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Nitrogen and phosphorus fractions as indicators of organic soil quality

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The state of the environment is currently evaluated by indicators of air and water quality. Sustainable land use requires an assessement of soil quality. Soil quality indicators should relate soil processes to management practices. The supply of N and P contributes to crop productivity, but can degrade air and water quality. In this paper, we will present organic soil N and P attributes that can make up soil functions. Nitrate was the only detected mineral N form in organic soil materials with pH (0.01M $CaCl_2$) exceeding 4.4. Lowest C/N ratio of cultivated sapric soil materials was 15, showing high nitrate-supplying capability. Total P concentration was between 760 and 1960 mg P kg^{-1} both in organic and inorganic forms when pH (0.01M $CaCl_2$) increased above 4.7, the recommended minimum pH value for cultivated organic soils. Lowest C/P ratio as organic forms was 340 for sapric materials containing less than 22% ash, indicating organic P sequestration capability (C/P > 300). However, the low N/P ratio of 23 (i.e. 340/15) also indicated capability for organic P availability to plants. Since N and P are related to organic matter transformations, the C/N/P/S multiratios of selected organic matter fractions, analyzed as compositional data (computation procedure presented), need further consideration as integrated N and P attributes in combination with pH and climatic indexes, in order to adapt N and P diagnosis and recommendation models to specific organic soil agroecological zones.

Key words: Soil quality indicators, nitrification, phosphorus fractionation, pH, C/N/P/S ratio

INTRODUCTION

The state of the environment is evaluated by indicators of air, water and soil quality. Air and water quality have received considerable attention in relation to global climate as well as human and animal health. According to Doran and Parkin (1994), soil quality is the capacity of a soil to function within ecosystem boundaries to sustain biological productivity, maintain environmental quality, and promote plant and animal health. Soil quality indicators should encompass ecosystem processes, be amenable to modelling, integrate soil properties and processes, and be user-friendly, easy to measure in the field, sensitive to changes in management and climate, and, as far as possible, obtained from existing data bases (Doran and Parkin, 1994). They must lead to scientificallysound, long-term sustainable solutions for specific soil management units within a given agro-ecological zone, and facilitate the decision-making process at various spatial and temporal scales of intervention.

Ammonium-ammonia contamination of surface waters and nitrate contamination of surface and ground waters are considered at risk to the environment. However, peat acids have a high ammonia-sorption capacity that would minimize ammonium-ammonia contamination risks (Vaillancourt et al., 1999). Phosphate is an important contributor to surface water eutrophication. In Ontario, phosphate discharges originate mainly from agricultural fields, including cultivated organic soils (Miller, 1979). A soil P saturation approach effectively assessed P contamination risk and probability of crop response to P fertilizers in Canadian acid light-textured soils (Khiari et al., 2000). In several Canadian organic soils, the P saturation concept could hardly be applied since inorganic phosphate is chemically retained to a small extent (Parent and MacKenzie, 1985).

Organic soils differ from mineral soils in many other respects, such as higher organic matter content and porosity, lower bulk density and optimum pH for plant growth, and more rapid transformation rates after drainage and cultivation. The organic soil function regarding water regulation and accumulation degrades irreversibly with entry of oxygen in the soil profile as a result of drainage and cultivation (Pons, 1960). Crop productivity is also enhanced as soil chemical and biological properties are improved by liming acid organic soils to optimum pH levels (Lucas and Davis, 1961). Soil N and P transformations are closely related to soil C evolution (Stevenson, 1986). Soil sequestration capacity for N and P must change with increased aeration and pH, as enhanced biological activity promotes C loss and peat humification.

Our objective was to examine, in existing soil datasets from eastern Canada, N and P fractions that are sensitive to pH changes, and to select sensitive soil quality attributes for monitoring N and P environmental risks.

