

# A simplified extraction schema to for the analytical characterization of apple orchard soils

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## Abstract

**Purpose** Standardized procedures for agricultural soil analysis use different extractant solutions, to determine one or just a few elements, which needs a lot of time and manpower. Within this work, it was tried to substitute traditional methods by the use of multi-element determination techniques, like inductively coupled plasma optical emission spectrometry (ICP-OES) and inductively coupled plasma mass spectrometry (ICP-MS) applied to a few solutions.

**Material and methods** ICP-OES and ICP-MS have been applied to a sequence of extracts obtained with 0.16 M acetic acid and 0.1 M oxalate buffer pH 3, which are more suitable for the plasma than traditional salt extractant solutions. Dilute acetic acid should characterize exchangeables plus carbonates, and oxalate buffer the pedogenic oxides. Aqua regia extractions in glass have been replaced by pressure digestion with KClO<sub>3</sub> in dilute nitric acid, which yields results equivalent to aqua regia, and additionally permits the determination of total sulfur, as well as acid-leachable boron and silicon. Total digestion was done in PTFE beakers by fuming with HNO<sub>3</sub>/HClO<sub>4</sub>, subsequently with HF, and final uptake in 1+1 HCl.

**Results and discussion** The method was applied to 44 soils from apple orchards of different soil types and climatic zones. P and K obtained from standard acetate-lactate extract as well as B obtained from the Baron extract correlated with the results from the acetic acid extract better than 0.9. Just Mg from the CaCl<sub>2</sub> extract (Schachtschabel) was independent from all

other Mg fractions. The results of the total digests could be verified by XRF analysis of the solid, Ti recovery was the most critical item. The results for Ca, Cu, Mg, Mn, Sr, Pb, and Zn obtained from KClO<sub>3</sub> digest and from totals, were strongly correlated. Factor analysis showed that the fraction mobilized by dilute acetic acid contained Ca-Mg-carbonates as well as Al-Ba-Na in the first factor, K-P-S in a second, whereas Mn-La-Li formed a group of its own. The pedogenic oxides, obtained from Al-Fe-Mn-Ti released in oxalate, carry most of the cationic trace elements, whereas the anions P-S-B-Si and the essentials Cu-Mo form different groups. Among the main elements, the quasi-total data were much less intercorrelated than the totals. The rare earth elements formed a strongly intercorrelated group as well after total digestion as in the oxalate leach.

**Conclusions** The proposed method permits to obtain information about common cations including trace elements, and the nonmetals phosphorus, silicon, sulfur, boron, and iodine simultaneously, which could be a gate to find new relations among them. The two-step procedure permits to predict availabilities in shorter and longer periods of time. Data from the extract in dilute acetic acid for K, P, and B can substitute traditional methods of soil analysis.

**Keywords** Heavy metals · Mobile fractions · Nonmetals · Rare earth elements · Soil nutrients

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## 1 Introduction

Ecological cycling processes generally depend on the amounts of nutrients, contaminants, and others, as well as the speed and conditions of transfer among the items in question. In case of metalliferous deposits, both total load, concentrations, and mobilization potential have to be

considered. In agriculture, soil analysis is mainly done to monitor available nutrients as well contaminants, in order to find the optimum fertilization resp. remediation strategy. Fertilization needs have to be predicted, which necessitate estimations of mobilizable and thus plant-available soil fractions. Bioavailability from soil or sediments is a biologically mediated process over a period of time. Selective leaching methods provide a snapshot of chemical speciation, which should yield assignments either to a probability of dissolution, or assignments to main solid phases, like humics and soil biota, carbonates, pedogenic oxides, clay minerals, silicates, and sulfides. Traditionally, modeling of plant-available nutrients in soils has been done from a series of different extractions, some just for one single parameter. Clear assignments to chemical speciation in the solid, however, permits the prediction of mobility changes under changes of pH and redox potential, in particular in terms of migrations in groundwater horizons. Root exudates, on the other hand, contain a lot of complexing organic acids, which can attack many chemical phases simultaneously.

Established methods to quantify plant-available soil fractions have often been tested in field trials, in particular with cereals. From this, a classification scheme to indicate deficient, sufficient or excess nutrient supply has been derived to enable fertilization recommendations. In the future, increasing costs for manpower in industrialized countries will render it impossible to perform several extracts on one sample, using different procedures for each parameter. The goal of this work is therefore to obtain a simplified procedure within two or three steps, targeting both on nutrients, main elements, hazardous elements, and others, by using ICP-OES as a multi-element method for final determinations.

If more information is required, sequential extraction procedures are an essential tool for understanding the origin, mode of occurrence, mobility, and transport of metals.

## 2 Material and methods

A total of 44 soils were sampled from apple orchards, dried, and sieved <2 mm as usual. They cover a broad range of pH, carbonate, total N, and humics content, as well as “available” nutrients (Table 1).

According to Austrian standard ÖNORM L 1080, humics have been defined as 1.72\*organic carbon. Similarly, 1 l of CAL-extractant solution contains 15.4 g of Ca-lactate  $\text{CaC}_6\text{H}_{10}\text{O}_6 \cdot 5\text{H}_2\text{O}$  (=0.05 M), 7.9 g of Ca-acetate  $\text{CaC}_4\text{H}_6\text{O}_6 \cdot \text{H}_2\text{O}$  (0.045 M), and 17.9 ml glacial acetic acid (0.313 M), and should have a pH=4.1. One gram of soil is shaken with 20 ml of extractant solution (or at aliquot proportions) (ÖNORM L-1087). The standard extraction for boron (termed B-Baron) is done by shaking 4 g of soil with 20 ml of a solution containing within 1 l 20 g ammonium acetate, 66 g ammonium sulfate, and 60 ml acetic acid (1.05 g/ml) for 90 min (ÖNORM L-1090). The Austrian guidelines for proper fertilization (2006) have been based on these parameters to set proper values for sufficient, adequate, and resp. insufficient nutrient supply.

