

Spatial variability of soil phosphorus in the Fribourg canton, Switzerland



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ABSTRACT

Phosphorus (P) is the second essential nutrient for plant growth but can become an ecological and economical concern in case of over-fertilization. Soil P dynamic is influenced by many parameters like soil physical–chemical properties and farming practices. A better understanding of the factors controlling its distribution is required to achieve best management of P in cropping systems. In Switzerland, the FRIBO network was launched in 1987 and consists of 250 sites covering a wide diversity of soils (Cambisols, Gleysols, Rendzinas, Lithosols, Luvisols, Fluvisols) and three different land uses (cropland, grassland and mountain pasture) across the Fribourg canton. A spatial investigation of the different P forms (total, organic and available) for the FRIBO network led to the following main conclusions:

- (i) The P status in agricultural soils was significantly different among the three land uses encountered, with the highest mean values of available P found in croplands, from 2.12 (CO₂ saturated water extraction) to 81.3 mg.kg⁻¹ (acetate ammonium + EDTA extraction); whereas total P was more abundant in permanent grasslands (1186 mg.kg⁻¹), followed by mountain pastures (1039 mg.kg⁻¹) and croplands (935 mg.kg⁻¹). This full characterization of the soil P status provides important data on P distribution related to soil properties and land use.
- (ii) Environmental variables such as altitude, slope, wetness index or plan curvature, derived from the digital elevation model (DEM) only explained a small part of the spatial variation of the different P forms (20 to 25%). Thus, the geostatistical analyses revealed that land use plays a significant role in soil P distribution. Improved predictions of the spatial distribution of P-related forms at landscape scales are needed and would require additional data points and variables such as parent material, soil types and terrain attributes.

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1. Introduction

Phosphorus (P) is an essential nutrient for plant growth, and without fertilization its availability can be limiting in agricultural systems (Aerts and Chapin, 2000). For the last decades, European and north-American farmers have been intensively applying P fertilizers to prevent P plant deficiencies. This phenomenon has led to the current P crisis, creating both ecological and economical concerns. Reserves of easily extractable phosphate rocks are dramatically decreasing, and some scenarios predict disappearance in the next 100 years (Gilbert, 2009). On the other hand, the potential for negative impacts of this nutrient on the environment is widely recognized (Gillingham and Thorrold,

2000; Sharpley et al., 2000; Withers et al., 2005). In Switzerland, agriculture is considered a major contributor to environmental pollution, especially eutrophication of surface waters due to diffuse phosphate losses from agricultural lands (Braun et al., 2001). Therefore, there is a crucial need to accurately understand P dynamic in agro-systems in order to achieve best P management practices while maintaining/improving both farm profitability and environment quality.

Phosphorus in soils can be found in inorganic or organic forms, the latter representing from 20 to 80% of total P (Stevenson, 1994), yet only inorganic forms of P (HPO₄²⁻, H₂PO₄⁻) can be taken up by plants. As a result, the majority of studies that investigated soil P status and its consequences, only focused on soil P availability, most often estimated via only one chemical extraction method and not always the same (Jia et al., 2011; Jordan-Meille et al., 2012; Needelman et al., 2001). However, Demaria et al. (2005) demonstrated that most of these

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chemical extraction methods under- or over-estimate the availability of P for plants. Thus, many studies suffer from lack of details in the characterization of soil P status and, in some cases, this lack of knowledge may lead to unnecessary soil P build-up. Awareness of the P crisis has been highlighted in the last couple of years by many studies that have investigated P status and its consequences at different spatial and temporal scales. For example, it has been shown that P flux heterogeneity, observed at the national scale (Senthilkumar et al., 2012a) and regional scale (Senthilkumar et al., 2012b), is most often due to industrial and agricultural activities. Moreover, soil P content expresses certain heterogeneity even at the field level (Juang et al., 2002; Umali et al., 2012), leading to site-specific fertilization recommendations. Thus, the large spatial variability of available P in agricultural soils does not allow for standard fertilization practices to be efficient and without risks at the regional scale and even at the field scale (Wong et al., 2012). Long-term investigation of soil P availability evolution has almost always reported increased soil P content over time in agricultural soils. This was the case in the Netherlands during the 20th century (Reijneveld et al., 2010) and in the Brittany region (France) over a 23-year period (Lemerrier et al., 2008). In both studies, increasing soil P content (either total P in the Netherlands or available P in Brittany) was correlated with increasing numbers of livestock. Recently, Jia et al. (2011) revealed an available P increase of more than 950% in a Chinese region (Pingluo county of Liaoning) between 1981 and 2006. These authors also demonstrated that the weak spatial dependency of P distribution was explained by increasing fertilizations which weakened the effect of climatic, soil and terrain variability. Regarding total P, Liu et al. (2013) demonstrated that stocks of total P of the Loess plateau (China) were greatly modulated by land use, precipitation and temperature. Investigations of the spatial distribution of different soil P forms have been performed in different places, such as Germany (Leinweber et al., 1997), but, to our knowledge, no such attempt exists in Switzerland.

The dense collection of soil samples for accurate spatial predictions of soil properties is expensive and time consuming, and many interpolation techniques have been developed for predicting soil properties for sites with no measurements (McBratney et al., 2000). Ordinary Kriging (OK) has been widely used in studies related to natural resources since the 1970s. However, with the emergence of desktop Geographic Information Systems (GIS) and the increased availability of remote sensing data in the 1990s, the use of secondary/auxiliary environmental variables in mapping and predicting soils and their properties has increased (Hengl et al., 2004; McBratney et al., 2000). The use of auxiliary environmental variables is advantageous for two reasons: (i) the acquisition is relatively less expensive compared to field-intensive methods, and (ii) it allows for prediction of soil properties at unmeasured locations based on the relationships between soil properties and environmental variables (Hengl et al., 2004; McBratney et al., 2000). One of the most accepted and widely used methods implementing this approach is Regression Kriging (RK) (Gessler et al., 1995; Hengl et al., 2004; McBratney et al., 2000; Moore et al., 1993; Odeh et al., 1994, 1995).

The Fribourg canton is located on the western edge of the Swiss Alps. It is mainly composed of agricultural lands within plain and mountain ecosystems and offers a broad diversity of soil properties and farming practices as well as terrain. To our knowledge, no study has estimated and quantified the proportion of soil P variability explained by intrinsic factors (soil properties) and the proportion due to extrinsic factors (e.g., land use). Also, no map showing the explicit spatial distribution of various P forms is available for the Fribourg canton. A regional scale investigation within this area allowed us to: (i) characterize the soil P status (total, organic, inorganic, and available P); (ii) evaluate the spatial variability of the different soil P forms and analyze the relationships between soil P forms and selected soil properties (independent from farming practices) and land use; and (iii) predict spatial distribution of soil P forms using geostatistical methods in order to identify areas where better P fertilization procedures are needed.