MATERIAL AND METHODS

The following chemical analyses were performed on air-dried soils as standard procedure. Compared to field-moist conditions, proportion of inorganic P in labile forms may be enhanced in air-dried soils, and proportion of organic P in labile forms may be reduced. Despite differences in sampling times during the growing season, leading to soil mineral N differences attributable to plant uptake and nitrification, it was assumed that proportions of amonium and nitrate was little affected by the sampling period. No N or P fertilizers were added as treatments. No rock phosphate had been applied to the soils.

The N dataset

Twenty-four air-dry surface soil samples (0–15 cm) were obtained from a collection of virgin or cultivated organic soils from four eastern Canadian provinces (Table 1) (Parent, 1984). There were eight samples each of fibric, hemic and sapric peat materials. The pH was measured in a 0.01 M $CaCl_2$ solution using a 1:2 (mL:mL) soil:solution ratio (Van Lierop, 1981). Ash content was determined by loss on ignition (LOI) by burning soil samples at 550 °C during 16 h in a mufle furnace. Total C was computed as LOI times C content of peat for a given decomposition degree (Naucke et al., 1990). Total N was determined by micro-Kjeldahl digestion followed by steam distillation (Bremner, 1965a). The C/N ratio was computed as total C divided by Kjeldahl-N.

Soil samples were extracted with 2 M KCl (Bremner, 1965b), and determined colorimetrically for ammonium and nitrate using a Technicon Auto-Analyzer II (1977). Since initial soil conditions and time of sampling may affect NH_4^+ and NO_3^- levels in the soil, we used the proportion of mineral N as NH_4^+ and NO_3^- as nitrification index. Doing so, the ammonium percentage was the additive inverse of the nitrate percentage.

The P dataset

Twenty-four air-dry sapric surface soil materials were collected from cultivated organic soils in southwestern Quebec (Sasseville, 1991). Three surface soil samples were also obtained from a lime experiment on a newly broken acid organic soil in central Quebec (Sasseville, 1991). Agricultural lime was incorporated in the 0–15 cm surface layer at rates of 0, 6 and 12 t $CaCO_3$ ha^{-1} using a rototiller. Soil samples were collected in the 0–20 cm layer three years after lime had been applied. The 27 soil samples were fractionated for P, excluding the ultra-sonification extraction step, according to Wagar et al. (1986) (Table 2).

The six P fractions were as follows: resin-P, inorganic $NaHCO_3$-P, organic $NaHCO_3$-P, inor-

Table 1. Chemical properties of 24 surface Eastern Canadian peat materials used to define N functions.

Sample ¥	C/N ratio	Kjeldahl-N %	pH (0.01 M $CaCl_2$)	Ash content %	NH_4-N § %	NO_3-N § %
Fibric peat materials						
1 : V_1	82	0.6	3.0	1.8	100	0
2 : V_2	43	1.1	3.2	2.6	100	0
3 : V_3	49	1.0	2.6	1.6	100	0
4 : V_3	37	1.2	2.7	3.6	100	0
5 : V_4	44	1.0	3.4	4.2	96	4
6 : C_2	36	1.1	5.7	12.4	0	100
7 : C_2	30	1.3	5.8	13.2	0	100
8 : C_1	39	1.1	5.2	9.1	0	100
Hemic peat materials						
9 : V_3	29	1.8	2.7	2.0	86	14
10 : C_4	31	1.4	5.7	9.7	0	100
11 : C_4	28	1.5	5.9	13.6	0	100
12 : C_3	27	1.8	4.8	9.1	0	100
13 : V_3	21	2.3	3.2	9.6	90	10
14 : C_3	19	2.4	3.7	7.5	57	43
15 : C_3	22	2.2	3.8	6.5	39	61
16 : C_3	26	1.9	4.2	7.8	43	57
Sapric peat materials						
17 : C_3	21	2.2	4.5	10.1	0	100
18 : C_3	18	2.4	5.0	14.2	0	100
19 : C_3	15	2.8	5.1	17.4	0	100
20 : C_3	16	2.6	5.1	18.2	0	100
21 : C_3	18	2.4	5.3	14.9	0	100
22 : C_3	16	2.6	5.4	18.1	0	100
23 : C_3	20	2.1	6.3	18.6	0	100
24 : C_3	16	2.5	6.0	18.5	0	100

