous addition of Al and Fe through intense chemical weathering of primary minerals containing Al and Fe and the inhibited crystallisation of Fe and Al oxides in the presence of soil organic matter (Schwertmann, 1966). The ratio between total content and oxalate-extractable proportion decreased in the sequence  $\text{Al} > \text{Fe} > \text{Mn}$ , indicating a declining tendency to form crystalline oxides. The oxalate-extractable sesquioxides were quantitatively dominated by  $\text{Fe}_{\text{ox}}$ . Therefore, we assume that particularly  $\text{Fe}_{\text{ox}}$ , but also  $\text{Al}_{\text{ox}}$ , substantially contribute to P sorption in mountain grassland soils. In comparison to  $\text{Fe}_{\text{ox}}$  and  $\text{Al}_{\text{ox}}$ ,  $\text{Mn}_{\text{ox}}$  may play only a minor role in P sorption, primarily because of the generally much lower concentration in soil. It is worth mentioning, that calcareous soils (Rendzinas, Para-rendzinas) also contained appreciable amounts of  $\text{Al}_{\text{ox}}$ ,  $\text{Fe}_{\text{ox}}$  and  $\text{Mn}_{\text{ox}}$  (on average  $45$ ,  $60$  and  $7 \text{ mmol kg}^{-1}$ , respectively), at least in the layer 0-10 cm. Besides carbonate particles and clay minerals, these amorphous and poorly crystalline sesquioxides (particularly Fe oxides) are presumably very important P sorbents, even in calcareous soils.

The majority of studied soils had high concentrations of  $\text{P}_t$  in the layer 0-10 cm. The mean value amounted to  $1198 \text{ mg kg}^{-1}$ . This agrees to a median value of  $1277 \text{ mg kg}^{-1}$  in the layer 0-5 cm of Swiss grassland soils reported by Keller and Van der Zee (2004). In the Eastern Italian Alps,  $\text{P}_t$  concentration in grassland soils ranged from  $724$  to  $932 \text{ mg kg}^{-1}$  in the uppermost 20 cm (Scotton et al., 2014). Since the  $\text{P}_t$  concentration in soils usually range from  $500$  to  $800 \text{ mg kg}^{-1}$  (Stevenson and Cole, 1999), we assume that permanent grassland soils in mountainous regions are characterised by high concentrations of  $\text{P}_t$  in the topsoil. In the study area, bulk density in terrestrial permanent grassland soils usually varies from  $0.8$  to  $1.4 \text{ g cm}^{-3}$  in the 0-10 cm layer, depending primarily on the root biomass,  $\text{C}_{\text{org}}$  concentration and intensity of utilisation (Bohner, unpublished data). Assuming a soil bulk density between  $0.8$  and  $1.4 \text{ g cm}^{-3}$ , the range of  $\text{P}_t$  content in the studied soils was on average in the order of  $1000$  to  $1700 \text{ kg P ha}^{-1}$  in the uppermost 10 cm. This means that usually less than 3 % of soil  $\text{P}_t$  can be removed by the harvested biomass each year from the soil layer 0-10 cm. Thus, in mountain grassland soils considerable time is required to appreciably reduce the concentration of  $\text{P}_t$  in the soil by biomass harvesting. Provided that the  $\text{P}_t$  concentration in long-term extensively used and never manured permanent grassland soils gives a rough indication of the native soil  $\text{P}_t$  content, then this level in the top 10 cm of the studied grassland soils seems to be in the order of  $900 \text{ mg kg}^{-1}$  (Table 4). This large native  $\text{P}_t$  pool in the A horizon of mountain grassland soils can be attributed to various factors, among which the continuous P inputs by rock weathering and bioaccumulation, the high concentrations of  $\text{Fe}_{\text{ox}}$  and  $\text{Al}_{\text{ox}}$  in topsoil that fix P and prevent it from leaching, the slow rate of  $\text{P}_{\text{org}}$  mineralisation due to unfavourable climatic conditions and the absence of tillage for many years (no dilution effect) seem to be most important. Because of the generally large  $\text{P}_t$  concentrations in topsoil, we assume that the rate of P replenishment of the soil solution from the solid phase is the limiting factor for P supply to plant roots rather than the total amount of P present in the soil. Consequently, plant species with an elevated P solubilising potential may have a competitive advantage over species with a high P uptake capacity in mountain grasslands, because the former can better utilise high soil P reserves. In the studied topsoils,  $\text{P}_t$  correlated positively with all measured P forms, PSC, DPS,  $\text{Fe}_{\text{ox}}$  and  $\text{Mn}_{\text{ox}}$  (Table 5). This suggests that  $\text{P}_t$  influences both readily and sparingly soluble P fractions in grassland soils. There was, however, no significant correlation with  $\text{C}_{\text{org}}$ , indicating that the concentration of soil organic matter has no major influence on the  $\text{P}_t$  concentration in the A horizon of humus-rich mountain grassland soils.

