

Compositional analysis of phosphorus pools in Canadian Mollisols

D. ABDI^{1,2}, N. ZIADI² and L-É. PARENT¹

¹ERSAM, Department of Soil and Agri-Food Engineering - Laval University, Quebec, Canada,
dalel.abdi.1@ulaval.ca; leon-etienne.parent@fsaa.ulaval.ca

²Agriculture and Agri-Food Canada - Soils and Crops Research and Development Centre, Quebec,
Canada. Noura.Ziadi@AGR.GC.CA

During cultivation, the internal phosphorus cycle of Mollisols (Chernozems) of the Canadian Prairies is perturbed by crop sequences including wheat phases, tillage practices, and regular applications of fertilizers. To monitor these changes, a proximate sequential phosphorus (P) fractionation procedure was developed by Hedley et al. (1982) to extract inorganic and organic P fractions as very labile (resin-P), labile ($\text{NaHCO}_3\text{-P}$), slowly available (NaOH-P), and very slowly available (HCl-P) pools. Models used so far to monitor P pools do not address the interactive behaviour of P fractions constrained to a closed compositional space. Compositional data analysis using isometric log ratio (*ilr*) coordinates is appropriate for modelling the interactive P pools using sequential binary partitions of P pools. Our objective was to model changes of P pools in Mollisols in response to management and time using *ilr* coordinates. We used a dataset with treatments and another where a Mollisol was analyzed at time zero and 4, 65, and 90 yr after sod breakup. Seven P fractions were assigned to P reactivity groups to compute six *ilr* coordinates. The *ilr2* contrasting inorganic (geochemical) and organic (biological) P pools and *ilr4* between the most readily available and less P bioavailable pools were the most sensitive to crop sequence and fertilization. Using composition at time zero as reference, the Aitchison distance reached a plateau after the 4th year in the Bm horizon compared to continuous change in the Ah horizon. Time changed the P balance of cultivated Mollisols primarily in the inorganic vs. organic P pools. The risks of yield loss and environmental damage can be minimized using soil tests that quantify the rapidly bioavailable inorganic P pools and crop management strategies that promote biological P pools.

1. Introduction

Mollisols (Chernozems) form an important soil group used for large scale grain production in the Canadian Prairies. They are naturally fertile soils well supplied with plant nutrients such as phosphorus. These soils have been perturbed by tillage practices and applications of phosphatic fertilizers and manure P. As a result, soil and crop management influenced the internal soil P cycling of Mollisols. Phosphorus fractionation procedures can quantify the P pools likely to change slowly or rapidly in soils under perturbation.

Hedley et al. (1982) proposed a sequential extraction procedure to chemically assess the availability of soil organic and inorganic P forms. Cross and Schlesinger (1995) classified the Hedley et al. (1982) interactive P pools into rapidly plant-available (resin-P and $\text{NaHCO}_3\text{-P}$) and refractory (NaOH-P , sonic P, HCl-P , and residual P) pools. The oxalate-extractable P (P_{ox}) estimates the inorganic P accumulation from fast and slow reactions with iron (Fe_{ox}) and aluminium (Al_{ox}) hydroxides (Lookman et al., 1996). Inositol phosphates that may account for more than 50% of soil organic P may also react with Fe and Al compounds in soils (Shang et al., 1990, 1992; Celi et al., 1999). Refractory and residual P pools contribute little to soil P cycling at time scale required for soil management. Since organic P usually declines in soils following cultivation (Stevenson, 1986)

chemical fractionation can assess long-term change in P pools in response to land use or soil management (Frossard et al., 2000).

Raw soil P fractions have been used to describe P distribution and model P dynamics in soils in state-space (Shuai and Yost, 2004), path (Tiessen et al., 1983), variance, regression and correlation analyses (e.g. McKenzie et al., 1992; Tiessen et al., 1984). Compositional data such as raw P fractions have severe limitations for linear modelling since they are constrained to a close space of strictly positive data spoiled by redundancy and spurious correlations. Gaussian laws cannot be applied to those data since it is impossible to obtain analytical data less than zero or more than 100%. For these reasons, P pools bear relative information about pool exchange processes. Raw P concentration data must be log ratio transformed before analysis by linear statistical procedures conceived for the real space made of both negative and positive values (Aitchison, 1986).