For selective leaching, 1 g soil was weighed into a centrifugation vessel, mixed with 20 ml of 0.16 M acetic acid (9.1 ml conc. in 1 l), covered with parafilm, and shaken overnight. After centrifugation and filtration through a dry filter (red ribbon, Schleicher & Schuell), the residue was mixed with 20 ml of 0.1 M oxalate buffer pH 3 (6.3 g oxalic acid+7.1 g ammonium oxalate in 1 l), and shaken for 2 h at ambient temperature and light. After centrifugation and filtration through a dry filter (like above), the residue was discarded.

For quasi-total digestion, 1 g of sample was weighed into PTFE pressure bomb vessels, 8 ml of a  $\text{KClO}_3/\text{HNO}_3$  solution (10 g  $\text{KClO}_3$  dissolved in 200 ml  $\text{H}_2\text{O}$ +80 ml  $\text{HNO}_3$  supr.) was added, closed and heated with microwaves, and finally made up to 25 ml (Sager 2011).

The entire procedure was performed in plastic vessels, in order to avoid contaminations with B and Si from glass surfaces.

**Table 1** Characterization of the tested soils by routine parameters

pH (0.01 M $\text{CaCl}_2$ )	4.5–8.0	P in CAL extract	23–254 mg/kg
$\text{CaCO}_3$ (Scheibler)	<0.5–25 %	K in CAL extract	27–655 mg/kg
Humics	1.2–7.5 %	Mg in $\text{CaCl}_2$ extract	69–297 mg/kg
Total N	0.05–0.39 %	B in Baron extract	0.3–3.6 mg/kg

Routine parameters:

Chemical analysis of soils—determination of acidity: ÖNORM L 1083

Chemical analysis of soils—determination of carbonate: ÖNORM L 1084

Chemical analysis of soils—determination of humus by dry combustion of carbon: ÖNORM L 1080

Chemical analysis of soils—determination of total nitrogen by dry combustion: ÖNORM L 1095

Chemical analysis of soils—determination of “plant-available” phosphorus and potassium by the calcium-acetate-lactate (CAL) method: ÖNORM L 1087

Chemical analyses of soils—extraction with calcium chloride solution for the determination of magnesium: ÖNORM L 1093

Chemical analysis of soils—determination of “plant-available” boron: ÖNORM L 1090

Total digestion was done in open PTFE dishes on a heating block by fuming of 1 g of soil with  $\text{HClO}_4/\text{HNO}_3$ , then repeatedly with HF, uptake in 1+1 HCl, till no residue was left, and made up to 50 ml. Some results could be successfully checked by XRF. The element most resistable to dissolution proved to be titanium.

Calibrant solutions for undiluted and 1+1 diluted measurement of trace element concentrations were prepared in the respective buffer solutions. Samples diluted 1+9 till 1+99 were run versus usual aqueous calibrants (Sager 2005). In addition to the ICP-OES, an ICP-MS was available for the determination of Rb, Cs, the rare earth elements in the total digests, and iodine in the  $\text{KClO}_3\text{-HNO}_3\text{-H}_2\text{O}$  digest. It turned out that the total and quasi-total Mo-data received from the ICP-OES were too low because of a U-shaped background from the high salt matrix, whereas this effect seemed to be much less for the mobile fractions, provided the calibrants had been prepared in the same extractant solution.

### 3 Results and discussion

#### 3.1 Results of the leaching procedure

Data from total soil digests show that the investigated samples cover a wide range of soil composition, e.g., 0.3–10.8 % Ca and 3.4–6.2 % Al, and all trace elements are at ambient levels. Table 2 shows the mg/kg, and Table 3 shows the percentages of elements mobilized in dilute acetic acid (pH=2.9), oxalate and  $\text{KClO}_3\text{-HNO}_3\text{-H}_2\text{O}$  pressure digestions. In the simplified sequential leaching sequence of dilute acetic acid and oxalate buffer, which act at about the same pH, K, and Ca together preferred to be mobilized in the first extract. Beneath exchangeables, weak acid should dissolve calcite and also dolomite, leaving Fe and Al largely untouched. Because most of K and Na is bound to micas and feldspars, exchangeable K and Na look rather low. In the acetic acid extract, the ICP-OES was not sensitive enough to detect Be, Cr, Fe, Mo, Pb, V, as well as Y and the rare earths in all samples.

Complexation with oxalate at about the same pH than beforehand released larger amounts of the siderophile element Be, Co, Cr, Cu, Li, Ni, Sc, V, as well as the anions As, P, S, and Si, together with main elements Al, Fe, and Mn, presumably because of the dissolution of the pedogenic oxides. Just Ca, K, and Na were lower. Mg, Na, B, and Ba got mobilized within both steps at about the same level. Some Cd, Mo, Pb, and rare earths were below the detection limit of the ICP-OES in the oxalate leach. The respective affinities of these groups are no surprise and have been found in four- or five-step sequenced applied to sediments and soils as well. The actual dissolution patterns depend on the amount of pedogenic oxides present, their crystallisation status, as well as on the amount and sorption sites at humics, carbonates, and clays (Sager 1992). The

affinities of sorption–desorption could be shown by sequential leaching of the same solids before and after loading from rainwater or tapwater (Sager 1991a, b, c; Sager and Vogel 1993).