The  $\text{P}_{\text{org}}$  concentration in the top 10 cm of the studied soils was very high compared to the concentration commonly found in soils (Stevenson and Cole, 1999). The mean value was  $811 \text{ mg kg}^{-1}$ , which was equivalent to 71 % of soil  $\text{P}_t$ . Thus,  $\text{P}_{\text{org}}$  was by far the major P form in the studied topsoils. According to Stevenson and Cole (1999),  $\text{P}_{\text{org}}$  usually constitutes between 20 and 80 % of  $\text{P}_t$  in the surface layer of soils. In mountain grassland soils, the conditions for the accumulation of P in organic forms seem to be fairly suitable. The slow rate of  $\text{P}_{\text{org}}$  mineralisation due to the cool climate (low soil temperature and long-lasting frost, which limit microbial activity) and the protection of  $\text{P}_{\text{org}}$  against mineralisation through binding of  $\text{P}_{\text{org}}$  to the surfaces of sesquioxides are primarily

responsible for the high  $P_{\text{org}}$  concentration in topsoil. The protective effect of sesquioxides on soil  $P_{\text{org}}$  is corroborated by the observed positive correlations between  $P_{\text{org}}$  and  $\text{Fe}_{\text{ox}}$  or  $\text{Mn}_{\text{ox}}$  (Table 5). In particular,  $\text{Fe}_{\text{ox}}$  seems to be an important soil factor affecting the retention and stabilisation of  $P_{\text{org}}$  in grassland soils. Furthermore, in permanent grassland there is no tillage which promotes the mineralisation of  $P_{\text{org}}$  in soil. The organic P pool in grassland soils is potentially available to plants (Cole et al., 1977). To become plant available,  $P_{\text{org}}$  must be mineralised. The mineralisation of most organic P compounds in soil is mediated by the action of extracellular phosphatase enzymes. This process is largely controlled by microbial activity (Richardson et al., 2009). Since mountain grassland soils usually contain large amounts of  $P_{\text{org}}$  in topsoil, the rate of  $P_{\text{org}}$  mineralisation rather than the amount of  $P_{\text{org}}$  present in soil determines P supply to plants. Consequently, management practices which promote the mineralisation of organic P compounds in soil during the growing season (especially at the time of maximal P uptake by plants in spring) contribute to a more efficient use of soil P by plants. In general, measures that increase the size and activity of the soil microbial biomass, enhance the activity of phosphatases in soil and improve the accessibility of  $P_{\text{org}}$  to phosphatases are of utmost importance to the P nutrition of grassland vegetation. In this context, avoiding topsoil compaction also plays an important role, because a low soil bulk density and a good soil structure (crumbly instead of platy) facilitate vigorous root growth and, thus, enable a greater access to soil P. In addition, bulk density and soil structure determine the pore-size distribution in soil and the habitable pore space for soil microorganisms including arbuscular mycorrhizal fungi, thereby influencing the accessibility of  $P_{\text{org}}$  to phosphatase enzymes and soil microorganisms. Since in mountain grassland soils a high percentage of the  $P_{\text{t}}$  content in topsoil is usually organic, an accurate estimate of the potential phytoavailability of  $P_{\text{org}}$  would be very helpful with respect to P fertiliser recommendations. Unfortunately, at present there are no routine soil test methods available in Austria to measure the easily mineralisable  $P_{\text{org}}$  in grassland soils. As expected,  $P_{\text{org}}$  was correlated positively with  $P_{\text{t}}$  (Table 5), indicating that  $P_{\text{org}}$  and  $P_{\text{t}}$  are closely connected. Surprisingly,  $P_{\text{org}}$  did not correlate with  $C_{\text{org}}$ . It seems that the concentration of soil organic matter has little influence on the concentration of  $P_{\text{org}}$  in the studied topsoils. This is in agreement with Sharpley (1985), who found that an increase in soil organic matter content does not always result in a direct increase in  $P_{\text{org}}$  content. The lack of significant correlations between  $C_{\text{org}}$  and  $P_{\text{t}}$ ,  $P_{\text{org}}$ ,  $P_{\text{i}}$  or  $P_{\text{ox}}$  suggests that in humus-rich mountain grassland soils the build-up of soil organic matter is presumably not an appropriate measure to increase the soil P reserves.

