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Some observations on the effects of length of sample storage, sample type, and sample depth on the determination of pH in soils collected in the vicinity of the Horne smelter at Rouyn-Noranda, Quebec[1]

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Abstract: As a routine part of laboratory practice, soil pH is commonly measured several months after sample collection. To determine the effect of sample storage time on soil pH, samples were analyzed the same day as collection, and in the laboratory at one, two, and six months after collection. The samples were collected as part of the Metals in the Environment (MITE) research at Rouyn–Noranda, Quebec.

The pH of A-, B-, or C-horizon soils did not change with storage time, although the pH of humus was less acidic by 0.65 six months after collection. The pH of humus and A-horizon soils collected from sites underlain by clay are less acidic than sites underlain by till, whereas B- and C-horizon samples have a similar pH for samples underlain by clay or till. In general soils become less acidic with depth.

Résumé : Communément, dans la pratique de laboratoire, on mesure le pH des sols plusieurs mois après la collecte des échantillons. Afin de déterminer l'effet du temps d'entreposage sur le pH des échantillons de sol, on a analysé des échantillons de sol le jour de la collecte, puis au laboratoire à des intervalles de un, deux et six mois après la collecte des échantillons. Les échantillons avaient été recueillis à Rouyn-Noranda (Québec) dans le cadre de la recherche sur les métaux dans l'environnement (MEDE).

Le pH des horizons A, B ou C des sols n'a pas varié avec le temps, mais le pH de l'humus était devenu de 0,65 unités de pH moins acide six mois après la collecte. Le pH de l'humus et des échantillons d'horizons A de sol recueillis à des sites dont le sous-sol est constitué d'argile, est moins acide que celui des échantillons provenant de sites dont le sous-sol est constitué de till. La composition du matériau sous-jacent n'influence pas le pH des échantillons des horizons B et C. En général, les sols deviennent moins acides à mesure que la profondeur augmente.

[1] Contribution to the Metals in the Environment Program

INTRODUCTION

Regional soil samples were collected at 87 sites within a radius of 100 km from the Horne Cu-Zn smelter located at Rouyn–Noranda, Quebec (Fig. 1) as part of the Metals in the Environment (MITE) – Point Sources Program. The soil samples were collected to determine the regional extent of metal loading from the smelter. Soil pH is one of the variables considered to effect concentration and mobilization of trace metals. In past projects, pH was determined in the laboratory up to six months or longer after sample collection. The purpose of this study is to determine if sample storage has a significant effect on pH measurements. In order to determine if variation in pH occurs during long-term storage, a suite of samples were analyzed in the field and in the laboratory at one, two, and six months after collection. A comparison of pH measurements with respect to depth and type of parent material was also investigated in order to determine any variations in pH between humus and mineral soils formed on till or sandy sediment, and those formed on lacustrine silt and clay. Samples used in this study consist of humus, A-horizon, B-horizon, and C-horizon soils collected from podzolic soils developed on till or sandy sediment, and from poorly developed luvisolic soils formed on lacustrine silt and clay. The number of samples and subsamples from each soil horizon are listed in Table 1.

METHODS

During regional humus and mineral soil collection, a subsample was separated and stored in an ice-packed cooler to avoid high temperatures inside a vehicle on hot summer days. Humus was collected after the litterfall was removed from the sample site. Soils with an A-horizon are not common in the area and where they do occur, they are thin (0.5–2.0 cm). Samples of B-horizon soils were collected from 20–25 cm below the top surface of the humus. C-horizon samples were collected at a depth of about 1 m and often represent the parent material. For long-term storage the original sample was put in a plastic bag sealed with elastic bands and placed in a metal pail. The pails were stored outside for up to one month before being transferred to a basement storage room at the Geological Survey of Canada.

Table 1. Number of samples and subsamples collected from the humus and mineral soils.

	Day of collection	1 month	2 months	6 months
Humus	80	5	24	80
A-horizon	24	1	9	24
B-horizon	85	6	28	85
C-horizon	90	7	27	90

Table 2. Specifications of the Omega PHH-7X pH pen (taken from instructions sheet supplied with instrument).