Isometric log ratio (*ilr*) transformation with orthonormal bases are sequential binary partitions (SBP) of compositional data (Egozcue and Pawłowski-Glahn, 2005). For D phosphorus fractions, there are $(D-1)$ SBP's. The conceptual model of Tiessen et al. (1984) shows mass exchange among P pools. A conceptual framework for binary partitions includes partitions between rapidly and slowly bioavailable P pools (Hedley et al., 1982) and between geochemical (inorganic) and biological (organic) P pools (Cross and Schlesinger, 1995). The Aitchison distance can be computed across *ilr* coordinates as a distance between perturbed and reference compositions.

The objective of this study is to present the conceptual model that describes relationships among soil P pools and to decompose these relationships into sequential binary partitions and *ilr* coordinates. Time and treatment variations in P pools are analyzed using datasets on the effect of crop sequence and fertilization on P pools and on time change in P pools in two Mollisols of the Canadian Prairies.

2. Material and methods

McKenzie et al. (1992) fractionated soil P in dryland grain crop sequences (continuous wheat, wheat-fallow and wheat-wheat-fallow) on a Lethbridge sandy clay loam (Calcereous Dark Brown Chernozem) given nitrogen and/or phosphorus fertilizers for 14 to 19 years. On the other hand, time change in P pools balance was modelled by Tiessen et al. (1983) in a Blaine Lake silt loam (Orthic Black Chernozemic) following chronosequence starting with native prairie (time zero) over 4-, 60- and 90-years of crop sequences.

The P pools were quantified using a modified Hedley et al. (1982) procedure. Sonic P pools that account for a small fraction of total P pools were amalgamated with their respective P pools. Residue inorganic and organic P pools that are undefined P pools were amalgamated into a single residue P pool. A modified Tiessen et al. (1984) conceptual model relating P pools is presented in Figure 1. There geochemical and biological P pools (Cross and Schlesingere, 1995) can be partitioned into slowly and rapidly bioavailable P pools (Hedley et al., 1982). Residue P represents the slowly bioavailable P pools as illustrated in Tiessen et al. (1984). The main P pools for partitions were thus the geochemical, biological, and residue P pools. The first sequential binary partition (SBP) was between residue P and other P fractions (Table 1). The second partition was between the geochemical and biological P pools. In the geochemical pool, there was only one unidirectional transformation, the one from primary minerals to solution P, leading to the third partition. Other P pools are bidirectional between rapid or slow geochemical or biological species (Figure 1).