¥ V = virgin and C = cultivated ; numerical indexes : 1 = New-Brunswick, 2 = Newfoundland, 3 = Quebec and 4 = Nova Scotia

§ Proportion of mineral N (NH_4-N + NO_3-N) in percentage ganic NaOH-P, organic NaOH-P, and residual or HCl-P. For each fraction, organic P was computed by difference between total P and inorganic P. Total soil P was determined after soil dissolution in a perchloric-nitric acid mixture. Phosphate concentration in solutions was determined colorimetrically (Murphy and Riley, 1962). Comparing the sum of individual P fractions to total P extraction, the average P recovery was 99% (95–102%). Total soil organic P was computed as the sum of individual organic P fractions. The C/P ratio was computed as total C divided by total organic P. The easily available P is made up of the resin and $NaHCO_3$-P fractions. The NaOH-P fractions are considered moderately available. The residual P fraction was assumed sequestered in humus.

Statistical analysis

Soil N and P attributes were related graphically to pH and partitioned using the Cate-Nelson procedure (Nelson and Anderson, 1984). The P fractions were expressed on a soil weight basis or as row-centred log ratios for compositional data (Aitchison, 1986). That procedure adjusts each

Table 2. Chemical analyses of 27 surface organic soil materials from eastern Canada used to define P functions.

Sample no.	pH (0.01) M $CaCl_2$	Ash	Resin P	$NaHCO_3$ P_i	$NaHCO_3$ P_o	NaOH P_i	NaOH P_o	Residual P	Total P
		%	mg kg^{-1}						
Survey soils									
1	5.74	22.3	144	146	199	382	366	723	1960
2	4.80	20.4	33	6	79	241	244	577	1180
3	6.58	66.9	19	83	142	121	172	583	1120
4	5.55	10.4	131	0	85	11	182	571	980
5	4.09	8.9	161	0	282	16	156	145	760
6	4.96	8.9	199	86	77	45	166	507	1080
7	4.72	7.8	105	0	18	0	38	339	500
8	6.69	16.9	105	299	369	230	227	550	1780
9	4.07	7.6	146	23	159	90	19	63	500
10	6.02	16.2	170	191	195	334	109	541	1540
11	5.43	16.3	170	86	72	207	140	425	1100
12	5.90	15.3	139	116	114	331	402	778	1880
13	5.42	13.1	122	59	53	62	222	402	920
14	4.88	8.5	201	15	107	23	187	466	999
15	6.07	22.7	222	138	62	74	22	348	1066
16	5.90	13.9	127	56	87	182	53	211	716
17	5.68	11.0	225	161	99	124	192	268	1069
18	4.66	7.3	185	10	101	12	146	54	508
19	5.65	12.7	99	75	115	275	427	680	1671
20	5.37	13.1	214	78	93	62	191	511	1149
21	4.42	7.8	65	8	121	18	59	104	375
22	4.64	9.3	90	0	56	41	44	149	380
23	6.36	54.8	74	161	81	286	310	600	1512
24	5.57	41.0	132	125	120	316	311	609	1613
Lime experiment soils									
0 t ha^{-1}¥	3.4	9.9	77	33	70	46	133	245	604
6 t ha^{-1}	4.7	16.0	154	114	48	68	185	409	978
12 t ha^{-1}	5.9	13.7	120	197	51	71	264	467	1170
	Polynomial trend §		Q	L	L	NS	L	L	L

¥ t $CaCO_3$ ha^{-1}

§ Q, L, NS : quadratic, linear and nonsignificant, respectively (Parent et al., 1992) fraction F_n to geometric mean G of the six P fractions mentioned above as follows:

$$G = \prod_{n=1}^{6} (F_n)^{1/6} \quad (1)$$

$$V_{F_n} = \log(F_n / G) \quad (2)$$

Relationships between P pools were described by principal component analysis of row-centred log ratios of P values in each compartment (SPSS Inc., 1996). Only eigenvectors showing eigenvalues greater than 1.0 were varimax-rotated. The P pools were illustrated graphically from factor loading plot.