Range	0.00 – 14.00 pH
Resolution	0.01 pH
Accuracy @20°C	±0.2 pH
Typical EMC deviation	±0.1 pH
Calibration	Manual 2 points
Electrode	Combination pH electrode
Environment	0° - 50° , 95% RH
Battery type	2 x 1.4V
Life	3000 hr
Weight	90 g

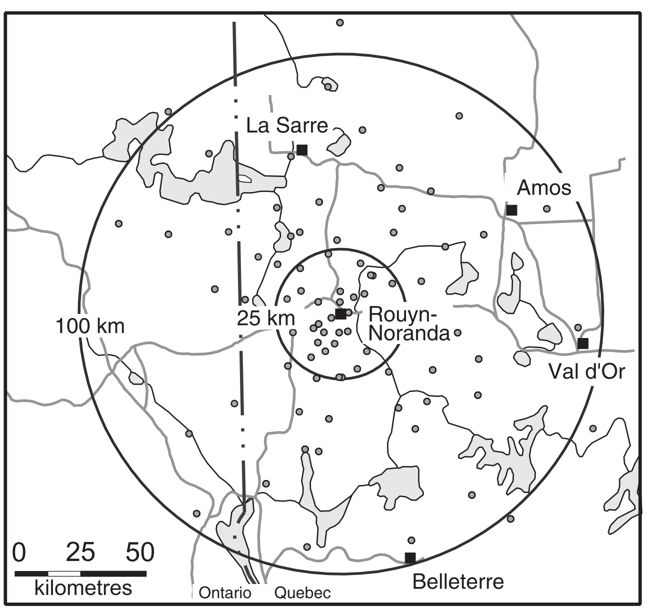

Figure 1. Distribution of sample sites within a 100 km radius of Rouyn–Noranda.

Figure 2. The Omega PHH-7X pen was used to determine the pH of samples in both field and laboratory measurements.

For pH analyses in the field and in the laboratory, samples were processed using the methods outlined by Sheldrick (1984) and Thomas (1996). Samples were sieved to 2 mm to remove large roots or pebbles. Ten grams of air dried soil or humus was placed in a 250 mL glass beaker. Twenty millilitres of 0.01M calcium chloride ($CaCl_2$) was decanted into the beaker containing the sample. If the sample absorbed the calcium chloride as is the case for most humus samples, an additional 20 mL of $CaCl_2$ was added. If the second 20 mL of calcium chloride was absorbed, as it was for most humus samples after six month storage, distilled water was added in increments of 10 mL until a liquid paste formed. The sample and solution was mixed with a glass stirring rod four times over a 30 minute period. The samples were then left to settle for 30 minutes.

Table 3. Measured pH values taken at time of collection and at one, two, and six months. Mineral soil in the 'parent material' column represents samples collected from soils formed over till and sandy sediments whereas clay represents soils formed over either massive or varved lacustrine silt and clay.

