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CONFERENCE CONTRIBUTION

V. J. G. Houba · I. Novozamsky

Influence of storage time and temperature of air-dried soils on pH and extractable nutrients using 0.01 mol/L $CaCl_2$

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Abstract The stability of pH and certified amounts of nitrate, ammonia, total soluble nitrogen, total soluble organic carbon, magnesium, sodium, potassium and phosphorus obtained by extraction from air-dried (40 °C) soil samples by 0.01 mol/L $CaCl_2$ solution during storage at –18 °C, 4 °C, ambient temperature, 40 °C and 70 °C was investigated in one calcareous soil and one acid sandy soil. Even at storage times of 45 and 90 days, extractable amounts changed. Extractable amounts of P, NH_4-N, total soluble N and soluble organic C increased even at a storage temperature of 40 °C. The pH was lower for samples stored at a temperature of 70 °C and also the Mg concentration became lower at elevated storage temperatures after 45 days in both soils. It is suggested that reference materials certified for values using unbuffered extractants should be stored at a temperature not higher than 4 °C.

Introduction

Quality control samples, such as internal reference materials normally used for continuous quality control via Quality Control Charts (QCCs), are often used for several years. Knowledge of the stability of the (analytical) values of interest during storage is therefore important.

Stability tests are always an integral part of the production process of CRMs and RMs. However, normally these stability tests are carried out over relatively short periods and measures are taken for proper storage afterwards. In practice, the produced materials will be used for longer periods by the customer, while the conditions of storage may not always be optimal.

The problem of the stability of certified values is less in case of total (or almost total) contents of elements. This, however, is not necessarily the case for analytical values obtained after extraction with weak unbuffered extractants [1]. The reasons for this instability of dry soil samples is not quite clear, but suggestions have been made that the physical structure of organic matter could change with time [2, 3]. For manganese extractable with 0.01 mol/L $CaCl_2$ it was shown that in air-dried soils stored at 20 °C the values increased drastically [4].

In the present study the stability of the contents of extractable nutrients and pH in $CaCl_2$ extracts of soils has been investigated.

Materials and methods

Pretreatment of soils

In 1995 a few hundreds kg of a top soil of a river sediment (river Rhine), located in Wageningen, the Netherlands, were collected, dried at 40 °C and milled to the fraction < 0.5 mm. This sample was subdivided into buckets of 50 L at the Nederlands Meetinstituut (NMI), (Eygelshoven, the Netherlands) [5]. Each bucket was further subdivided into portions of 100 g into sealed plastic flasks using the automatic equipment described earlier [6, 7]. During this last subdivision every 50th sample was set apart for a homogeneity test. Later, another stability test was started using a non-calcareous sandy soil prepared in the same way.

Storage periods and temperatures

Fifteen (representative) bottles, each containing 100 g of the pretreated and homogenized soils, were chosen for stability experiments. All bottles were analyzed in duplicate to control the homogeneity of the selected bottles and to determine the original values (i.e. starting point) of the stability test (storage time = 0). From these bottles always three were stored at –18 °C, 4 °C, ambient temperature, 40 °C and 70 °C. This yielded, for every storage temperature, 3 × 2 values for the calculation of mean and standard deviation. The highest temperature chosen may seem rather high, but it should be realized that often stored soil samples are exposed to such conditions (e.g. glasshouses, tropical days). Subsamples were taken after 1.5, 3, 6, 12, 18 and 24 months of storage for the calcareous soil and 1.5, 3 and 6 months for the sandy soil.

V. J. G. Houba (✉) · I. Novozamsky
Department of Soil Science and Plant Nutrition,
Wageningen Agricultural University, P.O. Box 8005,
6700 EC Wageningen, The Netherlands

Table 1 Relative influence of storage time and temperature on pH and nutrients extracted with 0.01 mol/L $CaCl_2$ of a calcareous river clay soil (data samples stored at –18 °C set at 100).