RESULTS AND DISCUSSION

The N function

Ammonium represented most of the mineral N in the surface layer of organic soils at pH values below 3.6 (Fig. 1). Little nitrate was present below pH 3.6. A shift from ammonium to nitrate occured above pH 3.6 (Fig. 1). Between pH 3.6 and pH 4.4, both ammonium and nitrate were present in similar proportions. Above pH 4.4, only nitrate accumulated in soil. In cultivated organic soils, a critical water pH value of 5.4 is targetted for growing agricultural crops (Van Lierop, 1982), i.e. 4.7 after conversion to pH (0.01 M $CaCl_2$) (Van Lierop, 1981).

Nitrate and pH can be assessed using field methods. However, describing spatial distribution of organic N transformations across large areas of organic soils would be an unaffordable task. Since soil moisture and temperature influence rate of organic matter transformations (Browder and Volk, 1978), water and heat balance indexes as assessed by agrometeorological and remote-sensing methods would also be useful to incorporate into the N function. A minimum set of soil attributes such as soil pH and nitrate level, as well as climatic attributes, coupled with a cost-effective data collection strategy, is needed to monitor the N function of nitrification at field and subfield levels, adapt N inputs to soil nitrate accumulation, implement practical solutions, and agrade soil, air and water quality related to N.

The P function

Since organic P accounts for 67–75% of total P in organic soils (Parent et al., 1992; Koch-Rose et al., 1994), P sequestration would be primarily related to soil biological capability to convert inorganic P into stable organic P. Total P concentration in our organic soils varied from 716 to 1960

Table 3. Soil P fractions and their row-centred log ratios in contrasted pH (0.01 M $CaCl_2$) groups below and above 4.7 (mean ± standard error).

P form	Amount in surface soil (0–15 cm) mg kg^{-1}		Row-centred log ratio (0–15 cm) unitless	
	pH < 4.7	pH > 4.7	pH < 4.7	pH > 4.7
Resin P (inorganic)	118 ± 14	140 ± 14 ns	0.40 ± 0.08	–0.07 ± 0.08 **
$NaHCO_3$ inorganic P	11 ± 4	110 ± 18 **	–0.96 ± 0.16	–0.31 ± 0.11 **
$NaHCO_3$ organic P	115 ± 26	112 ± 18 ns	0.30 ± 0.08	–0.17 ± 0.05 **
Easily available P ¥	245 ± 35	362 ± 35 **	-	-
NaOH inorganic P	32 ± 9	172 ± 30 **	–0.39 ± 0.14	–0.08 ± 0.07 **
NaOH organic P	85 ± 17	218 ± 26 **	0.18 ± 0.10	0.11 ± 0.07 ns
Moderately available P §	116 ± 16	391 ± 49 **	-	-
Residual P (organic)	157 ± 31	511 ± 36 **	0.47 ± 0.13	0.53 ± 0.05 ns
Total P	518 ± 40	1274 ± 89 **	-	-

¥ Sum of resin-P and $NaHCO_3$-P fractions

§ Sum of NaOH fractions

ns. *. **: difference in P form between two pH groups under same heading not significant or significant at the 0.05 or 0.01 levels, respectively