2. Material and methods

2.1. Study area

The Fribourg canton is located in the western part of Switzerland (46°–47°N, 6°–7°E). Its climate is temperate continental with cold winters (lowest mean monthly temperature in January: -3.1°C) and mild summers (highest mean monthly temperature in July: 17.6°C). The study area has a mean annual temperature of 8°C and a mean annual precipitation of 1118 mm (the driest month is February with an average monthly precipitation of 63 mm, and the wettest is August with an average monthly precipitation of 129 mm). These values are based on meteorological stations data from the study area extracted from the Meteosuisse IDAweb database (<http://www.meteoschweiz.admin.ch/>). Temperature and rainfall are not equally distributed in the whole canton as the southwestern area experiences a colder and rainier climate due to higher altitude. Such climatic conditions could favor erosion and leaching of soil nutrients (Troitino et al., 2008). The area represents 1670.7 km² (4% of Switzerland) and includes different soil types (Cambisols, Gleysols, Rendzinas, Lithosols, Luvisols, Fluvisols) (Brunner et al., 2008) and different land uses (croplands, grasslands and mountain pastures) (Fig. 1). In 1987, the Agriculture Institute of the Fribourg canton set up a network to survey soil quality called FRIBO (Julien and Morand, 1995). Within this area, 250 sampling sites were selected, distributed along a 2*2 km grid. Since 1987, 50 sites have been sampled each year. Thus, every 5 years, all the 250 sites have been sampled within what we call a “cycle.” In this study, we used the FRIBO data collection of the 4th cycle (2002–2006) to investigate the spatial variation of different P forms. Five out of the 250 sites

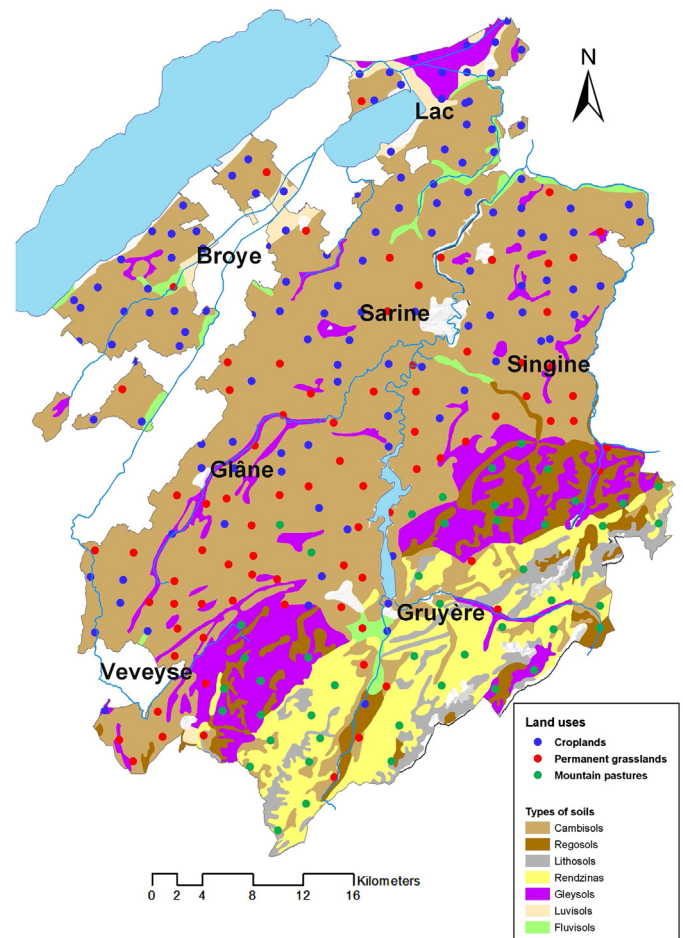


Fig. 1. Map of soil types and location of the 250 sites in the FRIBO network and their corresponding land use.

were removed from our analyses due to the extreme organic matter (OM) content, triggering outliers in almost all measured P variables. Among the remaining 245 sites, 3 different land uses were present: 134 croplands, 67 grasslands and 44 mountain pastures.

Usually, croplands follow a meadow-maize-wheat barley-rapeseed rotation but other crops are also cultivated, such as sugar beet, potatoes and peas. P fertilization in Switzerland is calculated according to the Swiss fertilization guidelines for crops and grassland (Sinaj et al., 2009) and applied mostly as chemical fertilizer (superphosphate) in croplands and as cattle manure in permanent grasslands and mountain pastures (Sinaj et al., 2009). Before 1993 many farmers used Thomas slags as P fertilizer in croplands, permanent grasslands and mountain pastures, but it is impossible to have an overview on the applied quantities and their distribution.

The location of different land uses and soil types follows a NW–SE gradient (Fig. 1). Most of the croplands occur in Cambisols located in the northern and central parts, mostly on low hills with molasses partially covered with moraine as parent material, while most of the mountain pastures occur in Rendzinas, Gleysols or Lithosols located in the southern part, mostly in alpine regions on calcareous or flysch parent material (Fig. 1). Permanent grasslands were almost all located in between the two other land uses. Hence, the distribution of land uses is correlated with the distribution of soil types: croplands were matched with sandy soils and permanent grasslands were matched with clay textured soils (Brunner et al., 2008).

2.2. Soil sampling and analysis

At each site, 25 soil samples of surface horizon (0–20 cm depth) were taken within an area of 100 m². Plant residues were removed from the soil and the individual samples were pooled together to form a composite sample per site. The 245 sites were sampled from 2002 to 2006 (approximately 50 sites per year). All soil samples were air-dried, sieved at 2 mm and analyzed for different soil properties (Table 1). The pH-H₂O, total organic carbon (TOC), clay and sand

content and cation-exchange capacity (CEC) were measured according to standard methods (Agroscope et al., 1996). The content of amorphous iron (Fe) and aluminum (Al) hydrous-oxides (Fe-ox and Al-ox) were measured after extraction with ammonium-oxalate as in Loeppert and Inskeep (1996). The total content of Fe and Al hydrous-oxides (Fe-d and Al-d) were measured after extraction with a mixture of dithionite, citrate and bicarbonate, following McKeague and Day protocols (1966).

Soil total P concentration (P_T) was obtained by digestion of 0.25 g of soil previously treated in 5 ml of hydrofluoric acid (40%) and 1.5 ml of HClO₄ (65%) according to the AFNOR standard X31-147 (1996) followed by molybdate colorimetric measurement (Murphy and Riley, 1962). Organic P (P_O) was obtained according to Saunders and Williams (1955) and inorganic P (P_I) was calculated as the difference between P_T and P_O. Soil available P was characterized by different chemical extractions: P-H₂O extraction was performed with 1:10 soil:water ratio for 16 h (Demaria et al., 2005); P-CO₂ extraction was performed with a 1:2.5 soil:extractant ratio for 1 h using CO₂-saturated nanopure water at pH 3.5–4 and pCO₂ of 6 bar (Agroscope et al., 1996); P-AAE was extracted in a 1:10 suspension for 1 h by mixture of 0.5 M ammonium acetate, 0.5 M acetic acid and 0.02 M EDTA (Agroscope et al., 1996); P-NaHCO₃ was extracted by 0.5 M NaHCO₃ at pH 8.5 for 30 min with a soil: solution ration of 1:20 (Olsen et al., 1954). P-CO₂ and P-AAE chemical extractions are the Swiss reference methods for routine estimation of soil plant-available P. The determination of soil plant-available P with ammonium-acetate EDTA and NaHCO₃ was reported to be more affected by soil properties such as pH and carbonate content than P extracted by H₂O and CO₂-saturated water (Demaria et al., 2005). Demaria et al. (2005) found that H₂O and CO₂-saturated water underestimate plant-available P while NaHCO₃ and especially ammonium-acetate EDTA, according to the soil type, significantly overestimated it. The degree of soil phosphorus saturation (DSP) was calculated according to van der Zee et al. (1987) from the P (mmol kg⁻¹), Fe and Al (mmol g⁻¹) extracted by ammonium oxalate reagent (Loeppert and Inskeep, 1996).

Table 1
Descriptive statistics (minimum and maximum value, mean, median, standard deviation and coefficient of variation) of the soil physical–chemical properties, for all sites and depending on land use. Different letters among land uses indicate a significant difference ($P < 0.05$) on a given variable, based on ANOVA followed by Tukey–Kramer pairwise comparisons test.