	Humus				A-horizon				B-horizon				C-horizon				
Sample number	Field	1 month	2 months	6 months	Field	1 month	2 months	6 months	Field	1 month	2 months	6 months	Field	1 month	2 months	6 months	Parent material
98-HJB-5001	3.10			4.67	3.50			3.54	4.53			4.58	4.75			4.77	Mineral soil
98-HJB-5002	4.40			4.39	3.77			3.80	4.75			4.85	4.75			4.79	Mineral soil
98-HJB-5003	3.27			4.18					4.68			4.89	4.60			4.82	Mineral soil
98-HJB-5004	3.05			3.72	3.40			3.63	4.52			4.66	5.06			4.75	Mineral soil
98-HJB-5005	3.45			4.26	3.59			3.52	4.43			4.25	4.51			4.45	Mineral soil
98-HJB-5006	3.45			4.12	3.09			3.30	4.73			4.83	4.92			4.94	Mineral soil
98-HJB-5007	4.06			4.97	3.88			4.11	4.15			4.32	4.58			4.59	Mineral soil
98-HJB-5008	4.20			4.58					3.90			4.29	4.25			4.72	Mineral soil
98-HJB-5009	3.50			4.37	3.77			3.78	4.54			4.45	4.65			4.68	Mineral soil
98-HJB-5010	3.88			4.37					4.30			4.33	4.54			4.68	Clay
98-HJB-5011	4.27			4.58					3.74			3.73	4.10			4.32	Clay
98-HJB-5012	4.56			4.90									4.46			4.83	Clay
98-HJB-5013	3.10		4.28	3.44	3.57		3.45	3.61	4.61		4.30	4.68	4.99		4.97	5.17	Mineral soil
98-HJB-5014	5.34		5.23	5.85					4.52		4.50	4.67	4.61		4.58	4.79	Mineral soil
98-HJB-5015	3.84		5.23	3.96					4.27		4.25	4.27	4.55		4.43	4.41	Mineral soil
98-HJB-5016	5.23		4.98	5.18					4.41		4.01	4.39	4.53		4.31	4.45	Mineral soil
98-HJB-5017	3.66		3.98	4.71					3.51		3.83	4.12	4.40		4.27	4.56	Clay
98-HJB-5018	2.92		2.83	3.02	4.66		3.14	3.23	3.30		4.40	4.69	4.69		4.48	4.98	Clay
98-HJB-5019	4.21		4.38	5.11					4.33		4.00	4.29	4.55		4.68	5.17	Mineral soil
98-HJB-5020	3.91		4.28	4.71					3.50		3.26	3.62	4.45		4.05	4.42	Clay
98-HJB-5021	3.25		3.17	3.62					4.20		3.96	4.15	4.32		4.18	4.34	Mineral soil
98-HJB-5022	3.43		3.17	4.60					4.24		3.69	3.96	4.25		4.12	4.40	Clay