Storage time (months)	Storage temperature (°C)				Storage temperature (°C)				Storage temperature (°C)			
	4	RT[a]	40	70	4	RT[a]	40	70	4	RT[a]	40	70
	pH				NO_3-N				NH_4-N			
1.5	100 ± 0.1	100 ± 0.1	100 ± 0.1	99 ± 0.1	101 ± 2.2	102 ± 1.5	101 ± 2.4	100 ± 2.1	113 ± 17	122 ± 5.5	122 ± 1.7	238 ± 7.4
3	100 ± 0.3	100 ± 0.3	100 ± 0.3	97 ± 0.3	106 ± 15	107 ± 15	108 ± 16	106 ± 15	100 ± 2.9	108 ± 3.4	108 ± 3.4	242 ± 2.9
6	100 ± 0.2	101 ± 0.2	100 ± 0.2	96 ± 1.9	101 ± 2.2	96 ± 2.9	97 ± 2.9	95 ± 2.6	100 ± 12	108 ± 23	108 ± 12	242 ± 20
10	101 ± 0.1	101 ± 0.1	100 ± 0.1	95 ± 2.2	99 ± 2.6	100 ± 2.4	101 ± 3.1	101 ± 4.2	100 ± 1.5	130 ± 3.9	103 ± 1.9	400 ± 4.7
12	101 ± 0.1	101 ± 0.0	100 ± 0.0	95 ± 0.1	103 ± 5.8	97 ± 2.7	108 ± 13	122 ± 4.2	111 ± 20	134 ± 7.4	134 ± 16	620 ± 24
18	101 ± 0.5	101 ± 0.5	100 ± 0.5	95 ± 0.5	98 ± 1.8	97 ± 2.4	99 ± 1.6	95 ± 2.5	115 ± 16	115 ± 20	136 ± 20	609 ± 86
24	100 ± 0.2	100 ± 0.2	99 ± 0.2	91 ± 0.2	100 ± 2.3	98 ± 1.2	100 ± 2.1	99 ± 1.5	104 ± 2.7	121 ± 5.1	160 ± 3.1	751 ± 18
	Total soluble N				P				Na			
1.5	101 ± 3.3	104 ± 3.1	107 ± 3.9	137 ± 3.7	95 ± 4.4	95 ± 1.7	97 ± 2.1	143 ± 2.6	99 ± 0.9	101 ± 0.7	102 ± 0.6	106 ± 0.7
3	113 ± 15	112 ± 15	117 ± 15	156 ± 15	100 ± 6.1	113 ± 6.9	119 ± 6.1	219 ± 6.1	100 ± 1.1	97 ± 0.8	99 ± 1.0	107 ± 1.1
6	108 ± 3.5	104 ± 3.1	112 ± 3.2	177 ± 4.5	100 ± 36	100 ± 37	117 ± 51	750 ± 238	99 ± 0.6	99 ± 0.6	101 ± 0.7	111 ± 0.6
10	99 ± 12	107 ± 12	119 ± 19	176 ± 18	100 ± 7.9	100 ± 7.5	129 ± 10	250 ± 23	99 ± 0.5	99 ± 0.7	104 ± 0.3	117 ± 0.7
12	99 ± 10	95 ± 10	107 ± 11	158 ± 14	–	–	–	–	101 ± 0.9	101 ± 1.2	107 ± 1.4	122 ± 1.1
18	98 ± 4.7	101 ± 4.4	117 ± 6.8	197 ± 7.1	120 ± 62	90 ± 61	140 ± 99	640 ± 329	99 ± 1.3	101 ± 1.4	107 ± 1.4	122 ± 1.6
24	105 ± 5.5	108 ± 4.9	122 ± 4.5	250 ± 11	100 ± 5.4	100 ± 6.9	138 ± 15	291 ± 11	99 ± 4.1	99 ± 4.6	110 ± 3.3	129 ± 3.8
	K				Mg				Soluble organic C			
1.5	100 ± 0.6	102 ± 1.3	104 ± 6.9	92 ± 0.9	103 ± 0.9	104 ± 3.1	98 ± 0.9	82 ± 1.1	–	–	–	–
3	101 ± 3.4	98 ± 2.6	96 ± 2.8	92 ± 3.4	101 ± 1.3	99 ± 2.3	95 ± 0.0	81 ± 1.3	–	–	–	–
6	99 ± 3.2	97 ± 2.6	90 ± 2.7	97 ± 2.6	100 ± 1.4	97 ± 3.3	92 ± 0.9	79 ± 1.0	–	–	–	–
10	103 ± 3.7	102 ± 1.1	100 ± 0.3	108 ± 0.5	99 ± 0.7	98 ± 1.3	90 ± 1.3	78 ± 0.7	–	–	–	–
12	100 ± 3.1	98 ± 2.8	98 ± 2.6	108 ± 2.8	101 ± 2.6	100 ± 2.2	90 ± 2.1	81 ± 1.7	–	–	–	–
18	100 ± 3.3	99 ± 2.7	101 ± 3.7	112 ± 3.3	96 ± 3.2	91 ± 4.6	86 ± 3.2	79 ± 2.7	102 ± 3.7	107 ± 5.0	162 ± 8.1	572 ± 31
24	97 ± 4.1	95 ± 3.5	97 ± 3.9	93 ± 5.0	101 ± 4.0	97 ± 4.7	90 ± 3.2	84 ± 4.7	106 ± 5.0	114 ± 5.5	175 ± 8.2	674 ± 33