	Altitude	Slope	pH	TOC	Clay	Sand	CEC	Fe-d	Fe-ox	Al-d	Al-ox
	m	%	H ₂ O	g.kg ⁻¹			cmol.kg ⁻¹	g.kg ⁻¹			
<i>All sites (n = 245)</i>											
Min–max	430–1590	0–75	4.8–7.8	5.8–89.9	87.0–752.0	21.0–772.0	6.6–67.9	1.7–21.5	1.1–15.5	0.4–3.3	0.4–4.5
Mean	785	10.42	6.3	25.5	229.4	446.6	19.2	9.1	4.3	1.5	1.5
Median	713	6.0	6.2	22.6	200.0	477.0	17.0	8.5	3.8	1.4	1.5
SD	278.2	13.24	0.7	14.8	112.1	156.3	9.4	4.1	2.3	0.6	0.7
CV (%)	35.4	127.06	10.4	58.0	48.9	35.0	48.9	45.3	51.8	42.1	42.2
<i>Croplands (n = 134)</i>											
Min–max	430–995	0–31	5.0–7.8	5.8–75.4	87.0–581.0	111.0–772.0	6.6–67.9	1.7–18.2	1.1–9.2	0.4–3.0	0.4–3.2
Mean	619.8	5.65	6.5	16.2	179.0	515.9	14.2	7.4	3.2	1.2	1.3
Median	635	4.0	6.3	13.9	164.0	530.0	12.9	6.4	2.9	1.1	1.3
SD	123.9	6.60	0.6	8.2	70.5	119.1	7.2	3.3	1.5	0.5	0.6
CV (%)	20.0	116.81	9.6	50.5	39.4	23.1	50.7	44.9	44.9	43.7	43.4
Tukey rank	c	b	a	c	c	a	c	b	b	b	b
<i>Permanent grasslands (n = 67)</i>											
Min–max	460–1015	0–33	5.0–7.5	15.7–58.0	120.0–752.0	21.0–684.0	11.5–49.7	4.3–19.8	2.0–8.3	0.4–3.3	0.6–4.5
Mean	789.2	7.79	6.2	31.2	255.3	409.3	22.3	10.6	4.6	1.8	1.7
Median	820	7.0	6.2	29.6	229.0	420.0	20.8	10.5	4.3	1.8	1.7
SD	114.1	7.32	0.6	9.3	118.5	140.3	7.2	3.7	1.4	0.6	0.6
CV (%)	14.5	93.97	8.9	29.8	46.4	34.3	32.3	35.3	30.7	34.9	36.3
Tukey rank	b	b	b	b	b	b	b	a	a	a	a
<i>Mountain pastures (n = 44)</i>											
Min–max	880–1590	0–75	4.8–7.2	22.0–89.9	190.0–654.0	31.0–603.0	17.8–49.6	2.9–21.5	3.5–15.5	1.0–3.1	1.1–3.2
Mean	1282.0	28.98	5.8	44.9	342.4	293.9	29.5	12.0	7.3	1.8	2.1
Median	1312	27.5	5.8	40.6	343.0	280.0	27.6	11.2	7.0	1.7	1.9
SD	184.0	18.53	0.6	14.0	110.6	153.0	7.8	4.5	2.5	0.5	0.6
CV (%)	14.4	63.94	10.8	31.3	32.3	52.1	26.3	37.2	33.8	25.7	29.8
Tukey rank	a	a	c	a	a	c	a	a	a	a	a

2.3. Environmental variables for P status spatial predictions

The 5 m grid size Digital Elevation Model (DEM) of the study area was projected to the CH1903 Hotline Oblique Mercator Azimuth Center Geographic Coordinate System (GCS_CH1903). The high relief of the study area (430–2400 m) suggested that the 5 m grid needed to be resampled to a 15 m grid size in order to provide a smoother surface and reduce the level of local variability or noise in the elevation data. Bilinear interpolation was used for resampling. The System for Automated Geospatial Analysis (SAGA) (Conrad, 2006) was used to derive terrain attributes (slope, slope length, mid-slope position, curvature, planform curvature, profile curvature, standardized height, normalized height, SAGA Wetness Index, Vector Terrain Ruggedness, and Terrain Ruggedness) that were used as environmental variables for spatial predictions of various P forms. Soil types and land use were also used as environmental variables and were converted from polygons to grids in ArcMap 10 (ESRI, 2012) and given the same grid size and projection of the terrain attributes. In order to investigate the relationships between P status and environmental variables, the values of environmental variables were extracted for all 245 sites where various P forms were measured and/or calculated.

2.4. Statistical analysis

The dataset was analyzed two times independently: first in a classical way to investigate the global soil P status and its link with chemical–physical soil properties, and then within a geostatistics framework, in order to investigate the spatial variation of different P forms.

2.4.1. Classical statistics

The mean, median, standard deviation and coefficient of variation for each soil physical–chemical variable were calculated for the whole dataset and within each land use category (Table 1). We followed the same process for the set of variables used to characterize soil P status (Table 2). Then the multivariate dataset was analyzed via a principal

component analysis (PCA) to investigate the correlations among the different variables and the projection of the 245 sites in the plan 1–2 of the PCA, depending on land use.

Because of the high number of sites ($n = 245$ in total and superior to 30 within each land use), classical tests were performed on untransformed variables. A one-way analysis of variance (ANOVA), followed by the Tukey–Kramer test for pairwise comparisons, was used to detect whether both the soil physical–chemical variables and the P-related variables were significantly different depending on land use. All the classical statistics were performed using R 2.14.1 the package “ade4” (Dray and Dufour, 2007).

2.4.2. Geostatistics

In order to generate a continuous spatial prediction of P forms among the 245 sampling sites, other environmental variables derived from the DEM were used. With all the DEM-derived variables, we first performed a multivariate analysis to determine the multi-co-linearity among DEM-derived variables selected for P form predictions in conjunction with the principal component analysis (PCA). This was followed by a forward step-wise regression analysis (Table 4) to determine the best predictors for various forms of P based on the minimum Akaike Information Criterion (AIC) (Akaike, 1974, 1976). These analyses were conducted on the Logit transformed P forms (Table 3) to assure normal distribution of the data. The spatial structure of the different variables was determined by means of a semivariogram using the nugget/sill ratio as defined by Cambardella et al. (1994). The spatial dependence structure of P forms and residuals was modeled in VESPER based on automated variogram fitting (Minasny and McBratney, 2002). No anisotropy was found among the selected variables, therefore isotropy was assumed for all kriging calculations. All semivariograms were fitted with an exponential model (Table 5).

Regression-Kriging (RK), as suggested by Hengl et al. (2004), was performed to predict P forms using environmental covariates derived from the DEM, soil type and land use. Initially, normality conditions for target variables (P_T , P_O , P_I , P-AAE, P- CO_2 , P-NaHCO₃, P-H₂O and

Table 2

Descriptive statistics (minimum and maximum value, mean, median, standard deviation and coefficient of variation) of the P related variables, for all sites by land use. Different letters among land uses indicate a significant difference ($P < 0.05$) on a given variable, based on ANOVA followed by Tukey–Kramer pairwise comparisons test.