98-HJB-5023	2.81			3.55					4.12		3.81	4.16	4.50		4.23	4.59	Mineral soil
98-HJB-5023-C2													4.90		4.66	5.09	Mineral soil
98-HJB-5024	2.88			3.73	3.37		3.18	3.57	4.06		3.89	4.31	4.46		4.67	5.14	Mineral soil
98-HJB-5025	2.94		3.00	3.37	3.88		3.64	3.85	5.20		4.81	4.98	4.53		4.51	4.93	Mineral soil
98-HJB-5026	3.64		3.79	4.27					4.00		4.00	4.13	4.59		4.50	4.80	Clay
98-HJB-5027	3.63		4.12	4.65	3.71		3.68	3.92	4.33		4.18	4.73	4.57		4.51	4.85	Mineral soil
98-HJB-5028	2.71		3.22	3.52	3.02		3.02	3.10	4.36		4.27	4.48	4.84		4.72	4.90	Mineral soil
98-HJB-5029	3.56		3.50	3.70					4.13		3.99	4.11					Mineral soil
98-HJB-5030	5.32		5.30	5.81					5.36		5.24	5.63	4.89		5.43	5.79	Clay
98-HJB-5031	4.34			4.75					4.20		3.99	4.15	4.18		4.17	4.35	Clay
98-HJB-5032	3.36		3.42	4.07					3.62		3.48	3.67	5.56		5.40	5.34	Clay
98-HJB-5033	3.67		3.78	4.45					5.01		4.47	4.82	5.54		4.95	5.26	Mineral soil
98-HJB-5034	3.12		3.32	4.73	3.90		3.40	3.68	4.57		4.14	4.33	5.15		4.73	5.15	Mineral soil
98-HJB-5035	3.02		3.02	3.28	4.40		3.69	3.71	4.70		3.89	4.19	5.00		4.51	4.78	Mineral soil
98-HJB-5036	3.22		3.20	3.80					4.03		3.99	4.28	4.46		4.30	4.57	Clay
98-HJB-5037	2.66		2.85	3.30	3.63		3.39	3.55	4.27		4.28	4.26	4.57		4.50	4.68	Mineral soil
98-HJB-5037-B2									4.41		4.44	4.64					Mineral soil
98-HJB-5038	4.64		4.70	5.13					4.68		4.33	4.56	6.88		6.87	6.69	Clay
98-HJB-5039	4.29			4.32									5.86			6.85	Clay
98-HJB-5040	4.07		4.04	4.51					4.57		4.39	4.67	4.87		4.47	4.83	Mineral soil
98-HJB-5041	3.47			4.05	3.92			3.81	4.33			4.37	4.69			4.76	Mineral soil
98-HJB-5042	3.85			5.33					4.28			4.16	4.91			4.43	Clay
98-HJB-5043	4.51			5.56									5.17			4.67	Clay
98-HJB-5044	4.79			5.81									6.40			5.16	Clay
98-HJB-5045	3.95			4.74					3.70			3.92	4.55			4.61	Clay
98-HJB-5046									5.57			5.25	5.05			4.70	Clay