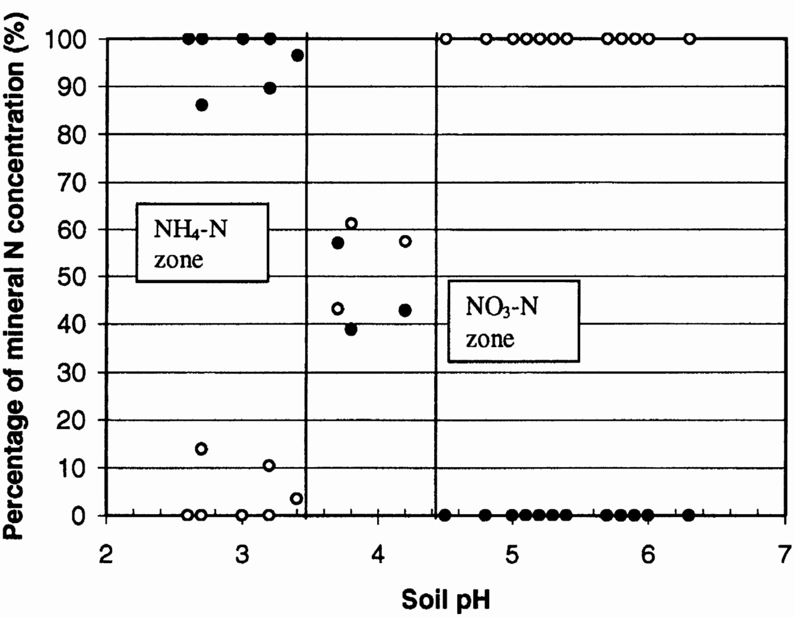

Fig. 1. Ammonium and nitrate percentages of mineral N in relation to pH (0.01 M $CaCl_2$) in organic soil surface materials.

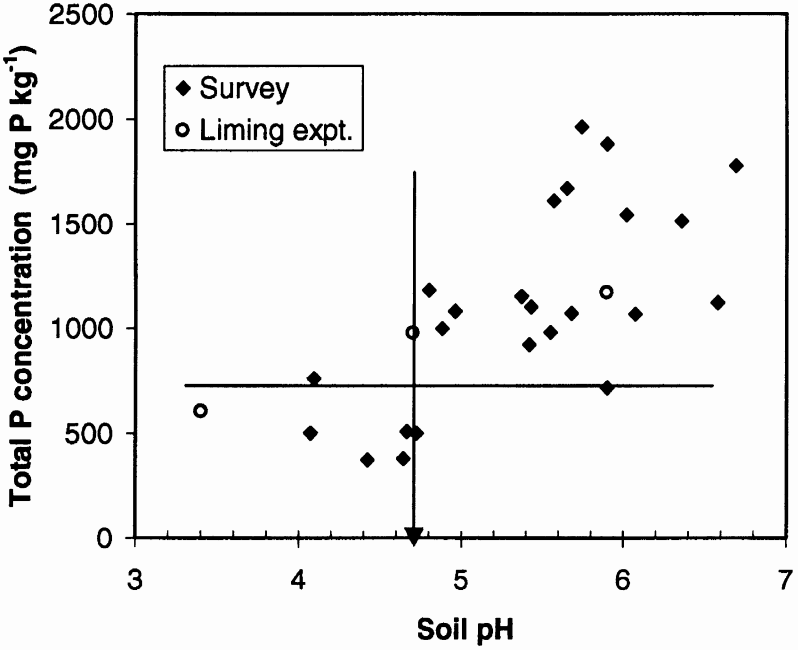

Fig. 2. Critical pH (0.01 M $CaCl_2$) for total P concentration in Quebec organic soils (lime experiment as empty dots to show the trend for an initially uniform soil receiving same amount of P fertilizers and grown the same crop).

mg P kg^{-1} when soil pH increased above 4.7 (Fig. 2). Most cultivated organic soils already have pH values exceeding 4.7, as recommended by public agencies (Van Lierop, 1982).