[a] RT = Room temperature (uncontrolled ambient temperature)

Analytical procedures

At each storage time the content of every bottle was carefully mixed and 2 times 3 g were weighed and extracted for 2 h using 30 mL 0.01 mol/L $CaCl_2$ in a temperature controlled room at 20 ± 1 °C. To minimize random errors, all analyses were performed in one series by one analyst. At the beginning and at every 10th position in a series an internal reference sample was included for quality control. During measurements the equipments were regularly tested using standard solutions. After the pH measurements in the settling suspension, the suspensions were centrifuged at 2000 g and in the clear supernatant the following parameters were measured: NO_3-N, NH_4-N, total soluble N, P, Na, K and Mg [8, 9]. Soluble organic C was determined after 18 months of storage of the calcareous soil and from the beginning in the experiment with the sandy soil. All data were corrected for the moisture content at 105 °C.

Results and discussion

To make data collected at different storage conditions and times better comparable, it was assumed that no changes take place at a storage temperature of –18 °C and these data were set at 100%. This assumption proved to be correct since no significant differences were found in the analytical results for this storage condition. All other analytical values were recalculated on this basis and the values found are given in the Tables 1 and 2. The uncertainty of these values was calculated following the procedure used by BCR [10] as follows:

$$Ur = (CV^2_T + CV^2_{-18\,°C})^{1/2} \times (\text{mean at T/mean at } -18\,°C),$$

in which: Ur = uncertainty of the relative value (ratios),
CV = coefficient of variance from analytical data,
T = storage temperatures 4, room T, 40 and 70 °C.

For the pH a small but significant decrease was found in both soils at a storage temperature of 40 and 70 °C. For NO_3-N no significant changes were observed. For NH_4-N and total soluble N an increase could be observed with increasing storage times at elevated storage temperatures. Even at the undefined storage at ambient temperature, a non-significant increase in the NH_4-N was observed. For P and total soluble N in soils stored at 70 °C significant increases in extractable quantities were found. In the case of soluble organic carbon already storage at 40 °C led to significant increases.

For Na a slight but significant increase in concentrations was found with storage time at a storage temperature of 40 and 70 °C in the calcareous soil, but not in the acid sandy soil. For K the results were not clear and seemed to be more or less constant in the calcareous soil, but decreased significantly in the acid sandy soil stored at 70° C. For Mg a significant decrease was found at a storage temperature of 70 °C in both soils, but also at 40 °C in the calcareous soil. Contrary to the other parameters, the decrease of extractable Mg content already occurred in the beginning of storage after 1.5 months, and there was no change thereafter.