$\text{KClO}_3\text{-HNO}_3\text{-H}_2\text{O}$  pressure digestions (Sager 2011) enabled complete recovery of Ca, Co, Cu, Pb, Zn, and P in a majority of samples. This is like from aqua regia, but the large advantage is the enhanced destruction of organics and the recovery of the nonmetals S, Si, B, and I. From open fuming with  $\text{HNO}_3\text{-HClO}_4\text{-HF}$ , no data for Si, B, and I are available because of volatilization, and sulfur was also lost occasionally. Therefore, the data from the closed system have been taken as 100 % within Table 3. Data from additional elements, which have not been determined in the mobile fractions, are given in Table 4.

The merit of this work is the simplification, causing less salt matrix and blanks, making more elements possible to be determined, and establishing connections to procedures traditionally used in the characterization of agricultural soils.

#### 3.2 Simulation of classical parameters

Extractions with Ca-acetate-lactate buffer pH 4.1 were originally developed to model the P-transfer and the yield of crop plants, irrespectively of the soil type and the P fertilizer used. Apatite is believed not to contribute to the P supply of arable crops and should not be attacked by this reagent. The original dataset contained results from eight experimental years, and four different types of P fertilizers applied to soils within pH 5.5–7.3. The buffer capacity is sufficient to let the pH increase during the extraction to pH 4.7 at maximum (Schüller 1969).

Though the pH of dilute acetic acid is much lower (pH 2.9), it hardly attacks crystalline apatite, but 0.5 M HCl is needed to recover it quantitatively (Psenner et al. 1984).

Though the correlation coefficient between P-CAL and P-Hac, K-CAL and K-Hac, and B-Baron and B-HAc proved to be 0.965, 0.935, and 0.852, respectively, closer fits than simple regressions may be obtained from linear combinations of more parameters, primarily to obtain the same slope and thus the same figures valid for classification of the result. Simulation of the K-CAL can be simply done by K-in acetic acid, corrected by P in acetic acid and humics:  $\text{K-CAL}=9.24+0.638*\text{K-Hac}+0.222*\text{P-Hac}+1.59*\text{humics}$ ;  $R=0.948$  (Fig. 1); the humics are given in %. Also, simulation of the P-CAL can be simply done by P-in acetic acid, and improved by K in acetic acid and total sulfur:  $\text{P-CAL}=0.843+1.262*\text{P-Hac}+0.003*\text{K-Hac}+0.054*\text{S-KClO}_3$ ;  $R=0.965$  (Fig. 2).

The simulation of the B-Baron can be improved by combining the acetic- extractable B with acetic acid extractable sulfate (Fig. 3):

**Table 2** Total and mobilizable amounts in apple orchard soils, mg/kg

	Hac		OX		KClO3		Total	
	Median	Range	Median	Range	Median	Range	Median	Range
<b>Main elements</b>								
Al	15.4	2.5–82.2	1278	528–2837	18818	12543–28549	49491	34015–61810
Ca	10997	1193–53472	39.1	13.2–63.0	13782	2124–120437	14214	2790–107585
Fe	2.16	<0.4–9.8	1892	646–9000	20600	12164–29639	24262	16998–35266
K	253	53–579	118	47–344		Impossible	17610	11615–22431
Mg	564	148–3652	610	64–4149	5900	2630–25716	7382	3691–27399
Na	14.6	7.0–47.2	12.8	5.1–26.7	132	31–206	6941	3661–10536
<b>Cations</b>								
Ba	11.6	4.8–21.2	11.1	1.9–44.0	93.9	41.6–172	320	241–434
Be	0.028	<0.004–0.082	0.231	0.072–0.406	0.78	0.54–1.18	1.908	1.21–4.17
Cd	0.058	0.037–0.089	0.025	<0.004–0.055	0.178	0.061–0.35	0.291	0.115–0.465
Ce	0.13	<0.10–0.29	<0.10	<0.10–2.26	28.8	16.8–54.6	46.1	29.5–69.1
Co	0.28	0.07–0.74	2.64	0.67–9.51	9.92	7.23–15.6	11.7	7.43–17.0
Cr	<0.06	<0.06–0.10	1.57	0.37–7.20	34.0	23.0–52.7	46.9	35.5–74.6
Cu	0.50	0.17–1.51	13.4	3.49–43.5	33.4	12.0–88.1	32.0	12.3–69.1
Ho	<0.10	<0.10	<0.10	<0.10	0.28	0.12–0.43	0.43	0.29–0.66
La	<0.10	<0.10–0.15	<0.10	<0.10–0.66	14.1	7.9–23.7	22.9	14.6–33.6
Li	0.20	0.04–0.61	0.54	0.14–2.56	21.1	15.9–33.7	35.0	29.6–52.6
Mn	67.6	42.2–331	151	10.0–893	532	312–946	628	421–1377
Ni	0.72	0.34–1.65	3.69	0.84–8.14	26.62	16.2–46.5	30.8	18.0–52.0
Pb	0.21	<0.20–0.54	1.88	<0.20–4.90	27.0	18.5–60.3	27.70	18.7–74.5
Sc	<0.10	<0.10–0.20	0.39	0.14–0.71	3.48	2.60–5.16	6.35	4.24–10.5
Sr	22.0	3.15–111	0.98	0.08–3.35	42.1	13.8–161	86.8	56.7–221
Ti	0.149	0.012–0.50	25.67	5.59–139.2	277	87–619	2152	1318–3718
V	0.04	<0.03–0.10	6.46	1.56–29.7	37.1	24.4–60.8	64.7	43.4–106
Y	<0.10	<0.10–0.14	0.20	<0.10–1.34	9.00	4.93–14.2	12.03	6.99–17.7
Zn	4.3	1.5–16.6	11.5	0.79–30.9	84.1	53.5–129	81.9	47.1–123
<b>Anions</b>								
As	0.26	<0.15–1.20	2.50	1.32–5.12	12.6	10.6–16.4	12.0	3.7–17.8
B	1.16	0.37–3.25	1.18	0.12–2.39	14.82	9.4–29.3		
Mo	<0.12	<0.12	<0.12	<0.12–0.21	<0.12	<0.12–0.31	0.50	0.18–0.95
P	28.3	5.6–80.9	326	118–566	821	449–1598	769	419–1540
S	15.2	6.7–30.3	31.9	21.1–80.3	296	144–487	226	97–373
Si	75	25–114	224	106–457	1080	589–1372		