As shown in Table 3, all P fractions except resin-P and $NaHCO_3$ organic P significantly increased when pH increased above 4.7. Concomitantly, proportions of resin-P and $NaHCO_3$ organic P fractions decreased, and that of $NaHCO_3$ and NaOH inorganic P fractions increased. The largest pools of organic P (NaOH organic P and residual P) did not change their proportions. Correspondingly, principal component analysis retained two eigenvectors with eigenvalues > 1.0 (Table 4). In the first eigenvector, resin-P and $NaHCO_3$ organic P loaded positively, and both $NaHCO_3$ and NaOH inorganic P fractions, negatively. In the second eigenvector, the $NaHCO_3$ and NaOH inorganic P fractions loaded negatively, and both NaOH organic P and residual P, positively. As a result, there were three groups of P pools (Fig. 3): rapidly available P (resin-P and $NaHCO_3$ organic P), rapidly to moderatly rapidly available inorganic P ($NaHCO_3$ and NaOH inorganic P), and slowly available organic P (NaOH organic P and residual P). Pool competition for P was assumed whenever loadings showed opposite signs in the same eigenvector.

As a result, resin-P and $NaHCO_3$ organic P pools feeding solution P would be replenished by $NaHCO_3$ and NaOH inorganic P pools. The $NaHCO_3$ organic P pool would be a transitory pool. Soil capability to incorporate inorganic P into moderately or slowly available organic P pools must be controlled by microbial and enzyme activities. In addition to soil test P measuring $NaHCO_3$-P pools, microbial P and phosphatase activity, as well as climatic factors as mentioned previously, could be combined in a soil P function describing mineralization of organic P, and incoporation of labile inorganic P into more stable organic P pools.

C/N, C/P and N/P ratios

Dual ratioing is the minimum transformation procedure for properly classifying compositional data, i.e. with a bounded-sum constraint of 100% (Aitchison, 1986). Nutrient dual ratios are often related to soil processes such as organic matter accumulation or mineralization. In particular, organic C, N, P and S are constituents of soil organic matter (SOM) that can be diagnosed as ratios for supporting interventions in specific organic soil management units.

Among soil key properties, the C/N ratio is indicative of the amount of organic N that can be mineralized in organic soils during a growing season (Kaunisto and Aro, 1996). Minimum C/N ratio for net N mineralization is generally assumed to be 25 (Stevenson, 1986). The C/N ratio in eastern Canadian peat soil materials was related to pH (Fig. 4) and soil management. For cultivated sapric materials, the C/N ratio varied between 15 and 21 (Table 1). The minimum C/N ratio of 15–16 was in keeping with average C/N ratios of 15–17 for cultivated cutover peatlands in Russia (Kreshtapova and Krupnov, 1998). The C/N ratio of sapric materials was higher than in acid mineral soils, which showed typical values between 10 and 13 with an average of 12 (Walker and Adams, 1958).

Organic C to P ratio is indicative of soil capability to accumulate organic matter (Walker and Adams, 1958) and to sequester P in SOM (Stevenson, 1986). According to Stevenson (1986), there would be no gain or loss of P with C/P ratios between 200 and 300. Above 300, soil solution must give up P to the microbes. In the lime experiment, C/P ratio of SOM decreased from 965 to 628 and 530 with liming rates of 0, 6 and 12 t ha^{-1}, respectively. The C/P ratio in SOM of organic soil materials containing less than 22% ash tended toward a value of 340, but decreased under 300 when ash content increased above 22% (Fig. 5). Hence, organic soils would favor organic P sequestration. In 21 New-Zealand acid mineral soils, organic C/P ratios averaged 60, varying between 34 and 111 (Walker and Adams, 1958). As a result, competition between plant and soil microbes would be greater in organic compared to mineral soils. However, crop response to P fertilizer is often insignificant in high-P cultivated organic soils even after 3–4 years of cropping without any P fertilizer application (Minotti and Stone, 1988). Organic P mineralization could be

Table 4. Varimax-rotated loadings describing the main P pools in organic soils.