The clear increase in soluble organic carbon with increasing storage time and temperature indicates, together with the changes in soluble total nitrogen, that the physi-

Table 2 Relative influence of storage time and temperature on pH and nutrients extracted with 0.01 mol/L $CaCl_2$ of an acid sandy soil (data samples stored at –18 °C set at 100).

Storage time (months)	Storage temperature (°C)				Storage temperature (°C)				Storage temperature (°C)			
	4	RT[a]	40	70	4	RT[a]	40	70	4	RT[a]	40	70
	pH				NO_3-N				NH_4-N			
1.5	100 ± 0.4	100 ± 0.2	98 ± 0.3	93 ± 0.1	101 ± 2.2	102 ± 2.5	99 ± 2.0	97 ± 2.5	106 ± 7.7	103 ± 4.0	113 ± 4.4	299 ± 11
3	100 ± 0.3	100 ± 0.2	99 ± 0.3	94 ± 0.1	98 ± 1.7	101 ± 3.8	97 ± 1.3	95 ± 2.3	99 ± 2.3	100 ± 0.8	123 ± 4.7	342 ± 23
6	100 ± 0.4	99 ± 0.2	98 ± 0.2	92 ± 0.2	97 ± 2.7	97 ± 2.8	94 ± 2.9	93 ± 2.7	96 ± 3.5	96 ± 3.4	131 ± 6.7	313 ± 20
	Total soluble N				P				Na			
1.5	100 ± 3.1	101 ± 2.7	101 ± 1.9	140 ± 4.5	95 ± 8.4	95 ± 5.0	100 ± 5.5	177 ± 8.2	95 ± 4.6	96 ± 4.2	96 ± 3.3	98 ± 3.4
3	100 ± 2.7	101 ± 1.7	104 ± 1.9	195 ± 16	103 ± 5.3	103 ± 4.4	118 ± 4.3	239 ± 11	100 ± 1.8	98 ± 4.4	95 ± 3.1	94 ± 3.6
6	96 ± 2.1	97 ± 2.5	106 ± 2.8	184 ± 12	97 ± 8.7	102 ± 8.4	128 ± 13	270 ± 26	95 ± 2.9	95 ± 1.8	94 ± 5.9	101 ± 2.7
	K				Mg				Soluble organic C			
1.5	100 ± 1.3	101 ± 1.6	102 ± 1.5	90 ± 1.9	97 ± 5.4	97 ± 5.5	97 ± 5.5	80 ± 4.5	101 ± 4.0	97 ± 3.0	109 ± 3.5	344 ± 12
3	99 ± 2.4	97 ± 1.9	97 ± 0.9	87 ± 2.5	103 ± 3.3	103 ± 3.6	97 ± 2.4	84 ± 2.2	99 ± 6.0	99 ± 4.9	122 ± 6.3	437 ± 20
6	93 ± 6.6	95 ± 8.4	97 ± 10	82 ± 5.9	95 ± 1.9	96 ± 2.3	94 ± 2.3	82 ± 2.5	98 ± 4.3	99 ± 7.1	142 ± 5.1	509 ± 15

[a] RT = Room temperature (uncontrolled ambient temperature)

cal properties of organic material in the soils change with storage time and increasing temperature. These changes are not observed at a storage temperature of 4 °C. This increase in soluble organic material, caused by not appropriate storage, can in itself influence extracting properties of weak, unbuffered extractants, especially when there is also an interest in extractable metal ions, able to form soluble compounds with organic ligands.

Conclusions

Since for pH and amounts of nutrients extracted with 0.01 mol/L $CaCl_2$ changes were observed already at 40 °C storage temperature, it was concluded that dry soil samples for certification purposes using a weak, unbuffered 0.01 mol/L $CaCl_2$ extract should be stored at low temperatures of at least 4 °C.

It is expected that storage at low temperatures is also necessary for other weak unbuffered extracts in case of (certified) reference materials.

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