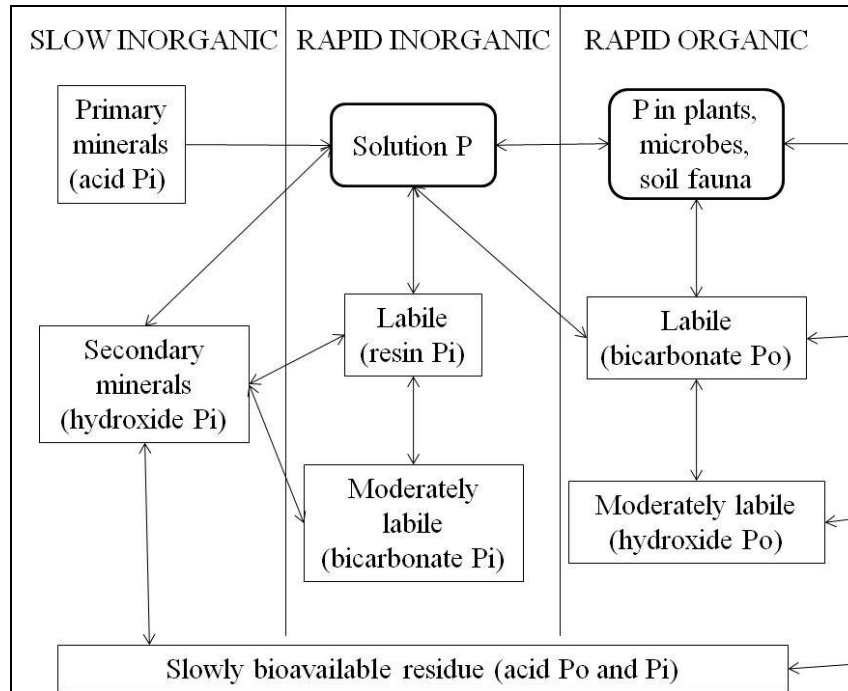


Figure 1: Conceptual relational model between P pools in Mollisols (modified from Tiessen et al., 1984).

<i>ilr</i>	Inorganic P				Organic P		Residue	<i>r</i>	<i>s</i>	Balance coefficient
	Resin	NaHCO ₃	NaOH	H ₂ SO ₄	NaHCO ₃	NaOH				
1	1	1	1	1	1	1	-1	6	1	0.926
2	1	1	1	1	-1	-1	0	4	2	1.155
3	1	1	1	-1	0	0	0	3	1	0.866
4	1	-1	-1	0	0	0	0	1	2	0.816
5	0	1	-1	0	0	0	0	1	1	0.707
6	0	0	0	0	1	-1	0	1	1	0.707

Table 1: Sequential binary partitions of soil P fractions (*r* is number of P fractions with plus sign and *s* is number of P fractions with minus sign)

3. Isometric log ratio transformation and the Aitchison distance

A *D*-part composition $x = [x_1, x_2, \dots, x_D]$ can be described by its parts as follows (Aitchison, 1986):

$$x = \mathcal{C}(x_1, x_2, \dots, x_D) = \left(\frac{x_1^{\kappa}}{\sum_{i=1}^D x_i}, \frac{x_2^{\kappa}}{\sum_{i=1}^D x_i}, \dots, \frac{x_D^{\kappa}}{\sum_{i=1}^D x_i} \right) \quad (1)$$

Where \mathcal{C} is the closure operator to unit κ . The isometric log ratio coordinate x_i^* is computed from SBP's as follows (Egozcue and Pawłowski-Glahn, 2005):

$$x_i^* = \sqrt{\frac{rs}{r+s}} \ln\left(\frac{g(x_+)}{g(x_-)}\right) \quad (2)$$

Where $g(x_+)$ is the geometric mean of P fractions in group x_+ and $g(x_-)$ is the geometric mean of P fractions in group x_- . The *ilr* sign indicates in what direction P pools change in response to treatment or over time. The Aitchison distance \mathcal{A} between two compositions is computed as follows across $D-1$ compositional dimensions (Egozcue and Pawlowsky-Glanh, 2006):

$$d_a^2(x, y) = \sum_{i=1}^{D-1} (x_i^* - y_i^*)^2 \quad (3)$$

$$\mathcal{A} = \sqrt{d_a^2(x, y)} \quad (4)$$

Where y_i^* is the reference composition.

4. The McKenzie et al. (1992) dataset

The response of Mollisol P pools to perturbation by cultural practices and by nitrogen (N) and phosphorus (P) fertilization regimes investigated by McKenzie et al. (1992) is presented in Table 2. In absolute terms, the P fertilization influenced more markedly the resin and NaHCO₃, and NaOH pools compared to other pools.

Treatment	Inorganic P fractions			Organic P fractions		Residue P	
	Resin	NaHCO ₃	NaOH	HCl	NaHCO ₃		NaOH
	mg kg ⁻¹						
	Uncultivated control						
None	8	6	12	218	7.5	73	254
	Continuous wheat						
Check (no N nor P)	19	8	20	201	4.4	52	219
Added N	15	8	22	195	8.9	65	215
Added N and P	78	26	44	215	9.5	66	220
Added P	73	19	36	212	6.3	62	223
	Wheat-wheat-fallow sequence						
Check (no N nor P)	19	8	23	199	5.0	53	214
Added N	15	7	21	203	5.1	62	218
Added N and P	51	16	32	216	4.9	57	222
Added P	61	15	30	213	4.4	50	220
	Wheat -fallow sequence						
Check (no N nor P)	43	14	36	217	7.8	59	210
Added N	37	13	33	212	8.4	61	213
Added N and P	59	18	38	221	9.0	64	213
Added P	68	17	39	226	6.8	57	215