The pH was measured using an Omega® PHH-7X pH pen (Fig. 2). Specifications for the PHH-7X pen are listed in Table 2. For each sample pH was measured by immersing the tip of the pH meter electrode in the $CaCl_2$ just above the sediment-solution interface (Fig. 2). Approximately ten to fifteen samples were measured each evening during field collection and the equivalent number at the corresponding one, two, and six month period. The pH meter was calibrated prior to and after each measurement session using 4.0, 7.0, and 10.0 pH buffer solutions.

RESULTS

Data from the pH measurement of humus and mineral soils acquired the day of sample collection, and at one, two, and six months afterwards are listed in Table 3 along with the parent material of the soil. In this table, the "field" column represents the pH of the sample as determined at time of collection. The data is displayed as bivariate plots in Figure 3, with

Table 3. (cont.)

	Humus				A-horizon				B-horizon				C-horizon				
Sample number	Field	1 month	2 months	6 months	Field	1 month	2 months	6 months	Field	1 month	2 months	6 months	Field	1 month	2 months	6 months	Parent material
98-HJB-5047	5.00			5.34					6.04			4.78	5.33			5.61	Mineral soil
98-HJB-5048	4.50			5.35					5.82			5.96	5.24			5.58	Mineral soil
98-HJB-5049	4.90			5.74					4.65			4.75	5.07			5.55	Clay
98-HJB-5050	4.29			5.25					4.62			4.29	4.43			4.87	Clay
98-HJB-5051	4.23			4.97					4.55			4.89	4.58			5.15	Clay
98-HJB-5051-C2													6.47			6.34	Clay
98-HJB-5052	3.03			3.79	3.30			3.68	3.92			4.14	4.13			4.33	Clay
98-HJB-5052-C2													4.14			4.52	Clay
98-HJB-5053	2.84			4.14					3.82			3.92	6.12			6.24	Clay
98-HJB-5054	4.22			5.25					4.26			4.31	4.30			5.11	Clay
98-HJB-5055	2.86			3.23	3.57			3.69	4.31			4.29	4.44			4.65	Mineral soil
98-HJB-5056	3.70			4.92					4.19			4.35	4.64			5.17	Clay
98-HJB-5057	4.87			4.88					4.38			4.29	4.91			5.23	Clay
98-HJB-5058	3.79			4.35					5.68			5.65	5.41			5.77	Mineral soil
98-HJB-5059									4.37			4.48	4.85			5.14	Mineral soil
98-HJB-5060	3.12			3.79					4.19			4.30	4.70			5.15	Mineral soil
98-HJB-5061	3.43			3.82	3.32			3.60	4.56			4.91	4.91			5.53	Mineral soil
98-HJB-5062	4.24			5.01					4.43			4.10	5.55			5.48	Clay
98-HJB-5063	5.39			5.47					5.15			5.44	5.91			6.15	Clay
98-HJB-5064	3.20			4.01					5.22			5.20	5.03			5.44	Mineral soil
98-HJB-5065	4.02			4.93	4.40			4.17	4.21			4.27	4.51			5.44	Clay
98-HJB-5066	2.84			3.14									6.04			4.69	Clay
98-HJB-5067	4.92			5.25					5.25			5.43	4.78			4.66	Clay
98-HJB-5067-C2													5.20			5.61	Clay
98-HJB-5068	4.10			5.02	5.18			5.08	4.23			5.01	6.05			6.06	Mineral soil
98-HJB-5069	4.70			5.30									5.63			6.25	Clay
98-HJB-5070	4.80			5.47	3.64			3.88	4.66			4.75	5.82			5.34	Mineral soil
98-HJB-5071	4.70			4.80					4.20			4.16	7.40			6.83	Clay
98-HJB-5072	5.04			5.79									4.59			4.96	Clay
98-HJB-5073	4.11			5.25					4.98			5.30	7.46			6.90	Clay
98-HJB-5074	3.39			3.73					5.41	5.26		4.95	6.08	6.28		6.44	Clay
98-HJB-5075	4.19			4.96					4.69	4.91		5.09	4.91	4.81		5.18	Mineral soil
98-HJB-5076	4.15	4.09		4.60					3.89	4.02		4.20	4.99	5.16		5.22	Clay
98-HJB-5077	4.85	5.20		6.14					4.35	4.78		4.44	4.28	4.47		4.79	Clay
98-HJB-5078	5.66	5.19		5.64					5.06	5.30		4.41	5.64	5.53		5.19	Clay
98-HJB-5079	3.80	3.38		4.01	4.25	4.00		4.23	4.36	4.49		4.01	4.91	4.63		4.50	Mineral soil
98-HJB-5080	3.56			4.98					4.65			4.45	5.48			5.30	Mineral soil
98-HJB-5081	4.29	4.28		4.69					5.54			4.73	4.50	4.57		4.75	Clay
98-HJB-5082	5.08			5.48					4.88			4.57	5.37			5.40	Clay
98-HJB-6001									5.05			4.31	5.15			5.36	Clay
98-HJB-6002									4.33			4.40	5.48			5.41	Clay
98-HJB-6003									4.57			4.55					Clay
98-HJB-6004									4.41			4.52					Clay
98-HJB-6005									4.29			4.35	5.43			4.75	Clay
98-HJB-6006									4.32			4.45					Clay
98-HJB-6007									4.59			4.68					Clay
98-HJB-6008									4.27			4.41	4.80			4.60	Clay
98-HJB-6009									4.39			4.39	4.63			4.45	Clay