$$B\text{-Baron} = -0.12 + 0.756*B\text{-Hac} + 0.029*S\text{-Hac}$$

As a hypothesis of explanation, it should be considered that the ionic strength is larger than the physiological salt content inside living cells, whereas the dilute acetic acid is in about the same range. Thus, living biomass might contribute more to P-CAL than to P-Hac. On the other hand, pH is lower for dilute acetic acid, thus increasing the ion exchange versus K. Iron is hardly soluble in dilute acetic acid, and the pedogenic oxides seem untouched by this reagent.

Exchangeable Mg, obtained from CaCl<sub>2</sub>-extract (usually termed as Schachtschabel's method) could not be predicted

from any other mobile Mg fraction within this setup, like leached with dilute acetic acid, acid oxalate, after KClO<sub>3</sub>-nitric acid digestion, or total digestion. Therefore, it was tried to obtain a fit from a linear combination of other parameters by partial correlation analysis. The simulation of Mg extracted by CaCl<sub>2</sub> is quite complex. Starting from the most significant binary correlations, and trying to hit the 0/0, the subsequent best fit was obtained:  $Mg\text{-CaCl}_2 = -28.7 + 0.354*Si\text{-Hac} + 6.92*Li\text{-KClO}_3 - 0.347*S\text{-KClO}_3 + 1225*N_{\text{tot}} - 56.6*\text{humics}$ ;  $R=0.978$ ; humics and  $N_{\text{tot}}$  are given in %.

It shows that the exchangeable Mg largely depends on the organic matrix and the weathering status of the silicates.

**Table 3** Percent mobilized with respect to total digest

	Hac		OX		KClO3	
Main elements	Median	Range	Median	Range	Median	Range
Al	0.027	0.005–0.18	2.94	1.15–5.12	38.6	28.3–53.0
Ca	54.3	24.8–100	0.34	0.013–1.78	100	54.1–100
Fe	0.012	< DL–0.05	9.34	2.43–30.6	82.9	66.1–100
K	1.43	0.24–3.29	0.67	0.27–2.14	Digestion matrix	
Mg	6.78	2.88–20.4	7.73	1.52–22.4	86.7	67.8–100
Na	0.19	0.10–0.67	0.17	0.07–0.60	1.78	0.55–4.41
Cations						
Ba	3.79	1.31–7.13	3.07	0.67–10.93	28.0	10.7–56.3
Be	0.99	< DL–5.71	10.68	4.94–18.50	42.4	18.5–76.3
Cd	20.2	9.2–51.2	7.73	< DL–39.9	64.3	26.1–100
Ce	0.13	< DL–0.49	0.11	< DL–2.96	67.3	45.1–100
Co	2.09	0.59–6.65	21.0	6.17–74.3	92.0	67.2–100
Cr	0.07	< DL–0.29	3.52	1.02–11.0	69.2	53.3–90.2
Cu	1.66	0.56–7.20	45.1	25.8–67.5	100	77.5–100
Ho	< DL	< DL	< DL	< DL–4.6	64.4	31.9–100
La	0.14	< DL–0.65	0.20	< DL–1.80	68.3	40.4–100
Li	0.58	0.12–1.17	1.54	0.42–6.27	58.2	44.7–100
Mn	11.0	3.81–42.6	26.1	1.76–83.2	81.2	57.4–100
Ni	2.24	1.17–5.50	13.3	2.21–33.4	91.5	51.2–100
Pb	0.83	< DL–1.62	8.04	0.55–19.2	93.5	72.0–100
Sc	< DL	< DL–0.20	4.83	< DL–11.8	57.7	32.4–91.1
Sr	26.0	4.25–63.0	1.32	0.05–4.39	49.5	18.8–96.5
Ti	0.007	0.001–0.026	1.26	0.33–4.68	11.7	5.5–26.0
V	0.06	< DL–0.14	10.5	3.59–32.4	56.4	42.6–75.8
Y	0.29	< DL–1.09	1.99	0.22–10.4	74.5	54.9–100
Zn	5.81	2.56–22.3	15.7	1.08–46.3	99.5	88.6–100
Anions						
As	3.55	< DL–7.9	21.2	7.7–43.5	92.2	83.9–93.5
B	7.41	2.02–20.8	6.81	< DL–14.9	100	
Mo	< DL	< DL–10.66	14.0	2.38–79.3	<sup>a</sup>	<sup>a</sup>
P	3.91	0.47–8.69	35.6	12.1–66.8	100	87.0–100
S	4.93	2.06–10.33	10.96	6.76–21.18	100	
Si	5.99	2.64–12.69	20.12	9.81–45.89	100	