Table 2: Mollisol P fractions following crop sequence and NP fertilization (data from McKenzie et al., 1992)

The effect sizes of treatments on P pools are reflected by *ilr* values (Table 3). The effect size of added P varied with fertilization and crop sequence. The effect of added P was most prominent in *ilr2*, *ilr3* and *ilr4* for continuous wheat and the wheat-wheat-fallow sequence while treatment effects were much smaller in the wheat-fallow sequence (Table 3). The dominance of wheat in the sequence affected markedly the balance between geochemical and biological pools and that between P in primary minerals and other inorganic pools.

Treatment	<i>Ilr1</i>	<i>Ilr2</i>	<i>Ilr3</i>	<i>Ilr4</i>	<i>Ilr5</i>	<i>Ilr6</i>
Uncultivated control						
None	-2.342	-0.251	-2.828	-0.048	-0.490	-1.609
Continuous wheat						
Check (no N nor P)	-2.095	0.709	-2.278	0.332	-0.648	-1.746
Added N	-1.961	0.124	-2.292	0.100	-0.715	-1.406
Added N and P	-1.412	1.122	-1.361	0.682	-0.372	-1.371
Added P	-1.589	1.224	-1.516	0.838	-0.452	-1.617
Wheat-wheat-fallow sequence						
Check (no N nor P)	-2.031	0.662	-2.229	0.275	-0.747	-1.669
Added N	-2.089	0.433	-2.379	0.174	-0.777	-1.766
Added N and P	-1.734	1.236	-1.719	0.664	-0.490	-1.735
Added P	-1.757	1.384	-1.693	0.862	-0.490	-1.719
Wheat -fallow sequence						
Check (no N nor P)	-1.634	0.895	-1.777	0.531	-0.668	-1.431
Added N	-1.682	0.736	-1.847	0.474	-0.659	-1.402
Added N and P	-1.513	0.950	-1.613	0.664	-0.528	-1.387
Added P	-1.563	1.217	-1.601	0.793	-0.587	-1.503

Table 3: *Ilr* coordinates of P pools following crop sequence and fertilization (data from McKenzie et al., 1992)

A clearer picture of P pools change is given by subtracting from the effect of treatments that of no cultivation (Table 4). As shown by the Aitchison distance (Table 4), check and added N were closest to uncultivated conditions across crop sequences, especially where wheat was dominant. Cultivation, crop sequence and fertilization increased the inorganic and organic pools compared to residue P, indicating more P bioavailability. The geochemical pool increased over the biological one across crop sequences (*ilr2*). The slowly and rapidly bioavailable inorganic P pools largely increased compared to P from primary minerals (*ilr3*) under continuous wheat and wheat-wheat-fallow compared to the wheat-fallow sequences. In general, the balance between slowly and rapidly bioavailable inorganic P pools (*ilr5*) slightly decreased compared to the uncultivated reference composition. Differences were also small in the balance between slowly and rapidly bioavailable organic P pools (*ilr6*) and the uncultivated reference composition.

Treatment	<i>Ilr1</i>	<i>Ilr2</i>	<i>Ilr3</i>	<i>Ilr4</i>	<i>Ilr5</i>	<i>Ilr6</i>	Aitchison distance
	Distance from uncultivated control						
	Continuous wheat						
Check (no N nor P)	0.247	0.961	0.551	0.380	-0.158	-0.137	1.475
Added N	0.381	0.376	0.536	0.148	-0.225	0.203	0.687
Added N and P	0.930	1.373	1.468	0.730	0.118	0.238	5.510
Added P	0.753	1.475	1.312	0.886	0.038	-0.008	5.251
	Wheat-wheat-fallow sequence						
Check (no N nor P)	0.311	0.913	0.600	0.323	-0.257	-0.060	1.464
Added N	0.253	0.684	0.449	0.222	-0.287	-0.157	0.890
Added N and P	0.608	1.487	1.109	0.712	0.000	-0.126	4.333
Added P	0.585	1.635	1.136	0.911	0.000	-0.110	5.146
	Wheat-fallow sequence						
Check (no N nor P)	0.708	1.146	1.051	0.579	-0.178	0.178	3.319
Added N	0.660	0.988	0.981	0.522	-0.169	0.207	2.718
Added N and P	0.829	1.201	1.215	0.712	-0.038	0.222	4.164
Added P	0.779	1.468	1.227	0.841	-0.097	0.106	4.998