Management intensity had a major influence on the P status in topsoil. In general, the concentrations (median values) of  $P_{\text{t}}$ ,  $P_{\text{org}}$ ,  $P_{\text{i}}$ ,  $P_{\text{ox}}$ , CAL-P,  $\text{H}_2\text{O-P}$  and the DPS value were higher in regularly manured or intensively used soils than in continuously unmanured and unfertilised or extensively used soils. The data clearly show that farm manure applications over many years can increase both the inorganic and organic P fraction as well as the DPS value in the top 10 cm of grassland soils. Several studies (e.g., Schellberg et al., 1999) have shown that long-term manuring or P fertilisation can lead to a P accumulation in grassland soils. We assume, therefore, that the observed differences in various soil P forms did not result primarily from a depletion of soil P reserves in extensively managed grassland due to continued P removal with the harvested biomass but rather originated from long-term annual farm manure additions to intensively managed grassland.

Most of the studied soils had high concentrations of  $P_{\text{ox}}$  in the layer 0-10 cm. A mean value of  $599 \text{ mg kg}^{-1}$  ( $20 \text{ mmol kg}^{-1}$ ) was found. This corresponds to 50 % of soil  $P_{\text{t}}$ . Thus,  $P_{\text{ox}}$  appears to be quantitatively an important P form in mountain grassland soils. Leinweber et al. (1997) found in northwest Germany in a region with medium and in a region with high livestock density in the soil layer 0-30 cm mean values of 14 and  $23 \text{ mmol kg}^{-1}$ , respectively. For Swiss grassland soils, a median value of  $658 \text{ mg kg}^{-1}$  ( $21 \text{ mmol kg}^{-1}$ ) in the uppermost 5 cm was reported by Keller and Van der Zee (2004). Since  $P_{\text{ox}}$  represents mainly sorbed P (Maguire et al., 2001), we assume that mountain grassland soils have the capacity to release large amounts of potentially plant available P into the soil solution via desorption, at least in the layer 0-10 cm. Plant roots are capable of mobilising sorbed P through exudation of carboxylates, especially citrate (Gerke, 2015). The results of the correlation analysis in Table 5 suggest that in the studied topsoils  $\text{Fe}_{\text{ox}}$  is more important than  $\text{Al}_{\text{ox}}$  for P adsorption.  $P_{\text{ox}}$  correlated negatively, though weakly, with soil pH, indicating that in the pH range of 7.4 to 4.4 the adsorption of P on sesquioxid surfaces increases as the pH decreases. We assume, therefore, that liming can promote P desorption in the A horizon of acidic, humus-rich mountain grassland soils, thereby increasing the P supply to plant roots.

The concentration of  $P_{\text{i}}$  correlated positively with soil pH and negatively with clay content (Table 5), indicating that acidic and clay-rich mountain grassland soils tend to have low stocks of  $P_{\text{i}}$ . The  $P_{\text{i}}$ , extracted by 0.1 M sulphuric acid, mainly represents Ca-bound P, which can be mobilised by plant roots through acidification of the rhizosphere (Gerke, 2015).

In the studied topsoils, mean ratios of  $C_{\text{org}}:N_{\text{t}}$ ,  $C_{\text{org}}:S_{\text{t}}$ ,  $C_{\text{org}}:P_{\text{t}}$  and  $C_{\text{org}}:P_{\text{org}}$  were found to be 10, 96, 51 and 66, respectively. According to Guggenberger and Haider (2002), the C:N ratios in surface soils usually range between 10 and 15, the C:S ratios between 60 and 100 and the C:P ratios between 50 and 100. The low ratios of C:N and C:P we found in many topsoils indicate an accumulation of well-humified organic material and a high humus quality. The mean  $C_{\text{org}}:P_{\text{org}}$  ratio (66) was quite low due to high concentrations of  $P_{\text{org}}$  and close to the C:P ratio in