P pool	Factor (1)	Factor (2)
	Rotated loadings	
Resin-P_i	0.873	0.032
$NaHCO_3$-P_o	0.809	–0.065
$NaHCO_3$-P_i	–0.619	–0.589
NaOH-P_i	–0.583	–0.497
NaOH-P_o	–0.052	0.858
Residual-P_o	0.074	0.848

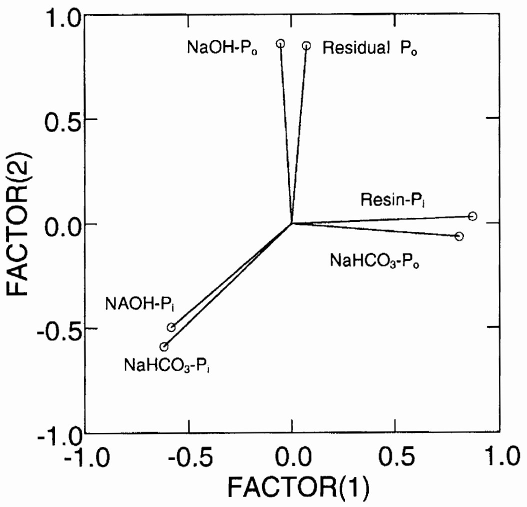

Fig. 3. Factor loadings plot for P fractions in organic soils.

significant during the season in cultivated organic soils. Indeed, proportion and concentration of the labile $NaHCO_3$ organic P fraction decreased as pH increased (Parent et al., 1992), indicating unstability of that fraction. The C/P ratio of each organic P fraction should be further investigated in relation to organic P mineralization potential, especially for the labile $NaHCO_3$ organic P pool. Rates of immobilization-mineralization reactions should also be determined.

Considering that surface sapric materials cultivated for many decades reached a C/N ratio of 15 and a C/P ratio of 340, the long-term N/P ratio should be 23 (C/P divided by C/N or 340/15) in those highly humified materials, compared to 25 to 50 in Finnish reforested cutover peats (Kaunisto and Aro, 1999). If microbial activity releases N and P from organic materials in the same ratio as they exist in the material (Kaunisto and Aro, 1996), and if mineralized N averages 425 kg N ha^{-1} per cm of organic soil subsidence by biological oxidation (Tate III, 1987), organic pools could release 21 kg P ha^{-1} (i.e. 425/23) per cm of subsidence in cultivated sapric materials. Depending on subsidence rate, more P than predicted from soil test P alone may become rapidly available to the crop. Hence, in topsoil sapric materials showing C/N ratios less than 25, the N/P ratio could be combined with subsidence rate in order to assess N and P release potential from SOM pools. Interestingly, $NaHCO_3$ extraction procedures have been proposed to assess both P (Wagar et al., 1986) and N (Fox and Piekielek, 1978) availabilities in soils.

C, N and P multiratios

Since organic C, N and P pools must be involved simultaneously in the fertility of drained organic soils and their degradation processes, the C/N/P ratio in soil organic fractions could be a more valuable attribute for N and P release or sequestration capabilities of organic soils, compared to C/N, C/P or N/P ratios taken alone. The C/N/P/S ratio would even be more meaningful for diagnosing organic matter transformations by soil microbes (Stevenson, 1986). The statistical analysis of such multiratios poses a mathematical problem that can be solved using compositional data analysis (Aitchison, 1986). Any P percentage in a SOM pool also analyzed for C, N and S must be transformed as follows, similarly the calculation procedure shown in Eq. 1 and 2:

$$R = 100\% - \%C - \%N - \%P - \%S \qquad (3)$$

where R is the filling value between 100% and percentages of C, N, P in the organic soil fraction examined for compositional data summing up to 100%. The R value closes the calculation system to 100%. The geometric mean of those proportions is computed as follows:

$$G = (C \times N \times P \times S \times R)^{0.2} \qquad (4)$$

The P variable V_P is a row-centred log ratio computed as follows:

$$V_p = \log(P/G) \qquad (5)$$

The C, N and S variables are computed similarly. The P variable V_P and the N variable V_N are the diagnostic variables to be related to release or immobilization rates of inorganic P and N fractions in organic soils. In the calculation procedure shown above, each variable was corrected for C, N, P and S levels in the organic soil fraction by dividing by the geometric mean of those components. Correspondingly, datasets must include complete elemental analyses (C, N, P, S) in or-