	P_T mg.kg ⁻¹	P_O	P_O/P_T %	P-AAE mg.kg ⁻¹	P-NaHCO ₃	P-CO ₂	P-H ₂ O	DSP %
<i>All sites (n = 245)</i>								
Min–max	353.8–2275.0	135.1–1443.0	13.8–88.3	1.9–439.1	6.5–158.1	0.2–21.2	0.2–31.1	4.8–87.8
Mean	1023.0	559.1	54.1	66.8	38.3	1.8	6.3	32.2
Median	976.8	521.0	53.5	47.6	36.0	1.1	4.9	30.6
SD	314.0	251.9	15.5	60.9	19.8	2.2	5.3	14.2
CV (%)	30.7	45.1	3.5	91.0	51.7	120.1	84.3	44.1
<i>Croplands (n = 134)</i>								
Min–max	475.2–2119.0	135.1–980.2	13.8–70.5	7.8–311.0	7.8–158.1	0.2–12.0	0.9–25.0	15.8–87.8
Mean	935.0	427.5	45.6	81.3	43.5	2.1	7.4	37.9
Median	876.4	406.6	45.7	67.9	41.9	1.5	6.2	35.5
SD	257.1	167.8	12.1	56.7	18.9	1.9	4.7	13.3
CV (%)	27.50	39.3	3.8	69.7	43.4	91.3	63.7	35.1
Tukey rank	b	b	c	a	a	a	a	a
<i>Permanent grasslands (n = 67)</i>								
Min–max	619.1–2275.0	241.7–1340.0	26.4–84.1	11.1–439.1	14.9–98.7	0.3–21.2	1.0–31.1	14.8–55.5
Mean	1186.2	703.0	59.8	67.6	38.5	1.9	6.7	30.8
Median	1139.6	701.3	61.5	43.7	31.0	1.0	4.2	28.5
SD	292.9	203.3	12.5	72.2	20.4	2.9	6.6	11.4
CV (%)	24.7	28.9	4.8	106.7	53.0	153.3	98.8	37.0
Tukey rank	a	a	c	b	a	a	a	b
<i>Mountain pastures (n = 44)</i>								
Min–max	353.8–1923.0	277.4–1443.0	45.6–88.3	1.9–96.4	6.5–52.6	0.2–2.1	0.2–7.2	4.8–30.2
Mean	1039.0	737.6	71.3	22.0	21.9	0.7	2.4	16.6
Median	963.6	682.3	71.4	16.1	20.4	0.6	1.6	16.8
SD	396.1	300.3	10.0	19.0	11.0	0.4	1.9	6.3
CV (%)	38.1	40.7	7.1	86.6	50.1	61.8	79.5	37.9
Tukey rank	b	a	a	c	b	b	b	c

Table 3
Skewness and kurtosis statistical moments for the untransformed and logit transformed P forms.

	Moments	P forms (Target predicted variables)							
		P _T	P _O	P _I	P-AEE	P-NaHCO ₃	P-CO ₂	P-H ₂ O	DSP
Untransformed	Skewness	0.76	0.71	1.05	2.76	0.85	5.72	1.65	1.04
	Kurtosis	1.13	0.72	2.42	11.79	0.71	46.22	3.4	2.84
Logit_transformed	Skewness	0.34	0.17	−11.59	−0.18	−0.71	5.74	−0.06	0.23
	Kurtosis	2.33	2.33	143.58	0.43	1.33	56.95	0.42	2.00

DSP) were checked via histograms distribution, skewness and kurtosis moments, and those that violated normality were logit transformed using JMP Version 9.0 (SAS Institute Inc., Cary, NC) statistical package (Table 3).

The logit transformation was conducted in two steps using first the following equation:

$$z^+ = \frac{z - z_{\min}}{z_{\max} - z_{\min}} \quad (1)$$

where: z^+ is the standardized variable (P status) varying between $z_{\min} < z^+ < z_{\max}$. The z_{\min} and z_{\max} were derived from the histogram distribution. The second step used the Eq. (2):

$$z^{++} = \ln\left(\frac{z^+}{1 - z^+}\right) \quad (2)$$

where: $0 < z^+ < 1$. The advantage of logit transformations is the standardization of the variable using physical minimum and maximum z values (Hengl et al., 2004).

Ordinary Kriging was performed on both predicted values for the target variables and error residuals. The predicted maps of target variable and error residuals were summed together to yield the final predicted maps of target variable. The final predicted maps were back transformed following Eq. (3):

$$\hat{z}(s_0) = \frac{e^{\hat{z}^{++}(s_0)}}{1 + e^{\hat{z}^{++}(s_0)}} * (z_{\max} - z_{\min}) + z_{\min} \quad (3)$$

where: \hat{z} is the predicted P form at the unknown location s_0 ; $e^{\hat{z}^{++}(s_0)}$ is the log coefficient of the predicted Logit P form at the unknown location s_0 , and z_{\max} and z_{\min} are the maximum and minimum values of untransformed P forms. The 95% confidence limits of the predictions were derived from the following Eq. (4):

$$\hat{z} \pm t(s_0) = \frac{e^{[\hat{z}^{++}(s_0) \pm t\sigma_{\hat{z}^{++}}(s_0)]}}{1 + e^{[\hat{z}^{++}(s_0) \pm t\sigma_{\hat{z}^{++}}(s_0)]}} * (z_{\max} - z_{\min}) + z_{\min} \quad (4)$$

where t is the threshold value of standard normal error and $\sigma_{\hat{z}^{++}}(s_0)$ is the standard deviation of the prediction error of transformed P forms.

The RK was performed using 165 out of 245 point observations with the remaining 80 points used for validation of the predicted maps of P forms. The Mean Error (ME) was used for measuring the bias in prediction while the Root Mean Square Error (RMSE) was used as a measure of the prediction precision. The ME is defined as in Eq. (5):

$$ME = \frac{1}{v} \sum [z^*(s_j) - z(s_j)] \quad (5)$$

where $z^*(s_j)$ and (s_j) are predicted and observed values of P forms and v is the number of samples used for validation. The RMSE is defined as in Eq. (6):

$$RMSE = \frac{1}{v} \left\{ \sum_{j=1}^v [z^*(s_j) - z(s_j)]^2 \right\}^{0.5} \quad (6)$$

The third accuracy assessment was the normalized RMSE by the total variation (Standard Deviation), as defined in Eq. (7):

$$RMSE_r = \frac{RMSE}{s_z} \quad (7)$$

where s_z is the total variation (Standard Deviation). ME should be close to zero for unbiased methods while RMSE should be as small as possible for unbiased and precise prediction. An $RMSE_r$ value of 40% indicates a satisfactory accuracy prediction; a value $>70\%$ indicates that the model explained less than 50% of the variability at the validation points and the precision is not satisfactory (Hengl et al., 2004).

In addition to the RK results, we investigated the local spatial autocorrelation of two P variables: P_T and available P, as estimated by P-H₂O. Using the geographical coordinates of the 245 sampling sites constituting the FRIBO database, we measured the local spatial autocorrelation of P_T and P-H₂O with the help of the OpenGeoda software (Anselin and McCann, 2009). This measure of local spatial autocorrelation has been carried out with Local Indicators of Spatial Association (LISA) developed by Anselin (1995). LISA indicators are statistics that measure spatial dependence and evaluate the existence of local clusters in the spatial arrangement of a given variable. They are based on Moran's I statistical index (Moran, 1950) to measure the global spatial autocorrelation for the variable of interest in the area under investigation. Moran's I ranges from -1 (inverse spatial dependence) to 1 (complete spatial dependence), with 0 indicating the absence of spatial dependence. We computed a LISA index based on a spatial weighting scheme determined on the basis of three criteria: (i) we considered the distance for which there is no neighborless sampling unit (3.5 km); (ii) we produced a correlogram showing that Moran's I was higher for short distances before rapidly and regularly decreasing (5 km) for each variable investigated (Fig. 2), and (iii) we considered the information produced by a connectivity histogram showing the density of points within spatial lags. As representativeness is required within the local domain defined, we decided to adopt a 10 km spatial lag, with a first class showing 12 units with 12 to 18 neighbors.