For mobile B, S, and Si, data from KClO<sub>3</sub>-HNO<sub>3</sub>-H<sub>2</sub>O pressure digestion have been defined as 100 %

< DL minor detection limit

<sup>a</sup> Mo determination in KClO<sub>3</sub> is interfered by the matrix (gets too low); in total digests, ICP-MS data were done

Again, the pedogenic oxides (Al-Fe-Mn) do not seem of importance for Mg-CaCl<sub>2</sub>.

When selected variables of the dataset are submitted to factor analyses, parallel trends and groupings of variables can be recognized. In combinations of the classical soil parameters P-CAL, K-CAL, Mg-CaCl<sub>2</sub>, and B-Baron with acetic acid extractables, they always appear together with their counterparts, except for Mg. Lime, indicated from Ca in acetic acid, effects many acid mobile trace elements, like Co, Ni, and Ti, but not the nutrients P-K-S-B. Acetic acid mobilizable Cu,

Zn, and Si behave rather individually among the samples investigated.

### 3.3 Extractant dilute acetic acid

Contrary to the release at pH 5 or pH 5.5 (Sager et al. 1990), which had been used in the past for the selective dissolution of carbonates, a dilute solution of acetic acid (pH=2.9) aims to release both exchangeable cations and also more firmly bound species, which require replacement by H<sup>+</sup>. Advantageous,



**Table 4** Range of further elements from total digests (I from KClO<sub>3</sub>)

mg/kg	Median	Range
Rb	86.0	55.9–119.6
Cs	3.98	2.71–5.86
La	22.9	14.6–33.6
Ce	46.1	29.5–69.1
Pr	5.50	4.33–7.89
Nd	20.6	16.1–29.2
Sm	3.90	3.07–5.76
Eu	0.839	0.644–1.177
Gd	3.57	2.62–5.39
Tb	0.487	0.350–0.766
Ho	0.430	0.295–0.664
Er	1.303	0.84–2.003
Lu	0.168	0.109–0.246
Bi	0.224	0.013–1.245
Tl	0.520	0.399–0.825
I	1.87	1.37–3.59

however, are higher concentration levels in the extracts and low additional salt matrix, which means less effect of blanks and more distance to the detection limits, resulting in higher precision. The precision of results for Cd–Cr–Cu–Ni–Pb–Zn obtained from extraction of soils by various salt solutions has been documented in ring tests within 11–49 %, in dilute acetic acid within 7–25 % (Sager 1999).

Clay minerals might also contribute to this fraction. The desorption of Pb, Zn, Cu, and Cd, which had been preadsorbed on various clay minerals, was found appreciable (more than half in most cases) into 0.1 M acetic resp. oxalic acid, but depended on the kind of clay and the cation in question (Farrah and Pickering 1978).

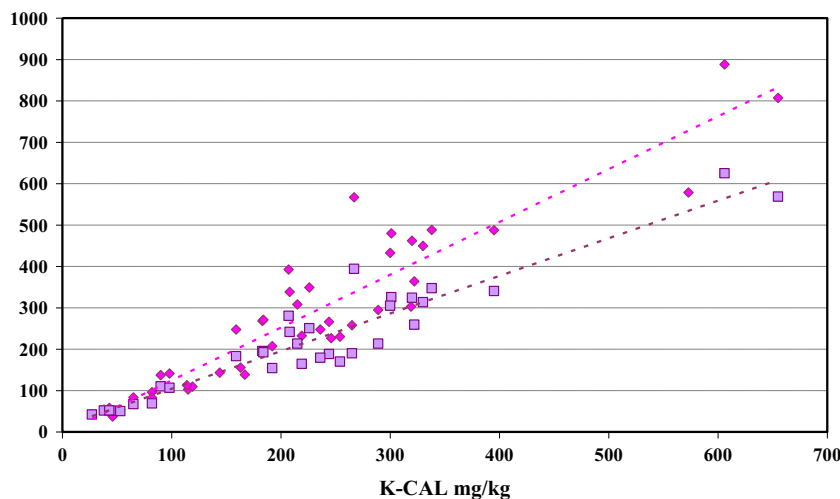
Acetic acid extractable P and K correlate highly significant linear with their counterparts in the acetic-lactic acid extract, which is routinely done in our lab, K extracted by diluted

acetic acid yielding a slope of 128 %, acetic acid extractable P a slope of 64 %, and B a slope 90.6 %. Thus, the limits need not be changed to obtain the same classifications as nonsufficient, adequate, or excess nutrient supply. In addition, the ICP permits to obtain mobile sulfur (sulfate) and silica as well. Silica is beneficial for the mechanical stability of green plants and protects against grazing by herbivores.