the soil microbial biomass of 60 (Cleveland and Liptzin, 2007). In general, a low  $C_{org}:P_{org}$  ratio ( $< 100$ ) is an important prerequisite for a high net P mineralisation rate in the soil. We observed a highly significant positive correlation between the  $C_{org}:P_{org}$  ratio and soil pH ( $r^2 = 0.44$ ,  $p < 0.001$ ). A probable explanation is that the retention and stabilisation of  $P_{org}$  in grassland soils increase as soil pH decrease. Hence, maintaining a favourable soil pH (pH  $CaCl_2$ : 6.2 – 5.0) may contribute to an enhanced P cycling within grassland ecosystems. Our findings agree with those of Turner and Blackwell (2013), who observed that soil pH has only a minor influence on the concentration of  $P_{org}$  in temperate arable soils although some forms of  $P_{org}$  accumulate preferentially under strongly acidic conditions, leading to a decline of the  $C_{org}:P_{org}$  ratio from about 70 in neutral soils to about 50 in strongly acidic soils. The mean  $C_{org}:N_t:S_t:P_t$  ratio in the soil layer 0-10 cm was 36:4:0.4:1. The C:N:S:P ratio in the soil organic matter of agricultural soils is typically about 100:10:1:1 (Helyar, 1998): Thus, the mass ratio indicates a relative enrichment of P in relation to C, N and S in many investigated grassland soils compared to agricultural soils in general. The C to nutrient ratios in topsoil were strongly affected by management practices. The median ratios of  $C_{org}:N_t$ ,  $C_{org}:P_t$ ,  $C_{org}:P_{org}$  and  $N_t:P_t$  were significantly or highly significantly lower in manured or intensively used soils compared with unmanured and unfertilised or extensively used soils. This indicates that the intensification of grassland management (manuring) may lead to a relative enrichment of N and P in the organic matter of grassland soils. Moreover, it seems that P accumulates in topsoil more easily than N under intensive grassland management, as indicated by the lower  $N_t:P_t$  ratio in manured and intensively used soils resulting from much higher concentrations of  $P_t$ . In the study area, the N:P ratio in farm manures commonly varies from 5 to 7, whereas N:P ratio in the grassland vegetation usually ranges from 7 to 8 (Gruber and Resch, 2009). Hrevusova et al. (2009) observed a similar N:P ratio (7-9) in alluvial grassland in the Czech Republic. Hence, the relative enrichment of P in relation to N in the surface horizon of manured grassland soils can largely be attributed to the lower ratio of N:P in applied farm manures than in the harvested biomass. In addition, annual P losses from grassland soils via leaching are usually lower than annual N losses through leaching, denitrification and volatilisation (Bohner et al., 2007), which also facilitates a selective accumulation of added manure and fertiliser P. Therefore, it is reasonable to assume that soil N rather than soil P is the primary growth-limiting mineral element in intensively managed mountain grassland, especially in plant stands with low cover of legumes. A similar conclusion has been drawn by Hrevusova et al. (2009) who reported that the biomass production of alluvial grassland in the Czech Republic was rather N- than P-limited.

The results of the correlation analysis suggest that soil reaction in the pH range of 4.4 to 7.4 had no or only a marginal influence on the concentrations and proportions of various soil P forms (Table 5). A higher negative correlation coefficient was observed only between soil pH and PSC, indicating that acidic mountain grassland soils usually have high PSC values in the topsoil due to large amounts of  $Fe_{ox}$  and  $Al_{ox}$ . Moreover, it is worth mentioning that soil pH was weakly negatively correlated with  $P_{org}$  expressed as a percentage of  $P_t$ . It appears that a reduced microbial activity under acidic soil conditions may contribute to an inhibited mineralisation of  $P_{org}$ . This conclusion is supported by other studies. For example, Harrison (1982) found that the rate of mineralisation of labile  $P_{org}$  increased over the pH range of 3.1 to 7.9 in woodland soils. Condrón and Goh (1989) observed an enhanced  $P_{org}$  mineralisation following lime addition to an intensively grazed pasture soil in New Zealand. Based on the results of these studies, we assume that liming may promote the mineralisation of  $P_{org}$  in strongly acid mountain grassland soils (pH  $CaCl_2$ :  $< 5.0$ ), which can result in increased P supply to plant roots and soil microorganisms. For these soils, reducing soil acidity via liming might be a more appropriate measure to increase soil P bioavailability and to improve soil fertility than pure additions of P with mineral P fertilisers. Especially legume growth and biological N fixation can be stimulated by lime applications to strongly acid grassland soils.

There was no or only a weak correlation between clay content and the soil parameters measured (Table 5). This indicates that in the studied topsoils clay content, which varied from 30 to 380  $g\ kg^{-1}$ , had no dominant influence on the concentrations of various soil P forms,  $P_t$  and the PSC. Similar results were obtained by other authors, who observed a lack of correlation between clay content and  $P_t$  (Subramaniam and Singh, 1997) or P sorption (Börling et al., 2001). It is possible that soil organic matter inhibits P sorption on clay surfaces via humus coatings in the A-horizon of grassland soils. In agreement with this, Soon (1991) found that clay content was less important for P sorption in the topsoils than in the subsoils. On the other hand, Maguire et al. (2001) reported a positive correlation between clay content and PSC. These disagreeing results may be attributed to the fact that clay mineralogy is much more important than clay content for the P sorption in soil (Fernandes and Warren, 1994). In particular, the number of positive charges on the surface of clay particles and the different affinity of clay minerals to the soil organic matter play a very prominent role for the P retention by clay minerals. Hence, clay content is not a suitable criterion for the P retention capacity in the A horizon of grassland soils.