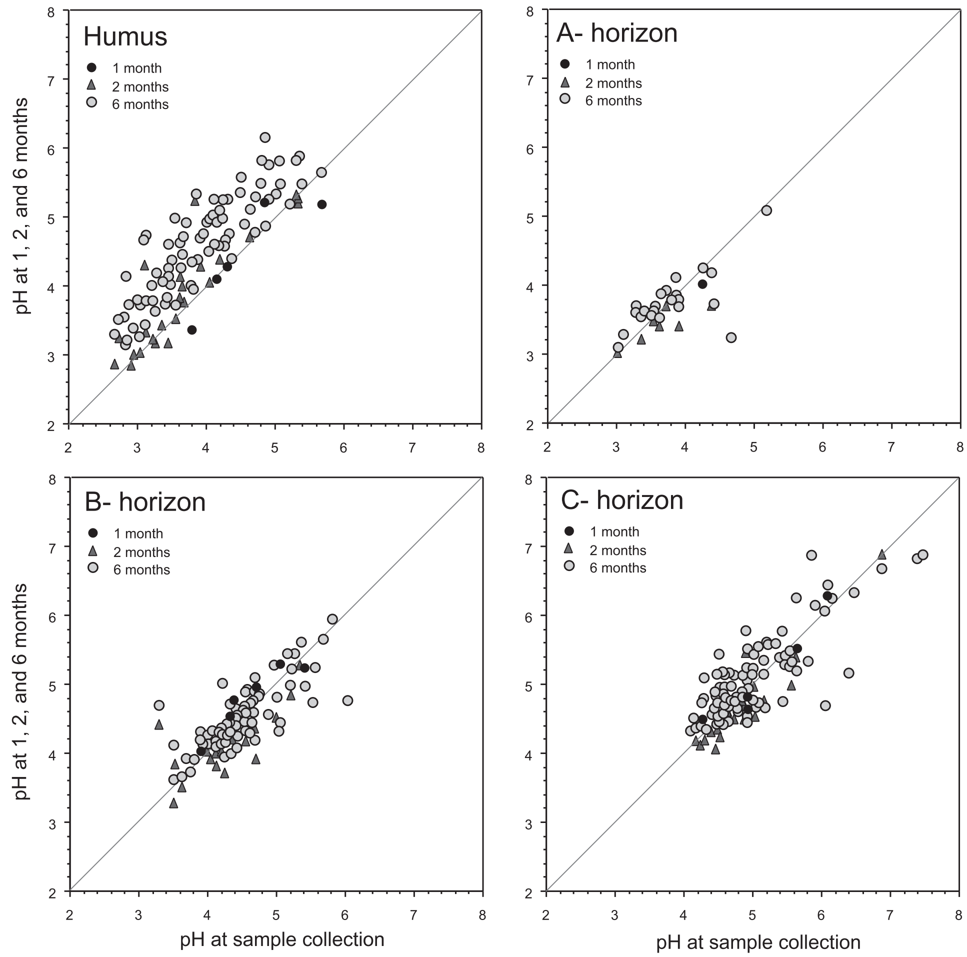

Figure 3. *Plots showing pH of humus and soil at sample collection versus pH at one, two, and six months after sample collection.*

derived statistics including mean difference, degrees of freedom (sample count - 1), t-values, and P-values listed in Table 4.

Humus

Humus displays the most significant change in pH between measurements taken at sample collection and laboratory determination (Fig. 3). At one month after sample collection, the pH was more acidic by a mean difference of 0.12, and after two months the pH was less acidic by a mean difference of 0.18 (Table 4). Both these values are within the accuracy of the pH meter (±0.2, Table 2). Therefore, there is little to no change in pH over this period. However after six months, the pH of 80 samples was less acidic by a mean difference of 0.65. A t-value of -15 and a low P-value (Table 4) indicate a consistent trend to decreasing acidity for humus samples measured in the laboratory after six months of storage.

A-horizon

Few A-horizon soils were sampled in comparison to the other soil horizons or humus (Table 1). Although there is not enough data at one month to draw any conclusions, the measurements at two months, a mean difference in pH of 0.39, indicates that the sample is more acidic than at sample collection. At six months the pH is similar to the value measured at sample collection.

B-horizon

After one month of sample storage, pH is less acidic by a mean difference of 0.18, and at two months pH is more acidic by a mean difference of 0.17. Both values are within the determination error of the pH meter (Table 2). At six months the field and lab determinations are similar (Fig. 3, Table 4). Therefore, there is little to no change in pH measured in the field or in the laboratory at one, two, or six months.

Table 4. Statistics on results of measurements. Mean difference, degrees of freedom, t-values, and P-values.

	Mean difference	Degrees of freedom	t-value	P-value
Humus				
1 month	.122	4	.814	.4612
2 months	-.181	23	-2.242	.0349
6 months	-.649	79	-15.074	<.0001
A-horizon				
2 months	.349	8	2.474	.0385
6 months	.028	23	.373	.7122
B-horizon				
1 month	-.167	5	-2.148	.0844
2 months	.169	27	2.678	.0125
6 months	-.027	84	-.755	.4525
C-horizon				
1 month	-.020	6	-.284	.7856
2 months	.134	26	3.096	.0047
6 months	-.101	89	-2.393	.0188

C-horizon

Values obtained from the determination of pH at one, two, and six months are similar with low mean differences with respect to the date of collection. The t-values and P-values indicate no significant difference in populations (Fig. 2, Table 4). There is little to no change in pH measured in the field or in the laboratory at one, two, or six months.