Table 4: *Ilr* differences in P pools between treatments and uncultivated check (data from McKenzie et al., 1992)

The *ilr4* is the most important balance for plant nutrition and the environment. Where no P was added, the wheat-fallow sequence showed the highest P bioavailability but also the highest risk for eutrophication of surface waters by dissolved P. Where P was added, crop sequences showed similar *ilr4* values and Aitchison distances. These results indicate that routine soil tests representative of *ilr4* are useful tools to address both agronomic and environmental issues. However, the biological dimension of the system (*ilr2*) can be manipulated on the long run by crop production systems that can decrease *ilr4* while maintaining the balance between organic pools (*ilr6*).

5. The Tiessen et al. (1983) dataset

Time change of P pools in horizons Ah and Bm has been studied by Tiessen et al. (1984) in a Mollisol after breakup of the natural prairie ecosystem followed by cultivation for 90 years (Table 5). The most prominent change was a decrease in the biological pools in both soil horizons.

After computing *ilr* coordinates at each time step, the degree of change in P balances can be measured as changes in each *ilr* coordinate and globally as the Aitchison distance (Figure 2). The slowly and rapidly bioavailable P pools decreased in both horizons compared to residue P (*ilr1*) and primary minerals P (*ilr3*) just after sod breakup and varied chaotically thereafter. The inorganic P pools decreased then increased (*ilr2*) probably due to humification following sod breakup and to cultivation thereafter. Resin P increased as a result of mineralization of root organic matter in the Bm horizon and decreased generally as a result of crop P uptake. Rapidly bioavailable inorganic

(*ilr5*) and organic (*ilr6*) P pools decreased compared to slowly bioavailable ones probably as a result of lesser microbial turnover following cultivation.

Above all, the Aitchison distance across *ilr* coordinates increased more rapidly in the Bm than the Ah horizons due to more rapid change in the most readily and the most slowly available P pools (Table 5). Thereafter, P balances remained stationary in the Bm horizon while there was considerable depletion of organic and residue P pools in the Ah horizon. Hence, few years after sod breakup, major changes in P pools occurred in the Ah horizon of this Mollisol where soil conservation practices must have largest effect on plant nutrition and environmental quality.

Time year	Inorganic P				Organic P		Residue P
	Resin	NaHCO ₃	NaOH	H ₂ SO ₄	NaHCO ₃	NaOH	
	mg kg ⁻¹						
	Ah horizon						
0	25.8	13.5	31.0	174	49.5	167	337
4	22.5	13.4	32.7	177	52.0	177	416
65	14.8	10.4	32.6	200	31.7	124	318
90	21.6	11.2	32.0	196	19.5	75	273
	Bm horizon						
0	9.1	5.3	18.4	199	16.6	63	236
4	8.0	3.3	18.4	190	16.5	72	290
65	6.3	4.2	22.8	221	15.1	66	242
90	7.1	3.9	17.9	228	9.7	47	254

Table 5: Effect of time on P pools in a Mollisol (data from Tiessen et al., 1984)

6. Conclusion

Using isometric log ratios to model P dynamics, the effect of crop sequences and fertilization on Mollisol P pools was primarily related to the dominance of wheat in the sequence and to P fertilization. More crops and less fallow in the sequence maintained soil P pools closer to uncultivated conditions.

The change of P pools over time was shown by an early change in balance where slowly to rapidly bioavailable P forms generally decreased compared to the recalcitrant residue and primary minerals P. Overall, the organic P pools decreased in the long run in both Ah and Bm horizons. Time change started rapidly then stabilized in the Bm horizon. The soil monotonically moved away from native conditions in the Ah horizon primarily due to loss of organic P.