In the majority of studied topsoils, only a small proportion (on average 0.8 %) of soil  $P_t$  was water-soluble and thus readily available to plant roots. The  $H_2O$ -P content in surface soil is crucial for P losses from grassland soils (Sharpley et al., 1986). As expected, the level of  $H_2O$ -P was positively correlated, though weakly, with DPS (Table 5). By contrast, there was no significant correlation between the level of  $H_2O$ -P and the PSC, indicating that in terrestrial grassland soils DPS is more important than PSC in controlling the level of  $H_2O$ -P.

CAL-P is used as a routine soil P test in Austria for P fertiliser recommendations. Adequate P status for grassland soils corresponds to a CAL-P value of at least 47 mg P kg<sup>-1</sup> in the layer 0-10 cm (BMLFUW, 2006). Based on this assumption, most of the studied soils (90 %) would be rated as P-deficient. However, this assessment contrasts with the high concentrations of P<sub>t</sub>, P<sub>org</sub> and P<sub>ox</sub> and the low C:P ratios we found in many topsoils. Moreover, Weißensteiner et al. (2014) calculated annual P budgets for various organic and conventional livestock farms in the study area and observed predominantly a balanced budget or even a P surplus (-3 to +20 kg P ha<sup>-1</sup>yr<sup>-1</sup>). The size of this P surplus largely depended on the input of P via concentrates. A long-term annual P surplus should enrich P in the topsoil. Thus, the predominantly balanced P budgets in the study area also disagree with the above interpretation of soil test data derived from routine soil P analysis. One reason for the apparent discrepancy might be that CAL-P underestimates the P status of humus-rich grassland soils, because it represents only inorganic orthophosphate and does not take into account easily mineralisable P<sub>org</sub> (Steffens et al., 2010). Thus, based on the results of this study, we advise a revision of the current Austrian soil P classification system for grasslands. The interpretation based on CAL-P values is incorrect and requires therefore a recalibration of the relationships between forage yield, P uptake by the vegetation and CAL-P value for different grassland sites. In particular, the range of critical CAL-P concentrations across the various soil P fertility categories should be lowered. In the soils investigated, the concentration of CAL-P was relatively low in comparison with the concentration of P<sub>t</sub>. On average, less than 3 % of soil P<sub>t</sub> was CAL-P, indicating that CAL-P represents only a small fraction of P<sub>t</sub>. CAL-P correlated positively, though weakly, with all measured P forms, PSC, DPS and Fe<sub>ox</sub> (Table 5). However, a higher positive correlation coefficient was obtained only for the relationship between CAL-P and H<sub>2</sub>O-P. Thus, care should be taken in using CAL-P as the sole criterion for the assessment of soil P status and the estimation of P fertiliser requirements of grassland vegetation. Nevertheless, CAL-P detects differences among grassland soils resulting from long-term differing management practices (manuring) and, therefore, provides a relative estimate of the soil P status, but does not predict the amount of P required for maximum forage yield. CAL-P can be used as a soil indicator of management intensity in permanent grassland on terrestrial soils. A high CAL-P value in topsoil (> 25 mg kg<sup>-1</sup>) demonstrates long-term intensive grassland management associated with high farm manure applications each year. From a nature conservation point of view, CAL-P can also be considered as an environmental indicator of habitat quality and vascular plant species richness in permanent grassland on terrestrial soils. In Austria, species-rich grassland plant communities are usually restricted to soils with less than 25 mg CAL-P kg<sup>-1</sup> in the layer 0-10 cm (Bohner, 2005).

Most topsoils exhibited high PSC values (on average 91 mmol kg<sup>-1</sup>), indicating that mountain grassland soils usually have the capacity to retain large amounts of native and applied P in the layer 0-10 cm. Similar PSC values (91 mmol kg<sup>-1</sup> in the top 5 cm of soil) were found in Swiss grassland soils by Keller and Van der Zee (2004). Much lower values (31-35 mmol kg<sup>-1</sup> in the layer 0-30 cm) were reported for German grassland soils by Leinweber et al. (1997). There was no significant correlation between PSC and C<sub>org</sub>, indicating that variations in soil organic matter content do not greatly influence the PSC in terrestrial permanent grassland soils. This is in agreement with the results of Borggaard et al. (1990), who also found no relationship between soil organic matter and the PSC. The PSC was not influenced by management practices and can therefore be regarded as a management-independent, soil-specific parameter that is useful in soil characterisation and long-term soil monitoring.