For each sampling site, the correlation between the observed variable and the mean of this variable within the spatial lag was calculated. The standardized scattergram of this relationship shows four distinct classes: (i) high values correlated with high weighted values; (ii) low values correlated with low weighted values; (iii) a low-high relationship, and (iv) a high-low relationship. The attribution of sampling sites to these four classes depends on the results of a significance test. This test consists of performing many random permutations ($N!$) among sampling sites to compare the observed index with the distribution of indices obtained from the random permutations (see details in Anselin, 1995). If the test is significant – the observed index is larger than the largest index obtained by means of permutations (or smaller in case of negative spatial autocorrelation) – a sampling site is attributed to one of the clusters. All sampling sites which are not significant are displayed in white. This permitted us to produce maps showing locations where there is significant spatial dependence of P_T and P-H₂O values.

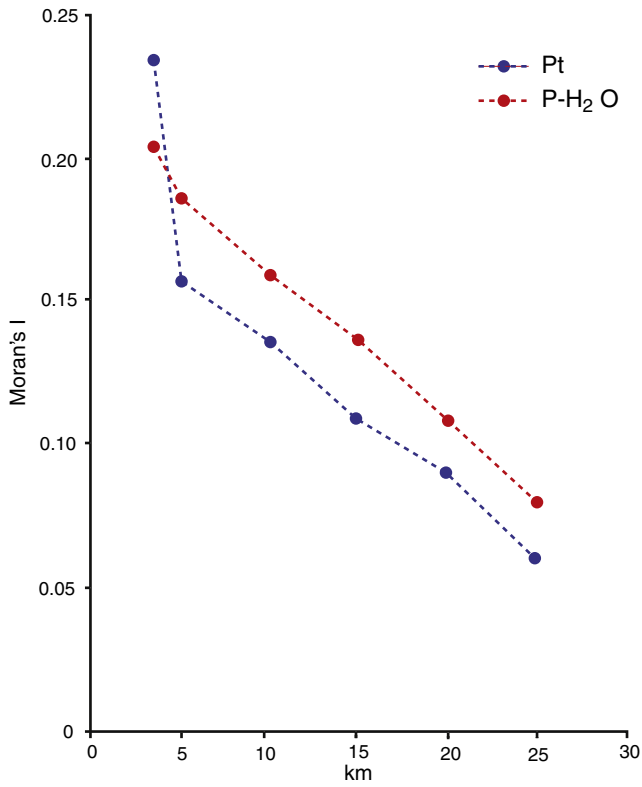


Fig. 2. Correlogram showing Moran's I for spatial lags ranging from 5 to 25 km.

3. Results and discussion

3.1. Physical–chemical characterization of soils

Soils of the Fribourg canton represent a large variety of physical–chemical properties. However, soils from the same land use category often shared similar properties (Fig. 3). Indeed, following a NW–SE gradient, soils on croplands were associated with the highest values of pH and sand content but also with the lowest values of TOC, CEC, Fe and Al oxides (Table 1). Soils on mountain pastures had properties opposite of those for croplands (low pH, high clay and TOC content), whereas soils on most grasslands were in between. All these variables, except pH, displayed high coefficient of variation (CV > 25%) in all land uses. These variations were greater in croplands for TOC, CEC and Fe and Al oxides, in grasslands for clay content and in mountain pastures for sand content (Table 1). The observed differences could greatly influence soil P status because some of these variables are considered as drivers of soil P sorption, desorption and isotopic exchangeability. Indeed, clay content, Fe and Al oxides enhance P sorption (Freese et al., 1992; Frossard et al., 1995; Singh and Gilkes, 1991; van der Zee et al., 1987), while soil organic matter is negatively correlated (Dubus and Becquer, 2001). Moreover, soil P desorption is strongly driven by pH (Simard et al., 1994). It has been demonstrated that pH and Fe-d are principal soil properties controlling isotopically exchangeable P (Demaria et al., 2013).

3.2. Soil P status in the Fribourg canton

As expected from the physical–chemical properties of soils, we observed that the three different land uses can also be discriminated according to their P status. Mean P_T was the highest for permanent

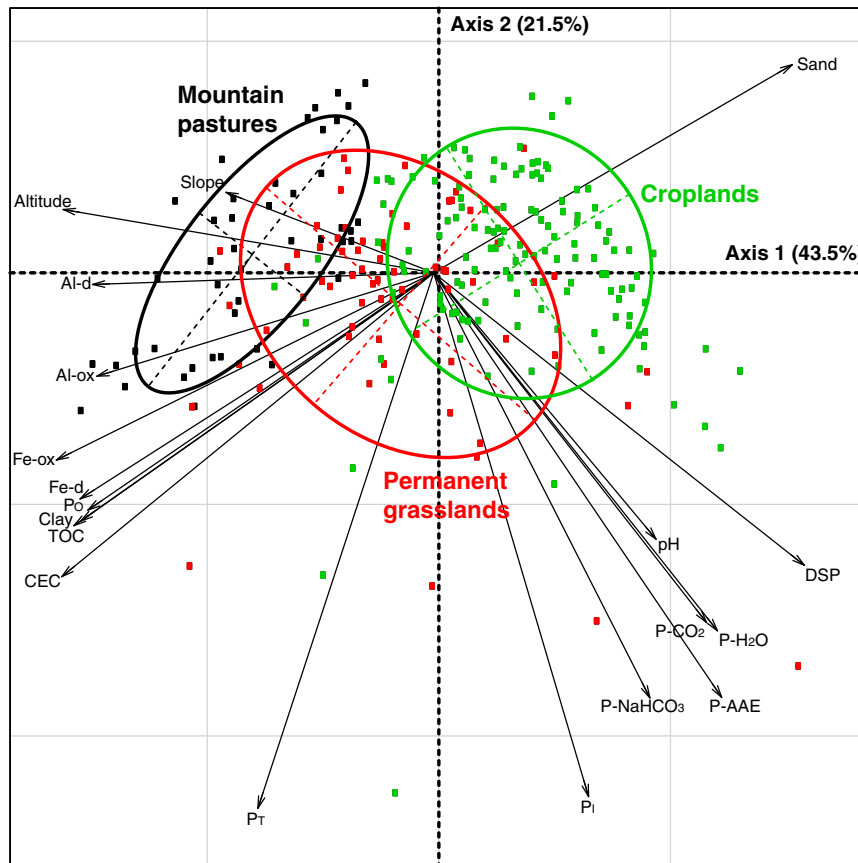


Fig. 3. Soil characterization through principal components analysis. Axis 1 represents 43.5% of the observed variance, axis 2 represents 21.5% of the observed variance. The 245 sites were projected in the Axis1/Axis2 plan and their positions were revealed with color dots: black dots correspond to pasture land; red dots correspond to grasslands and green dots to croplands.

grasslands with $1186 \text{ mg P.kg}^{-1}$ ($F_{2,243} = 14.96$, $P < 0.001$), representing an increase of 13% and 21% compared with mountain pastures and croplands, respectively. Our findings are not congruent with those of Reijneveld et al. (2010), who found that the P_T was higher in croplands than in grasslands. A recent study, in a broader study area in China (Liu et al., 2013), has shown that no significant difference occurred in terms of P_T within a set of croplands displaying different temperature and precipitation conditions. This reinforces the hypothesis that farming practices, especially fertilization, outweigh the effect of environmental conditions and thus lead to big differences among land uses.

The mean amount of P_O was also different for different land uses. The highest mean values were found in mountain pastures (737 mg.kg^{-1}) and grasslands (703 mg.kg^{-1}) as compared to croplands (427 mg.kg^{-1}). As expected, the opposite pattern was found for inorganic P (P_i , data not shown). This was corroborated by the mean proportion of P_O (P_O/P_T) in the soil, which was greatly higher in mountain pastures (71.3%), followed by grasslands (59.8%) and croplands (45.6%) (Table 2). These variations in the distribution of different P forms among land uses could be explained by the presence of livestock and continuous addition of cattle manure in mountain pastures, often responsible for increases of P_T and P_O (Reddy et al., 2000; Reijneveld et al., 2010; the presence of tillage in croplands (Dick, 1983); and by the fact that mountain pastures often are in higher and colder areas with conditions that could limit microbial decomposition of soil organic matter (Karhu et al., 2010).