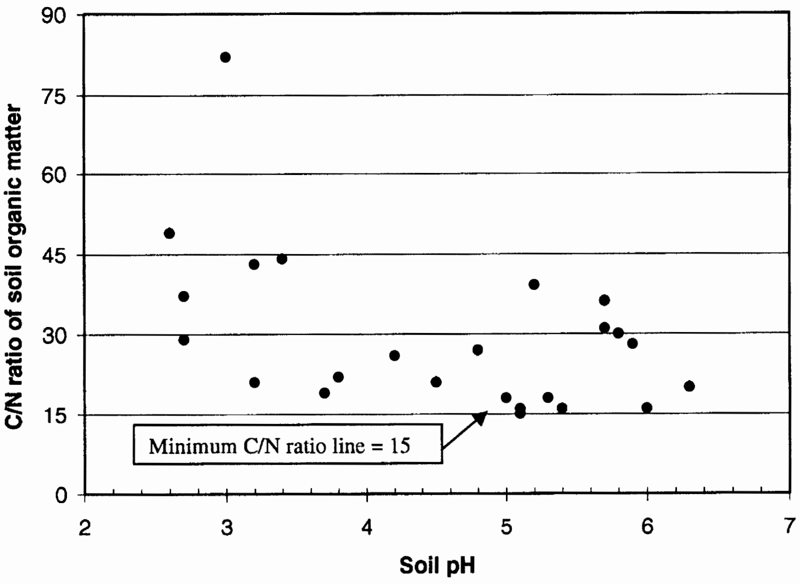

Fig. 4. Relationship between C/N ratio of soil organic matter and pH (0.01 M $CaCl_2$) in organic soil surface materials.

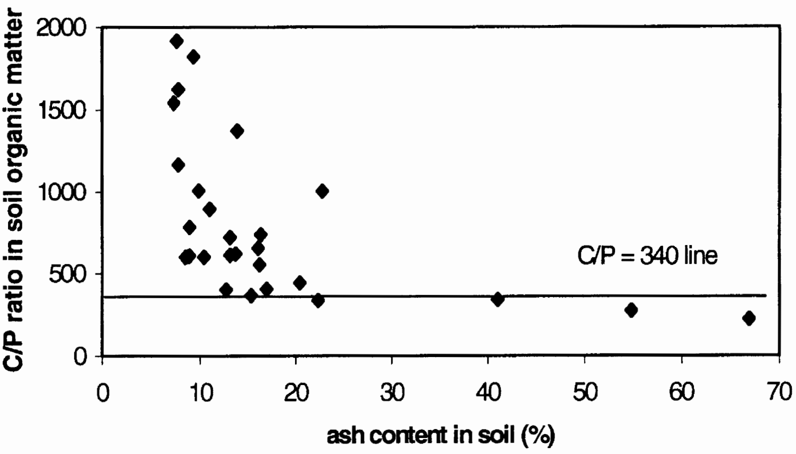

Fig. 5. Relationship between C/P ratio of soil organic matter and ash content in organic soil surface materials.

ganic soil fractions, which unfortunately was not the case in the presented datasets (Tables 1 and 2).

CONCLUSION

Soil quality indicators for N and P defining the state of the environment in organic soil agroecosystems must be easy to monitor. Sensitive attributes were shown to be pH, nitrate level, the P-extractable $NaHCO_3$ fractions, and, possibly, microbial P. With regard to the predominance of N and P organic pools and their usual computation as C/N, C/P and N/P ratios, the validity of the C/N/P/S ratio should be more closely examined as a compositional system analysis for diagnostic purposes. Organic soil quality indicators should help resource managers minimizing the environmental impact of agricultural practices on water and air quality over large areas, while sustaining the agricultural production on organic soils. Diagnosis of soil attributes and functions for N and P should be transferable to similar agroecological zones across the world.

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