In the majority of studied topsoils, DPS was quite low, presumably due to the high PSC in the surface layer and the relatively low management intensity in the study area. The DPS ranged from 3 to 57 % with a mean value of 22 %. Much higher mean DPS values in topsoils probably as a result of the more intensive grassland management were observed in German grassland soils (44 % in a region with medium and 80 % in a region with high livestock density at a sampling depth of 0-30 cm) by Leinweber et al. (1997) and in Swiss grassland soils (48 % in the layer 0-5 cm) by Keller and Van der Zee (2004). Even in soils with high PSC, a low DPS value is not a valid justification for a build-up of soil P reserves through excessive manuring, because P, which is retained by the Fe and Mn oxides, can easily be mobilised under water-saturated (reducing) soil conditions, thereby increasing the risk of elevated P losses from grassland soils via surface runoff and leaching. This is of utmost importance in mountainous regions with high precipitation and heavy snowfall. Especially during a rainfall or snowmelt period, even terrestrial grassland soils can experience temporary waterlogging, leading to an abrupt increase in P solubility, particularly in compacted and regularly manured, P-rich topsoils (Ajmone-Marsan et al., 2006). DPS was highly significantly and positively correlated with H<sub>2</sub>O-P in manured soils (r<sup>2</sup> = 0.43, p < 0.001), but there was no correlation in unmanured and unfertilised soils. In regularly manured grassland soils, the concentration of H<sub>2</sub>O-P was usually higher than in unmanured and unfertilised soils and increased with increasing DPS value (Fig. 1). The exponential relationship indicates that the strength of P bonding decreases as soils become more saturated with P. Above a critical DPS value of about 30 % H<sub>2</sub>O-P increased substantially, demonstrating the environmental risk associated with the build-up of large soil P reserves. Our finding supports the critical P saturation threshold of 30 %, as recommended by Leinweber et al. (1997). In the study area, DPS values greater than this threshold were observed in topsoils under intensively managed pastures and heavily manured meadows. This suggests that long-term excessive manuring and continued large P inputs from cattle excreta may lead to elevated DPS values in the topsoil, which promotes P losses in runoff and leachate. It should be noted, however, that unmanured and unfertilised,

calcareous grassland soils with a neutral to slightly alkaline soil reaction can also show high DPS values, even higher than 30 % (Fig. 1). A probable explanation is that the oxalate extraction overestimates sorbed P in calcareous soils (Börling et al., 2004). This is also corroborated by the two outliers among the manured soils (Fig. 1). Hence, the DPS, calculated from oxalate-extractable P, Al and Fe, cannot be used to estimate P losses from calcareous soils. Nevertheless, DPS can be regarded as a management-dependent soil parameter, which reflects the relative saturation status of carbonate-free grassland soils. Thus, the DPS seems to be a suitable indicator for estimating P losses in runoff and leachate from carbonate-free grassland soils. In addition, the DPS can also serve as basis for P fertiliser recommendations.

The present study has focused on terrestrial permanent grassland soils in a typical mountainous region of Austria, but other mountainous regions in Central Europe with similar soil types, parent materials, soil mineralogy, climate and intensity levels of grassland management (e.g., Alps, Jura, Carpathians, Central German Uplands) might also benefit from the results.

## 5. Conclusions

- (1) Terrestrial permanent grassland soils in a typical mountainous region of Austria frequently have high concentrations of  $P_i$ ,  $P_{org}$  and  $P_{ox}$  in the layer 0-10 cm and they are characterised by high PSC values and low C:P ratios in the A horizon. Native soil  $P_i$  concentration amounts to about 900 mg kg<sup>-1</sup> soil. Hence, the rate of P replenishment of the soil solution from the solid phase seems to be the limiting factor for P supply to plant roots rather than the total amount of P present in the soil.  $P_{org}$  is by far the major P form in topsoil (on average 71 % of  $P_i$ ). Consequently, management practices which promote the mineralisation of organic P compounds in soil during the growing season (e.g., lime applications to strongly acid soils, improvement in topsoil structure by avoiding soil compaction) may contribute to a more efficient use of soil P by plants. Permanent grassland topsoils, particularly those low in pH, possess the capacity to retain and to release large amounts of P primarily due to high concentrations of  $Fe_{ox}$ . In addition, they also possess a high potential for  $P_{org}$  storage.
- (2)  $Fe_{ox}$  and  $Al_{ox}$  are important P sorption parameters in the A horizon of terrestrial grassland soils, whereas clay content seems to be of minor importance. The DPS, based on oxalate extraction, is a suitable indicator for estimating P losses in runoff and leachate from carbonate-free grassland soils. A critical threshold value of 30 % was found.
- (3) Management intensity has a major influence on the P status in topsoil. Long-term excessive manuring and continued large P inputs from cattle excreta can lead to an accumulation of various inorganic and organic P forms in the topsoil. Intensively managed grassland soils with DPS values greater than approximately 30 % are critical source areas for environmentally substantial P losses by surface runoff and leaching. Soil N rather than soil P seems to be the most growth-limiting mineral element in intensively managed mountain grassland.
- (4) Permanent grassland soils in Austria are not generally depleted in P. To avoid unnecessary mineral P fertiliser applications, a revision of the current Austrian fertiliser P recommendation system for grasslands would be advisable.
- (5) Since  $P_{org}$  is the most important P pool in these mountain grassland topsoils and its P release for plant nutrition is not reflected by the current routine soil P tests such as CAL-P, novel analytical procedures for the routine determination of easily mineralisable  $P_{org}$  in grassland soils are urgently required and should be developed.