Different indicators characterizing available P ($P\text{-H}_2\text{O}$, $P\text{-CO}_2$, $P\text{-NaHCO}_3$, $P\text{-AAE}$) also revealed some significant differences among land uses. We observed that all these indicators were correlated together and with P_i (Fig. 3), providing equivalent results. They revealed that the highest concentration of available P was found in croplands, followed by grasslands and mountain pastures (Table 2). However, while values of $P\text{-AAE}$ revealed a significant difference between grasslands and arable lands, values of $P\text{-NaHCO}_3$, $P\text{-CO}_2$ and $P\text{-H}_2\text{O}$ did not. The DSP was significantly different among land uses as well ($F_{2,243} = 111.3$, $P < 0.001$), with pasture lands harboring the lowest mean value (16.6%) followed by grasslands (30.8%) and croplands (37.9%). In total, 171 sites exceeded the value of $\text{DSP} = 25\%$, which was estimated as the threshold beyond which P loss through leaching or erosion is highly probable (van der Zee et al., 1987). However, because this threshold was established for sandy acidic soils of the Netherlands, it may not be appropriately extended to other soil types (Beauchemin and Simard, 1999).

All these results are illustrated in Fig. 3, where all sites (dots) and all variables (arrows) included in Tables 1 and 2 as well as in the PCA analysis have been projected in the axis1–axis2 plan of the PCA. The three circles represent the area where a given site that belongs to a given land use should be placed (with a probability of 95%) and demonstrate that the three land uses are well segregated, especially along the first PCA axis.

Taken together, these results clearly show that croplands have the lowest quantity of total P but the highest quantity of available P and a very high DSP (Table 2). Permanent grasslands harbored both high total and available P while mountain pastures revealed a high total amount of P but low P availability and DSP. Due to the strong correlation between extrinsic (land use) and intrinsic (terrain attributes, soil type, soil properties) factors, estimating their respective role in soil P status was not obvious, and the analyses of spatial variability of these factors turned out to be necessary.

3.3. Spatial prediction of P status

3.3.1. Spatial autocorrelation between environmental variables for P forms and Regression Modeling

The analysis of the multi-co-linearity among environmental variables of P forms predictions in conjunction with the principal

Table 4
Summary results of the step-wise regression analysis for P forms.

P forms**	Selected predictors	R C (SLS*)	P-value	Adj R ²		
P_T	Intercept	−0.9935	<.0001	0.08		
	Norm. Height***	−1.0250	0.0002			
	Std. height***	0.0015	0.0024			
	Slope	−0.0122	0.0297			
P_i	Intercept	1.1661	0.0850	0.09		
	Altitude	−0.0033	<.0001			
	P_O	Intercept	−1.3133		0.0674	0.30
		Altitude	0.0011		0.0568	
$P\text{-AAE}$	Slope	−0.0185	0.0111	0.33		
	Norm. Height***	0.0017	0.0521			
	Std. height***	−1.1217	0.0065			
	Land use	−0.2733	0.0978			
	Intercept	0.1194	0.8269			
	Altitude	−0.0016	<.0001			
	DDG***	0.0015	0.0886			
$P\text{-NaHCO}_3$	Wetness index	−0.1104	0.0150	0.30		
	VTR***	−16.4610	0.0236			
	Intercept	−0.5481	0.0031			
	Altitude	−0.0009	0.0004			
$P\text{-CO}_2$	Slope	−0.0197	0.0010	0.19		
	Slope length	−0.0006	0.0685			
	Intercept	0.9831	0.4531			
	Altitude	−0.0035	<.0001			
$P\text{-H}_2\text{O}$	DDG***	0.0035	0.0252	0.32		
	Land use	−0.7016	0.0165			
	Intercept	−1.0948	0.0005			
	Altitude	−0.0008	0.0237			
DSP	Slope	−0.0301	0.0003	0.54		
	DDG***	0.0020	0.0449			
	Intercept	−0.3124	1.0000			
	Land use	0.2401	0.0200			
	Altitude	−0.0013	<0.0001			
	Slope length	−0.0004	0.0472			
Curvature	24.857	0.0316				
Plan curvature	−55.692	0.0083				

* Regression coefficients (SLS) – Standard least square estimation.

** Logit transformed P forms.

*** Standardized height; vector terrain ruggedness; downslope distance gradient.

component analysis (PCA) indicated that some of the environmental predictors were highly correlated. For example, the correlation coefficient (r) between slope and altitude was 0.64. Also profile and planform curvatures were highly correlated with curvature ($r = 0.84$ and 0.90 , respectively). The PCA showed that altitude, slope, standardized height, SAGA wetness index, vector terrain ruggedness and terrain ruggedness were major contributors to the first axis of the PCA ($r = 0.70$) whereas slope length and curvature were major contributors to the second PCA axis ($r = 0.60$ and 0.81 , respectively). The multivariate analysis and PCA results suggested that only 4 (mid-slope position, planform curvature, profile curvature, and normalized height) out of 13 terrain attributes were not related and did not contribute significantly to the first two axes of the PCA (data not shown).

The step-wise multiple regression analysis for each of the P forms further reduced the number of environmental predictors (Table 4).

Table 5
Semi-variogram parameters from Regression Kriging of P forms.

P status	Semi-variogram parameters					
	Nugget- C_0	Partial sill-C	Sill- $(C_0 + C)$	Nugget/sill ratio	Range (m)	AIC
P_i	0.37	0.55	0.91	40.07	41846	−51.6
P_i	0.00	21.51	21.51	0.00	47598	214.2
P_O	0.08	2.77	2.85	2.86	50000	52.1
$P\text{-AAE}$	0.52	2.16	2.69	19.54	47598	16.0
$P\text{-NaHCO}_3$	0.36	1.12	1.47	24.27	50000	−60.3
$P\text{-CO}_2$	1.61	6.54	8.15	19.73	54643	132.3
$P\text{-H}_2\text{O}$	0.73	1.79	2.51	28.96	50000	−1.6
DSP	0.14	1.30	1.44	9.7	50000	3.6