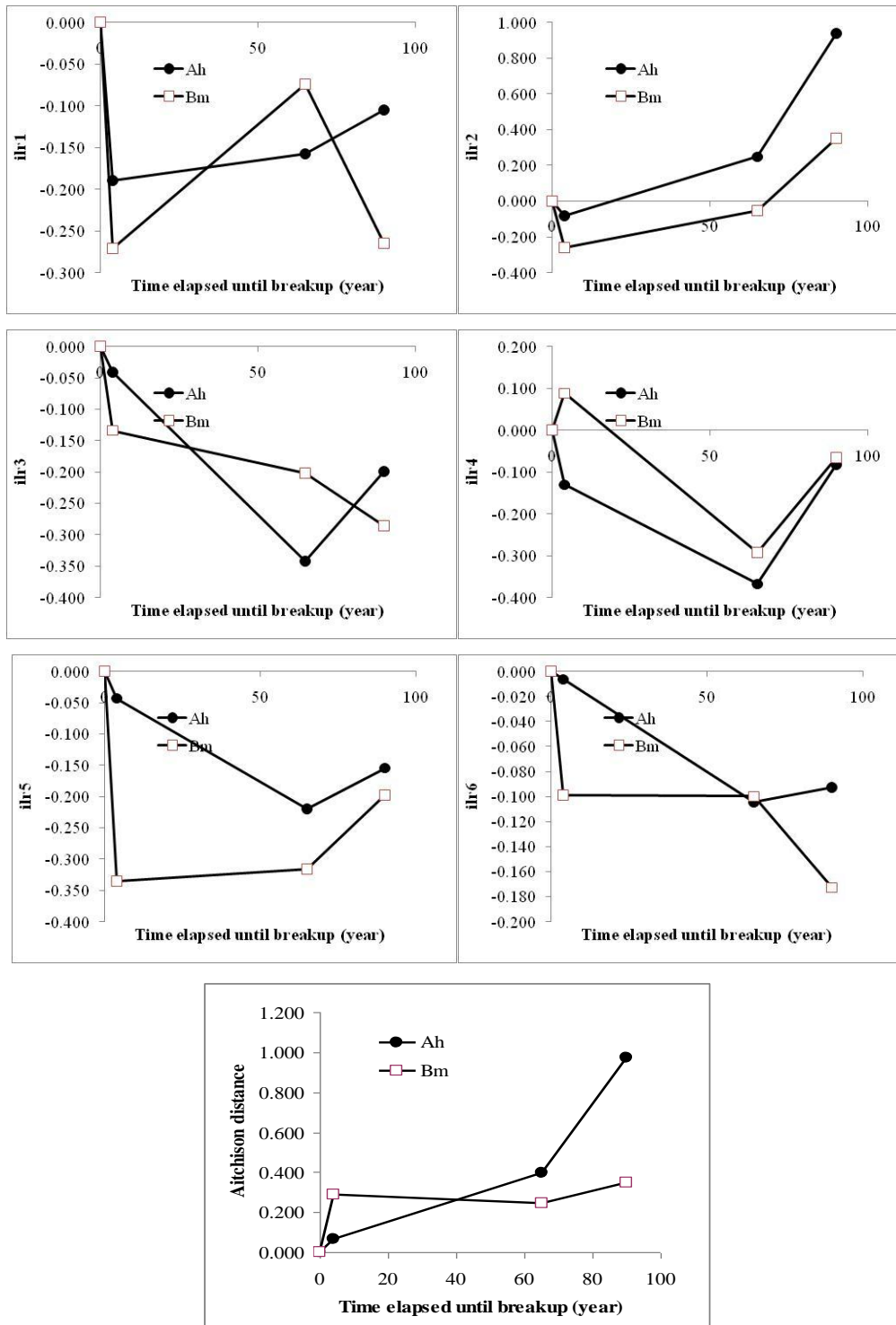


Figure 2: Time change in P balance distances from initial conditions in a Blaine lake soil (data from Tiessen et al., 1983).

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