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Table 1. Basic soil physical and chemical properties in the layer 0-10 cm (n = 106).

	pH	C <sub>org</sub>	N <sub>t</sub>	S <sub>t</sub>	C <sub>org</sub> : N <sub>t</sub>	C <sub>org</sub> : S <sub>t</sub>	N <sub>t</sub> : S <sub>t</sub>	sand	silt	clay
		g kg <sup>-1</sup>			ratio			g kg <sup>-1</sup>		
Median	5.6	42	4.9	0.5	9	81	9	380	510	110
Mean	5.8	43	5.1	0.5	10	96	14	370	490	140
Minimum	4.4	26	3.0	0.1	7	51	6	90	290	30
Maximum	7.4	75	11.6	0.9	13	288	70	650	730	380
V (%)	15	21	26	39	12	48	85	32	13	57

n, number of soil samples; V (%), variation coefficient (%); pH in CaCl<sub>2</sub>.

Table 2. Concentration of Al, Fe and Mn and element ratios in the soil layer 0-10 cm (n = 106).

	Al <sub>t</sub>	Fe <sub>t</sub>	Mn <sub>t</sub>	Al <sub>ox</sub>	Fe <sub>ox</sub>	Mn <sub>ox</sub>	Al <sub>t</sub> : Al <sub>ox</sub>	Fe <sub>t</sub> : Fe <sub>ox</sub>	Mn <sub>t</sub> : Mn <sub>ox</sub>
	mg kg <sup>-1</sup>			mmol kg <sup>-1</sup>			element ratio		
Median	17470	28118	874	78	105	11	8	5	1
Mean	17732	27681	925	78	104	12	9	5	2
Minimum	4552	6296	260	20	19	2	5	3	1
Maximum	34758	56880	2861	159	216	48	22	11	8
V (%)	30	38	48	41	38	68	34	33	64

n, number of soil samples; V (%), variation coefficient (%); Al<sub>t</sub>, Fe<sub>t</sub>, Mn<sub>t</sub>, total Al, Fe, Mn; Al<sub>ox</sub>, Fe<sub>ox</sub>, Mn<sub>ox</sub>, oxalate-extractable Al, Fe, Mn.

Table 3. P forms, P sorption capacity and degree of P saturation in the soil layer 0-10 cm (n = 106).

	P <sub>t</sub>	P <sub>i</sub>	P <sub>ox</sub>	P <sub>org</sub>	CAL-P	H <sub>2</sub> O-P	P <sub>org</sub>	C <sub>org</sub> : P <sub>t</sub>	C <sub>org</sub> : P <sub>org</sub>	N <sub>t</sub> : P <sub>t</sub>	PSC	DPS
	mg kg <sup>-1</sup>						% of P <sub>t</sub>		ratio		mmol kg <sup>-1</sup> %	
Median	1148	320	540	873	21	7	74	36	49	4	94	21
Mean	1198	388	599	811	27	9	71	51	66	5	91	22
Minimum	197	22	67	176	1	1	38	19	31	2	23	3
Maximum	2600	1624	1881	1335	204	36	96	381	428	30	159	57
V (%)	38	77	54	29	90	71	19	99	82	66	34	49

n, number of soil samples; V (%), variation coefficient (%); P<sub>t</sub>, total P; P<sub>i</sub>, inorganic P; P<sub>ox</sub>, oxalate-extractable P; P<sub>org</sub>, organic P; CAL-P, CAL-extractable P; H<sub>2</sub>O-P, water soluble P; P<sub>org</sub> % of P<sub>t</sub>, organic P as a percentage of P<sub>t</sub>; PSC, P sorption capacity; DPS, degree of P saturation.

Table 4. Effects of manuring and intensification of utilisation on selected soil chemical properties (median values) in the soil layer 0-10 cm (n = 106).