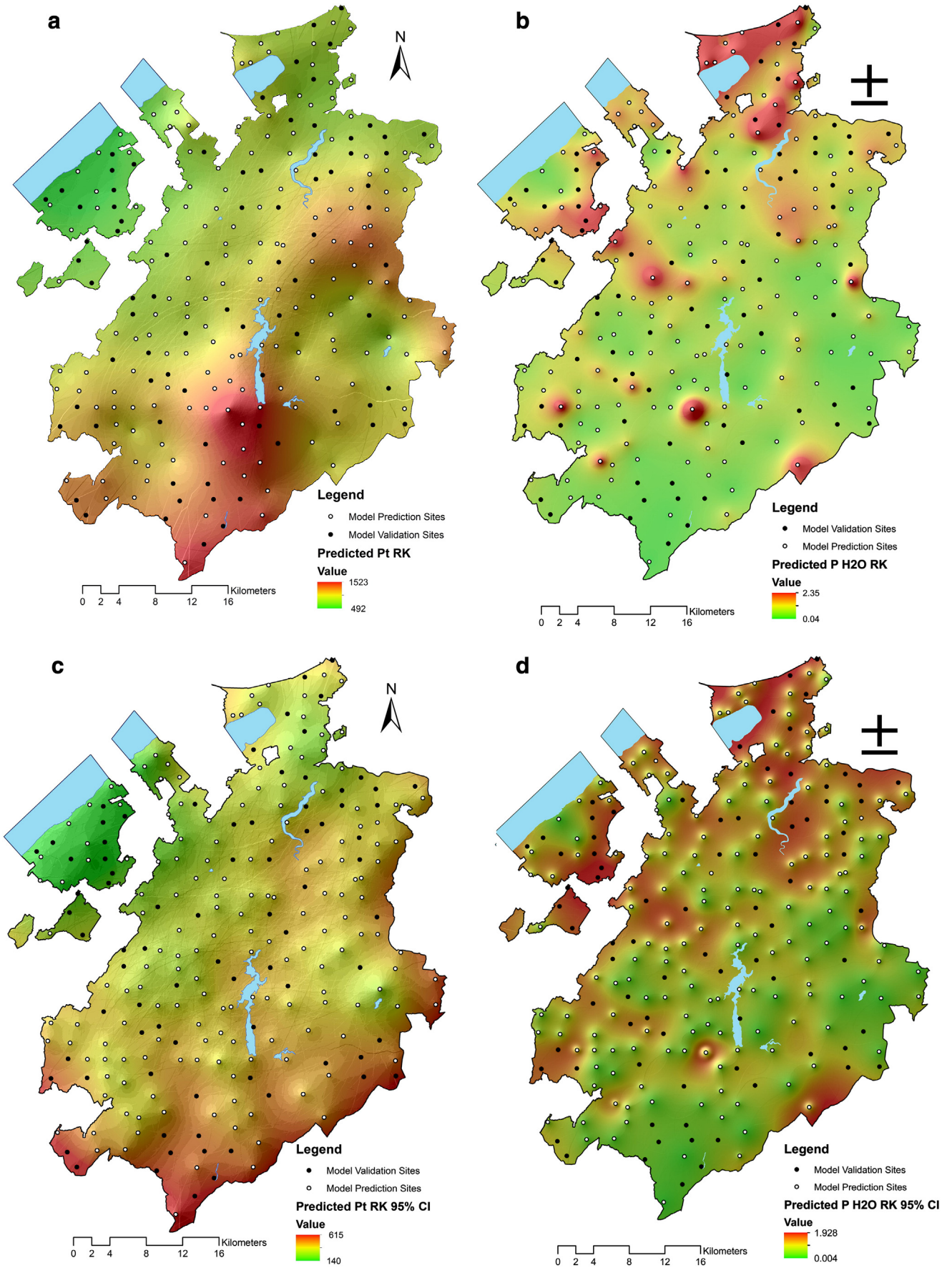


Fig. 4. Prediction maps of (a) total phosphorus (P_T); (b) available P estimated via water extraction ($P-H_2O$); (c) 95% confidence intervals of P_T and (d) 95% confidence intervals of $P-H_2O$ showing the site locations used for Regression Kriging modeling and validation.

Models with the lowest AIC were selected. The adjusted R^2 indicated that terrain attributes were the major contributors in explaining the spatial variability in various P forms ($P < 0.05$). Land use was significant only for P-CO₂ ($P = 0.01$) and DSP ($P = 0.02$). Overall, the selected environmental predictors could only explain 25% of the spatial variability in P forms and varied from 0.08 for P_T, the worst case scenario, to 0.54 for DSP, the best case scenario. The poor relationships between P forms and selected predictors points to (i) the greater influence of historical land use that may have modified these relationships, as demonstrated by other studies (Jia et al., 2011; Lemercier et al., 2008; Reijneveld et al., 2010), and/or (ii) the unsatisfactory sampling effort. Other studies have shown that the spatial distribution of P forms could also be related to geology, especially parent material (Wang et al., 2009). The use of auxiliary data, such as geology, land use or soil type, to further sub-divide the study area may improve the predictions by reducing the overall variability but better highlighting the environmental predictors–P form relationships. However, the stratification of the study area may need to be complemented by additional sampling sites in order to maintain a sizeable number of samples for spatial analysis.

3.3.2. The spatial prediction of P status using Regression Kriging (RK)

The nugget/sill ratio obtained from different P forms indicated that the spatial dependency varied from less than 1% to 41% (Table 5). Based on the scale edified by Cambardella et al. (1994), a nugget/sill ratio of less than 25% suggests a strong spatial dependency and a ratio between 25 and 75% would indicate a moderate spatial dependency whereas a value greater than 75% would indicate a weak spatial dependency. With the exception of P_T with a moderate spatial dependence and P_i with an undefined one, other P forms had a strong spatial dependence, especially P_o and DSP, which had a Nugget/Sill ratio of 2.86 and 9.7%, respectively. This result indicates that P_T was less sensitive to extrinsic factors than other P forms. To our knowledge, this is the first time that a study can identify a superior sensitivity of available form of a soil element to farming practices, as compared to the total amount of the same element. However, the wide range for all P forms (41,846–54,643 m) suggests that the autocorrelation is still present but at a coarse scale, limiting accurate predictions based on terrain attributes at finer scales such as landscape. Another interpretation of the nugget/sill ratio is the portion of the variation that one can expect to predict with the spatial model (Auerswald et al., 2009). As expected, the average nugget/sill ratio, excluding P_i, was 20%, which is comparable with the total variation (25%) explained by the multiple regression models relating environmental predictors and P forms.

Geographically speaking, the spatial distribution shows areas of high P_T values mostly south of the Gruyère Lake (Fig. 4a). Areas with the lowest P_T values appear close to Neuchâtel Lake in the northwest part of the canton. These patterns can partly be explained by partitioning of land uses within the Fribourg canton, confirming that croplands displayed the lowest P_T values. On the other hand, the distribution of available P, as revealed by P-H₂O RK, is more heterogenic and some sites strongly influence the prediction pattern (Fig. 4b). However, we can still observe a general pattern in which the northern part displays the highest values of available P and the southern part the lowest values, confirming the results of the classical statistics and the effect of land use. Moreover, the stronger heterogeneity in the distribution of available P, as compared to the one of P_T, definitely corroborates the higher sensitivity of available P to farming practices.

3.3.3. Assessing the level of uncertainty in the predicted P maps

Visual inspection of the RK model's uncertainty revealed that it was positively correlated with P values: the higher the P_T or the P-H₂O, the higher the uncertainty (Fig. 4c and d). In the case of P_T, we also observed an increasing uncertainty in the southern part of the study area due to the canton boundaries and the lack of observations outside the study area (Fig. 4c). Both Regression and OK interpolation methods performed

similarly as shown by the comparable accuracy indicator values (Table 6). The Mean Error (ME) showed a negative bias for all P forms. The Relative Root Mean Square Error (RMSEr) was greater than 70%, which indicated that the model accounted for less than 50% of the variability at the validation points, rendering the predictions unsatisfactory. As previously noted, the poor relationships between P forms and environmental predictors on one hand and the inadequate number of point observations on the other hand contributed to the weakly accurate predictions and lack of improvement from RK compared to OK. This is not entirely surprising as previous studies have shown that RK was not suitable when all the auxiliary variables could not be exhaustively sampled (Wu et al., 2010) and that generally OK performed better in agricultural lands (Zhu and Lin, 2010) or where the study area displayed a high heterogeneity of soil properties (Umali et al., 2012). Another potential explanation for this high level of uncertainty in our predictions is the non-corresponding scale of the sample location (approximately 2 km) with the one of environmental variables measurement (originally 5 m and then generalized to 15 m). We thus suggest that in the next cycles of the FRIBO network, more sampling sites should be included along with the use of a coarser DEM (maybe 25 m) in order to test for a reduced uncertainty in the prediction models.