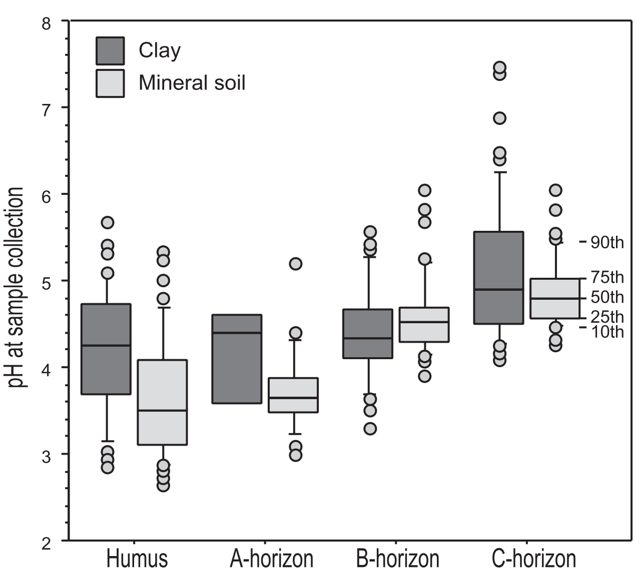

Figure 4. *The pH of humus, and soil determined at sample collection in relation to the underlying parent material. Each box diagram displays the 10th, 25th, 50th, 75th, and 90th percentile.*

Table 5. Statistics for pH of the total population and for the populations represented by mineral soils and clay.

	Mean	Standard deviation	Count	Minimum	Maximum
Humus total	3.93	0.75	80	2.66	5.66
Clay	4.20	0.71	41	2.84	5.66
Mineral soil	3.65	0.69	39	2.66	5.34
A-horizon total	3.78	0.50	24	3.02	5.18
Clay	4.12	0.72	3	3.30	4.66
Mineral soil	3.73	0.47	21	3.02	5.18
B-horizon total	4.49	0.52	85	3.30	6.04
Clay	4.41	0.56	44	3.30	5.57
Mineral soil	4.57	0.46	41	3.90	6.04
C-horizon total	5.00	0.68	90	4.10	7.46
Clay	5.11	0.83	50	4.10	7.46
Mineral soil	4.86	0.40	40	4.25	6.05

pH, parent material, and the soil profile

As stated earlier, soils collected for this study were formed on two different parent materials, 1) podzolic soils developed on till or sandy sediments, and 2) luvisolic soils formed on lacustrine silt and clay. The relationship between the pH of humus and mineral soils determined at sample collection to the type of underlying parent material is plotted as box diagrams in Figure 4. Each box diagram displays the 10th, 25th, 50th, 75th, and 90th percentile, with values below the 10th percentile and above the 90th percentile plotted as individual points. Humus and A-horizon soils formed over clay are less acidic than those formed over mineral soils. The mean, standard deviation, count, and minimum and maximum value of pH for the total population and for the populations represented by mineral soils and clays is displayed in Table 5. B-horizon samples collected over clays are slightly more acidic than samples collected over mineral soils (Fig. 4). C-horizon soils often represent the unweathered parent material. The pH of both clay and mineral soil show similar pH values for C-horizon samples (Fig. 4, Table 5), however samples with pH above the 90th percentile for C-horizon soils formed on clay are considerably less acidic than mineral soils.

The box plots depicted in Figure 4 display a decreasing acidity with depth for humus and A-, B-, and C-horizon soils formed on both mineral soils and clays for parent materials.

CONCLUSIONS

Data collected during this study indicates that the measurement of mineral soil pH at one, two, or six months after sample collection is similar to the pH at sample collection. Therefore it is not necessary to take pH measurements in the field to have accurate results. Samples collected from A-horizon soils did show a slight increase in acidity after two months but were similar in pH to field measurements after six months of storage. Samples of humus stored for either one or two months also have pH values measured in the laboratory that compare to values measured in the field. However, samples of humus, stored for six months, display a consistent trend of lower acidity and thus do not reflect the pH at sample collection.

Humus and A-horizon samples collected from soil profiles formed over glacial lacustrine silt and clay are less acidic than samples collected from soil profiles formed over till and sandy sediments. The pH of B- and C-horizon soils collected over till and sandy sediments and those of samples collected over glacial lacustrine clay are similar. Data from this study indicates a consistent trend for humus and soil to decrease in acidity with depth.

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