	Unmanured	Manured	P value	Extensive	Intensive	P value
H <sub>2</sub> O-P (mg kg <sup>-1</sup> )	4	8	0.000	5	8	0.001
CAL-P (mg kg <sup>-1</sup> )	11	24	0.000	19	26	0.004
P <sub>t</sub> (mg kg <sup>-1</sup> )	860	1199	0.000	987	1299	0.000
P <sub>i</sub> (mg kg <sup>-1</sup> )	314	320	0.191	237	422	0.000
P <sub>ox</sub> (mg kg <sup>-1</sup> )	324	600	0.000	451	651	0.002
P <sub>org</sub> (mg kg <sup>-1</sup> )	469	898	0.000	658	907	0.000
P <sub>org</sub> % of P <sub>t</sub>	64	74	0.605	76	71	0.017
C <sub>org</sub> : N <sub>t</sub>	12	9	0.000	11	9	0.000
C <sub>org</sub> : S <sub>t</sub>	115	82	0.000	91	82	0.111
C <sub>org</sub> : P <sub>t</sub>	91	35	0.000	53	34	0.000
C <sub>org</sub> : P <sub>org</sub>	145	51	0.000	74	51	0.003
N <sub>t</sub> : P <sub>t</sub>	6	4	0.000	6	4	0.000
DPS (%)	13	20	0.051	15	22	0.007

n, number of soil samples; H<sub>2</sub>O-P, water-soluble P; CAL-P, CAL-extractable P; P<sub>t</sub>, total P; P<sub>i</sub>, inorganic P; P<sub>ox</sub>, oxalate-extractable P; P<sub>org</sub>, organic P, P<sub>org</sub> % of P<sub>t</sub>, organic P as a percentage of P<sub>t</sub>, DPS, degree of P saturation.

Table 5. Correlation matrix (r values, Spearman rank correlation) of P forms, PSC, DPS and related soil properties in the soil layer 0-10 cm (n = 106). Correlation is significant at the 0.01 level.

	P <sub>t</sub>	P <sub>i</sub>	P <sub>ox</sub>	P <sub>org</sub>	CAL-P	H <sub>2</sub> O-P	P <sub>org</sub> %	PSC	DPS	Al <sub>ox</sub>	Fe <sub>ox</sub>	Mn <sub>ox</sub>	pH	C <sub>org</sub>	clay	sand
P <sub>t</sub>	1,00															
P <sub>i</sub>	0,81	1,00														
P <sub>ox</sub>	0,65	0,52	1,00													
P <sub>org</sub>	0,86	0,47	0,55	1,00												
CAL-P	0,46	0,28	0,47	0,42	1,00											
H <sub>2</sub> O-P	0,48		0,26	0,53	0,62	1,00										
P <sub>org</sub> %	-0,54	-0,92	-0,39				1,00									
PSC	0,34		0,60	0,35	0,32			1,00								
DPS	0,39	0,45	0,62	0,27	0,29	0,35			1,00							
Al <sub>ox</sub>			0,34					0,82	-0,33	1,00						
Fe <sub>ox</sub>	0,53	0,41	0,61	0,43	0,35		-0,30	0,87		0,49	1,00					
Mn <sub>ox</sub>	0,37			0,46				0,42		0,40	1,00					
pH		0,25	-0,25				-0,27	-0,64	0,32	-0,62	-0,55	-0,26	1,00			
C <sub>org</sub>						0,36				-0,26	-0,42		0,56	1,00		
clay	-0,35	-0,41			-0,29		0,34		-0,35						1,00	
sand	0,32	0,31			0,32	0,32									-0,81	1,00

P<sub>org</sub> %, organic P as a percentage of P<sub>t</sub>.

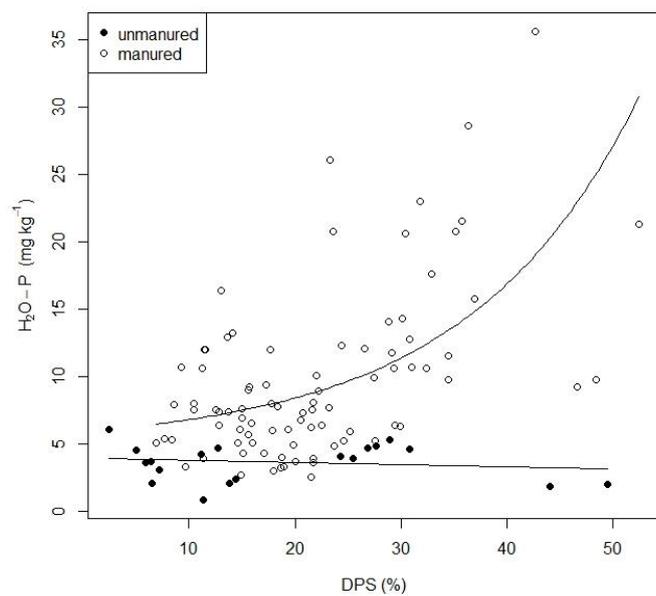


Figure 1. Relationship between the concentration of water-soluble P (H<sub>2</sub>O-P) and the degree of P saturation (DPS) for manured and unmanured permanent grassland soils in the layer 0-10 cm.