3.3.4. Local Indicators of Spatial Association (LISA)

The results of the LISA analyses confirmed the one we obtained via RK regarding the distribution of two P-related variables (P_T and P-H₂O) but also showed some interesting perspectives on how to manage them. Indeed, in the southern part of the region, which is dominated by pasturelands, we observed several sites ($n = 12$) displaying low P_T values significantly associated ($P = 0.01$) with their direct high P_T environment (Fig. 5a, red triangles). In the same area, we also observed few sites ($n = 5$) that displayed high P-H₂O values significantly associated ($P = 0.01$) with their direct low available P environment (Fig. 5b, red circles). These particularities can be explained by the topography. The sites with low P_T values are located on very steep slopes, making the spreading of any kind of fertilizers impossible. Some sites with high P-H₂O values are almost flat and close to the farm and thus receive more fertilizers. These sites and their neighborhood have to be carefully monitored in the future because they occur in the area of the Fribourg canton with the highest slopes and the highest rainfalls (data available at <http://geo.friportail.ch>), conditions that increase the risk of erosion and leaching.

On the other hand, in the northern part of the canton, mostly composed of croplands, we observed that several sites ($n = 22$) displayed low values of P-H₂O significantly ($P = 0.01$) associated with their neighborhood qualified by high values of available P (Fig. 5b, red triangles). Rossier et al. (2012) found a significant decrease of P-CO₂ values in croplands and explained it by a reduced fertilization since the

Table 6
Accuracy assessment indicators of kriging methods for various P forms.

P forms	Kriging method	ME	RMSPE	RMSEr	St Dev.	St Err.
P _T	Regression	−126	352	106	330	37
	Ordinary	−129	342	107	319	36
P _i	Regression	−113	300	107	279	31
	Ordinary	−164	281	123	229	26
P _o	Regression	−139	254	119	214	24
	Ordinary	−36	193	101	191	21
P-AEE	Regression	−20.9	69.2	104	66.4	7.4
	Ordinary	−24.1	64.9	107	60.6	6.8
P-NaHCO ₃	Regression	−18.8	28.4	132	21.4	2.4
	Ordinary	−19.1	28.7	133	21.5	2.4
P-CO ₂	Regression	−0.6	2.7	102	2.6	0.3
	Ordinary	−0.8	2.3	106	2.2	0.2
P-H ₂ O	Regression	−0.29	0.64	111	0.58	0.06
	Ordinary	−0.30	0.64	113	0.57	0.06
DSP	Regression	−2.88	11.28	114	9.94	1.10
	Ordinary	−2.71	10.64	115	9.25	1.03

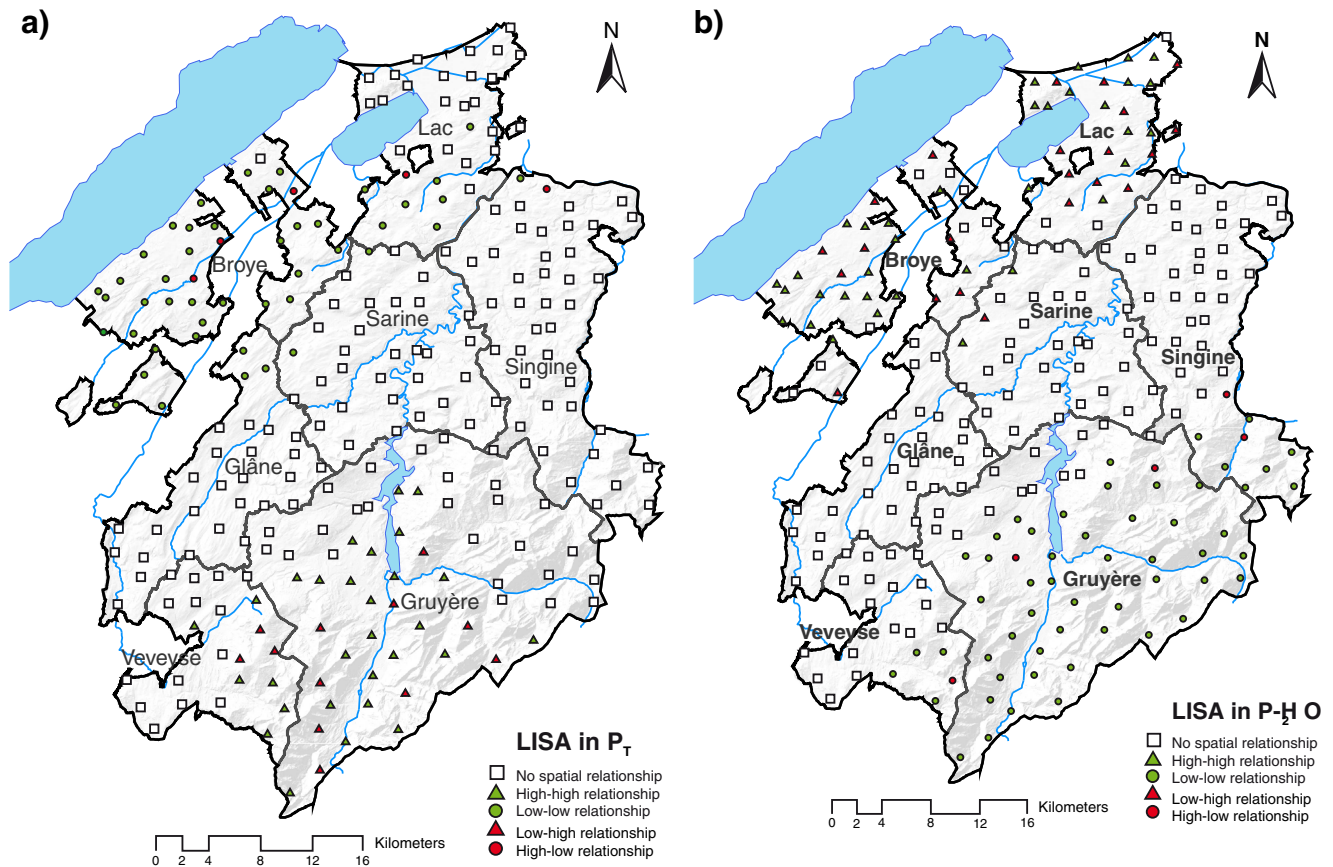


Fig. 5. Local index of spatial autocorrelation (LISA) for P_T (a) and $P-H_2O$ (b).

introduction of direct payments for ecological programs, such as integrated production in 1993 by Swiss government. This phenomenon is not happening in permanent grasslands and in mixed dairy-crop farms because in these areas the number of livestock is increasing as well as the amount of manure spread on the land.

4. Conclusions

Overall, we observed large variations of different P forms (total, organic and available) in the agriculture soils of Fribourg canton. Our results suggest that the difference of P forms among the 245 sites is related to farming practices, especially land use. Croplands have the lowest quantity of total P but the highest quantity of available P, with a very high DSP. Permanent grasslands harbored both high total and available P, and mountain pastures revealed a high total amount of P but low P availability and DSP. The poor performance of terrain attributes in spatially predicting various P forms indicates the overwhelming influence of land use practices and highlights the need for more geo-referenced observation points. The kriging interpolations were based on 165 points only (or approximately one observation point per 10 km²) which, given the general high relief characteristics of the Fribourg canton and diverse land use, did not adequately capture the relationships between terrain attributes and P forms distribution observable at finer scales, such as slope and landscape scales. However, the fact that available P appeared much more sensitive to extrinsic factors than total P is encouraging since P pollution is mainly due to leaching of available P in the soil solution. Lowering available P levels in agricultural soils seems feasible but would require better knowledge of the P status and

controlling variables such as parent material, soil types and terrain attributes.

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