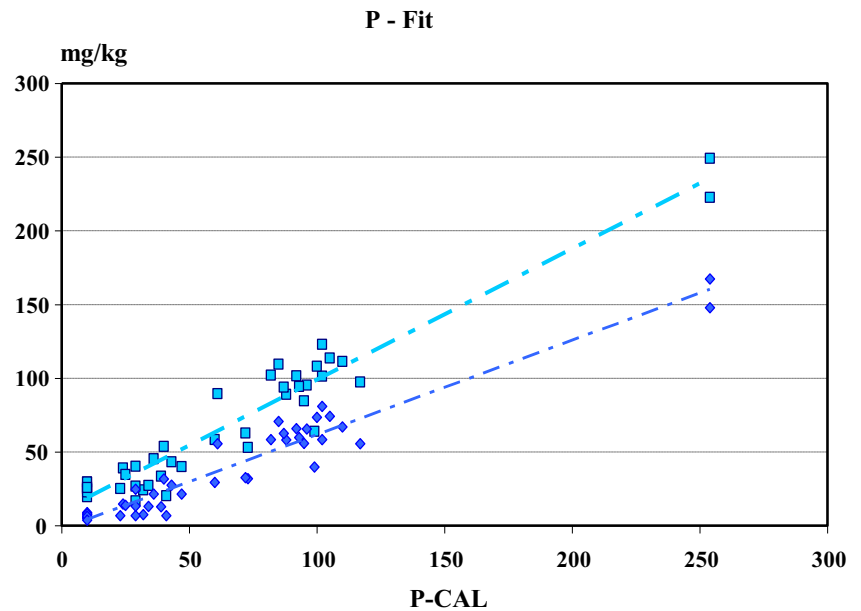
Factor analyses of element concentrations obtained from the selective leaching procedures together with total or quasi-total contents have been exerted in order to recognize significant groupings and relations. When the acetic acid mobilizable fractions are combined with the main elements from the KClO<sub>3</sub>–HNO<sub>3</sub>–H<sub>2</sub>O digest, just Ca and Mg go along with their respective counterparts, whereas the other main elements hardly show reasonable relations, but appear in different factors or with low factor weights. Particularly silicon acts rather individually. Acid-mobile B has a strong tendency toward Mg (Table 5).

Cd–Cr–Cu–Fe–Ni–Pb–Zn values obtained from extractions with dilute acetic acid have been certified for the international reference materials CRM 483 (sewage sludge treated soils from Northampton/England), CRM 484 (sewage sludge treated terra rossa from North-East Catalonia/Spain), and BCR 700 (sewage sludge amended soil from Hagen/Germany). Like usual in soil analysis, these materials were air-dried and sieved <2 mm, and homogenized to achieve a bulk variability of total main elements at or below the 1 % level, measured by X-ray fluorescence (XRF) (Ure et al. 1993; Quevauviller et al. 1997; Pueyo et al. 2001). Whereas ammonium acetate and calcium chloride extractable fractions from sludge-amended soils changed within a year of storage, the extracts obtained from dilute acetic acid were sufficiently stable to start a proper certification campaign (Ure et al. 1993). In the first paper, a 0.43 mol/l acetic acid was proposed for the single extraction, and a 0.11 mol/l acetic acid for the sequential extraction, followed by 0.1 mol/l hydroxylamine hydrochloride-nitric

**Fig. 1** K from CAL extract versus K extracted by diluted acetic acid (*diamonds*) (R=0.9353), and fitted data to obtain the same slope (*squares*) (R=0.9484), in mg/kg (*fitted line*); P-CAL=0.84+1.26\*P-Hac+0.003\*K-Hac+0.054\*S-KClO<sub>3</sub>



**Fig. 2** P from CAL extract versus P extracted by diluted acetic acid (*diamonds*) (R= 0.9653), and fitted data to obtain the same slope (*squares*) (R= 0.9654) (*fitted line*)  $P-CAL = 0.84 + 1.26 * P-Hac + 0.003 * K-Hac + 0.054 * S-KClO3$



acid of pH=2 (Ure et al. 1993). They used 0.5 g in 20 ml, or equivalent. Later, the precision of the sequence was improved by increasing the hydroxylamine concentration to 0.5 mol/l (Rauret et al. 2000). For the contaminated samples investigated, significant different results between results from the reciprocating shaker and the end-over-end shaker emerged (Quevauviller et al. 1997). This means at least, within a series, the shaking method has to be same throughout.

The  $CaCl_2$ ,  $NH_4NO_3$ , and  $NaNO_3$  extracts from the candidate reference materials CRM 483 and CRM 484 could not be certified because of too high standard deviations of the results obtained (Quevauviller et al. 1997).

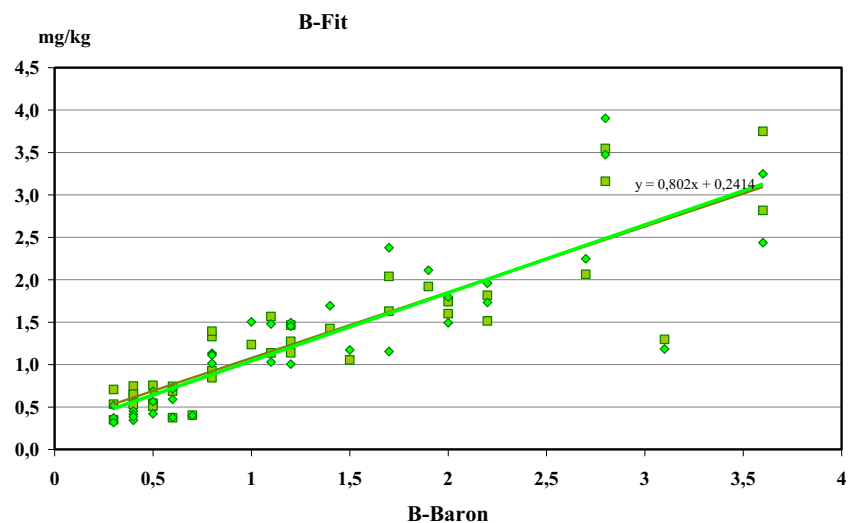
From soils of nine different regions of China, 0.43 M acetic acid extracted 0.13–8.53 % of total rare earth elements at ambient levels, DTPA extracted 0.17–24.5 % and 0.1 M HCl extracted 0.04–26.7 %. In a series of pot experiments

with these soils, the transfer of rare earth elements to wheat shoots and roots correlated significantly with the soil extract into 0.1 M HCl, whereas correlations with the amounts extracted with 0.43 M acetic acid resp. DTPA were insignificant. The amounts extracted by 0.01 M  $CaCl_2$  solution were generally too low to be detected even by ICP-MS (Li et al. 2001).

K uptake in ryegrass (*Lolium perenne*) was modeled by ammonium-acetate-exchangeable fraction and a fraction leached by 1 M HCl in a pot experiment. In the rhizosphere, soon a concentration gradient for both fractions developed. The K uptake turned out to exceed the ammonium-acetate-exchangeable K in variable amounts depending on the soil type and the K bound in the interlayers of soil clay minerals, particularly smectite and illite (Kong and Steffens 1989).

The 0.16 mol/l acetic acid used in this work, 20 ml applied to 1 g, is well within the range of the certified methods, and

**Fig. 3** Boron from Baron extract versus B extracted by diluted acetic acid (*diamonds*); fitted data to obtain the same slope (*squares*) result in almost the same



**Table 5** Factor weights from of factor analysis acetic acid extractables versus main elements

	Component						
	1	2	3	4	5	6	7
AlHAc	,565	-,426	-,007	-,107	-,055	,171	-,582
BHAc	,154	,753	,308	,420	-,043	,075	,179
BaHAc	,195	,719	,128	,113	,165	,172	,372
CaHAc	,751	,313	,468	,033	,164	,182	-,045
CdHAc	-,178	,154	,250	-,019	-,832	-,165	,074
CoHAc	-,726	-,294	,188	-,064	-,200	,204	-,446
CuHAc	,081	-,417	-,026	,181	,246	,635	-,012
KHAc	-,026	,233	,093	,863	-,246	,046	,175
LaHAc	,399	,004	,609	,000	-,151	,064	-,382
LiHAc	,040	,251	,881	,156	,051	-,004	,080
MgHAc	,060	,906	-,002	,160	-,005	-,025	,053
MnHAc	-,157	-,062	,900	,035	-,194	-,158	,051
NaHAc	,186	,829	,038	,142	-,086	-,184	,068
NiHAc	-,759	-,207	,088	,121	,007	,106	,095
PHAc	,107	,139	,060	,882	,188	,110	,133
SHAc	,464	,431	-,090	,611	-,088	-,214	-,253
SiHAc	-,095	,137	,039	,225	-,068	,046	,898
SrHAc	,434	,084	,798	,177	-,090	-,020	,025
TiHAc	,830	,028	,205	,076	,011	,242	,109
ZnHAc	-,018	,054	-,431	,173	-,138	-,540	,078
AlKClO3	-,537	-,141	,571	,014	,238	-,203	,394
CaKClO3	,779	,382	,117	,095	,204	,251	-,056
CeKClO3	-,665	,257	-,017	-,165	,078	,384	,205
FeKClO3	-,329	-,085	,440	-,064	,626	,161	,336
MgKClO3	,388	,755	-,058	,212	,266	,154	-,133
NaKClO3	,055	,394	,456	,315	,584	,042	-,127
SKClO3	-,091	,354	,264	,685	-,051	-,433	,137
SiKClO3	-,009	,256	-,251	-,015	,094	,846	,039
TiKClO3	,105	,333	-,198	-,297	,657	,159	,057

Extraction Method: Principal Component Analysis

Rotation Method: Varimax with Kaiser Normalization

Factor weights > 0.800 have been marked *yellow*, and factor weights 0.600 to 0.800 have been marked *grey*

improves the detection limit by a factor 2. Use of the original 0.11 mol/l would be equivalent to 27.5 % CaCO<sub>3</sub>, but the 0.16 mol/l are 40 % CaCO<sub>3</sub>, which seems to be sufficient to treat the local samples.

### 3.4 Discussion of the oxalic acid-ammonium oxalate extract

The oxalate buffer applied as the second step, acts at about the same pH, but with strong complexation capabilities. In highly calcareous soils, the pH during the extraction may rise to more than 4, thus decreasing the amount of extracted Fe and others.

Therefore, it was recommended to decalcify the samples prior to the oxalate leach, by shaking with 1 M Na-acetate buffer pH 4.75, or to add sufficient oxalic acid for the destruction of the carbonates (Del Campillo and Torrent 1992).

Former works of the author as well as others had shown that this extraction often carries a major fraction of trace elements, all depending on the grain size of the solid, indicating surface-related amounts (Sager et al. 1990; Sager 1992; Sager and Vogel 1993). These are surely available within a longer time span than the exchangeables, but also mobilizable by reduction, until sulfide precipitation occurs.



In the oxalate-leachable fraction, which is known to contain the pedogenic oxides as weathering products, most cations highly intercorrelated, as well as the anions P-S-Si-B, except Cu and Mo. The main group of the pedogenic oxides, lead by Al-Fe-Mn, clearly counteracts the carbonates, but they are independent of the basicity of the silicates, the latter being presented by total Al-Fe-Ti-Ce. Though well measurable, oxalate-mobile Si is almost independent from other fractions.

From a thermodynamic point of view, at equilibrium all iron oxides should dissolve both in oxalate as well as in EDTA at  $\text{pH} < 4.5$ . Beneath ferrihydrite, this also includes maghemite, magnetite, and lepidocrocite, i.e., all sites readily available for the adsorption of cations, anions, and pesticides Fe-oxide surfaces. Oxalate is very quick, and 2-h shaking is sufficient. Light-induced decomposition of oxalate, however, leads to the formation of Fe(II), which catalyzes dissolutions additional to the EDTA (Borggaard 1992), like goethite. From naturally precipitated goethite, desorption of Cu, Cd, Pb, and Zn at pH 4 was found to be marginal, and within 20–40 % at pH 3. Desorption from a naturally precipitated mixture of  $\text{MnO}_2$  and ferrihydrite was also low at a pH 3 (Tipping et al. 1986), but from goethite, equivalent desorption from the natural sample occurred at lower pH and less selectivity among the metals, then from  $\text{MnO}_2$ .

Natural ferrihydrites from soil-related environment commonly contain up to 9 % Si, which might inhibit the growth of more crystalline iron oxides such as goethite and hematite (Childs 1992). This explains why oxalate-mobilizable Si was also found in this work.

Within a long-term trial of 70 years at a sandy soil in Northern Germany, most extractable mobile phosphorus fractions were influenced by fertilizer application and liming, whereas oxalate-extractable Fe and NaOH-extractable P remained at constant levels. Acidification resulted in an increase in mobile P and P supply (Schweitzer and Pagel 2001).

Acid ammonium oxalate (pH 3.3) extracted three to five times more Mo from alkaline high Mo soils than bicarbonate-DTPA and ammonium carbonate at pH 9, but the plant uptake for crested wheatgrass (*Agropyron cristatum*) and alfalfa (*Medicago sativa*) in a pot experiment correlated equally for all three extractants (Wang et al. 1994).

When within a column experiment, the anions B-Mo-As-Se-S were adsorbed from a NPK fertilizer solution and washed with about 5 pore volumes, the acid oxalate leach of the remaining solids clearly recovered the adsorbed amounts (Sager 2002, 2004), thus indicating some significance of this reagent, in particular for those species which are not desorbable by weak acids only.

In solution, the stability of rare earth carbonate and oxalate complexes is highly correlated, and increases from La to Lu. The rare earth analogue Y behaves similar to Tb (Cantrell and Byrne 1987).

Oxalate resp. oxalic acid is secreted by various fungi, like wood-rotting basidiomycetes, mycorrhizal fungi, or fungi pathogenic to herbaceous plants, in order to facilitate cell wall penetration. In advance of mycelial invasion, oxalic acid permeates the host tissue, depletes calcium and others from cell walls, and causes visible necrotic lesions in herbaceous tissues, accompanied by the formation of calcium oxalate microcrystals (Dutton and Evans 1996).

### 3.5 Discussion of the $\text{KClO}_3\text{-HNO}_3\text{-H}_2\text{O}$ digest

As an alternative to the usual aqua regia digestion method, pressure digestion with potassium chlorate in dilute nitric acid was chosen. The method has been developed for the digestion of green plants but can be used for all kinds of food, and permits to start with 1 g of sample, which is fourfold compared with the amount suitable for the digestion with conc. nitric acid, because the water present inside adsorbs  $\text{CO}_2$  and  $\text{NO}_x$ . The closed system permits complete recovery of, e.g., boron, sulfur and iodine, but also tin and antimony and other trace elements, which are usually obtained from aqua regia.

Total iodine, which was obtained from the  $\text{KClO}_3\text{-HNO}_3\text{-H}_2\text{O}$  digest, significantly correlated with S and B obtained from oxalate, and to a lesser extent with Ba-B-Na-Mg obtained from acetic acid, but not with main elements or essential cationic trace elements. Its main input to the soil is presumably from atmospheric precipitation, and not from fertilization, but much about the local ecological cycling is still unknown.

In case of tropical teak trees, just 25–55 % of P gets recycled by litterfall, and some P gets trapped in the wood. Among a lot of P fractions obtainable from the soils, the P contents of the leaves correlated best with total P, because the organic P reserves are meaningful as well, as they make 80–90 % in the tested substrates (Glaser and Drechsel 1992).

## 4 Conclusions

Simplification of conventional soil analysis is possible by sequential leaching with dilute acetic acid and acid ammonium oxalate. Use of the ICP-OES multi-element capabilities permits to determine nutrients, essential traces, anions (P, S, Si), and contaminants in one run. Substitution of aqua regia reflux by pressure digestion with a solution of  $\text{KClO}_3$  in dilute  $\text{HNO}_3$  permits the quantitative recovery of important trace elements, as well as of the nonmetals P-S-I. Total digestion with hydrofluoric acid is required to determine the basicity of the silicates. K, Na, Li, Sc, Y, Ti, and the rare earth elements are among the most immobile elements. For quality control with respect to leaching with dilute acetic acid, reference materials are available, which have been certified for six trace metals.

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