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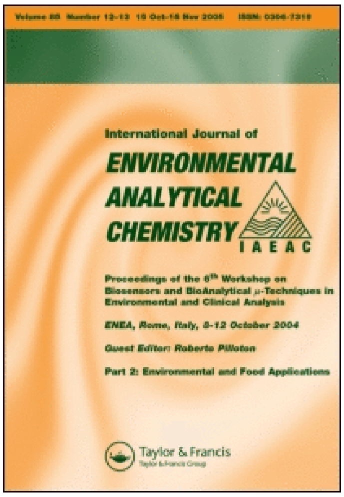

International Journal of Environmental Analytical Chemistry
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713640455

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To cite this Article Häni, Heinz(1990) 'The Analysis of Inorganic and Organic Pollutants in Soil with Special Regard to Their Bioavailability', International Journal of Environmental Analytical Chemistry, 39: 2, 197 — 208
To link to this Article: DOI: 10.1080/03067319008027697
URL: http://dx.doi.org/10.1080/03067319008027697

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Intern. J. Environ. Anal. Chem., Vol. 39, pp. 197–208
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THE ANALYSIS OF INORGANIC AND ORGANIC POLLUTANTS IN SOIL WITH SPECIAL REGARD TO THEIR BIOAVAILABILITY

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(Received 30 September 1989)

The most important inorganic pollutants in soil are the heavy metals. Problems related to the determination of the total and soluble content are discussed. Soluble contents are of interest in connection with studies about bioavailability. Because some of the heavy metals are essential for plant growth, most of the work about bioavailability has been done in the field of plant nutrition. Much less is known about the situation in polluted soils.

It was shown that neutral salt solutions which do not really change the pH of soil during the extraction procedure are best suited to define thresholds of excess. This is in contrast to much stronger extractants like EDTA or DTPA often proposed for the analysis of soils which are deficient in trace elements.

With three sets of experiments the correlation between the contents of cadmium, copper, nickel and zinc extracted by 0.1 M $NaNO_3$ (as an example of a neutral salt solution) and the plant response (phyto- or zootoxicity) are shown:

—pot experiments using soils which were contaminated by metal salt solutions

—pot experiments using soils from contaminated areas

—field studies in polluted areas. In these studies the aspect of heavy metal leaching was also considered.

The results were converted to indicative values in the Swiss Ordinance of Pollutants in the Soil. These indicative values derived from plant reactions were checked by the carbon mineralisation as an example of a soil microbiological process.

As it was found that organic pollutants are not easily taken up by plant roots the problem of bioavailability is much less important. However, the biodegradation and formation of metabolites has to be considered.

KEY WORDS: Heavy metals, soil, bioavailability, plant nutrition, phytotoxicity, zootoxicity, soluble content, total content.

1. INTRODUCTION

In the analysis of inorganic pollutants in soil one must distinguish between the determination of the total content as a measure of the degree of soil contamination and a soluble content which is of interest in relation to bioavailability or leaching into the groundwater. As it is not easy to achieve a complete dissolution of the soil, procedures with different acids are often chosen for routine work in order to approximate the total content. In this paper the dissolution strength for heavy

Table 1 Figures from glasshouse experiments: Ranges of heavy metal contents (total and soluble) which lead to phyto- (zinc and copper) or zootoxic concentrations in a given test plant in different soils. Zn, Cu: red clover (Trifolium pratense L.); Cd: rye grass (Lolium multiflorum Lam.) From Häni and Gupta[3]

		Soluble soil content (ppm)				
Element	*Total soil content (ppm)*	*NH_4OAc pH 4.8*	*NH_4OAc+ EDTA pH 4.65*	*DTPA pH 7.3*	*$NaNO_3$ 0.1 M (ppm)*	*Plant content*
Zn	70–218	7–30	—	7–30	0.8–1.3	200
Cd	0.8–4	—	0.3–1.2	—	0.06	1
Cu	83–127	3.5–12	—	6.6–32	1–2	20

metals of nitric acid proposed in the Swiss Ordinance on Content of Pollutants in the Soil (1986) is shown.

The earliest work on soluble contents was done with normal uncontaminated soils in the field of plant nutrition. Sillanpää[1] e.g., defines critical deficiency levels for copper and zinc extracted with acid ammonium acetate-EDTA (pH 4.65):

–copper < 0.8–1.0 ppm

–zinc < 1.0–1.5 ppm (+pH correction)

Attempts to set toxicity thresholds for heavy metals in polluted soils with the same or similar extractants (acid and/or complexing agent) produce a rather broad range (Table 1). As toxicity criterion the phyto- (copper and zinc) or zootoxic concentrations (cadmium) in a given test plant are used. Because it is difficult to define critical toxic levels for heavy metals in different soils, other much milder extractants like neutral salt solutions which do not really change soil properties during the extraction procedure (Table 1, $NaNO_3$ as an example of a neutral salt solution) were tried. In the Proceedings of a Seminar organised by the Commission of the European Communities, held in Münster,[2] it was concluded that neutral salt extractants provide the most promising chemical method for assessing bioavailability. Neutral salt solutions are used in sequential extraction procedures to determine metal ions bound in exchangeable form.[2] In the following, examples are given to support the significance of this mobile metal form in predicting biological effects. These findings were converted to indicative values of soluble (exchangeable) contents in the above mentioned Ordinance of Pollutants in the Soil.

In connection with organic pollutants the interest is not so much concentrated on the determination of soluble concentrations but rather on the biodegradation in soil. However, in relation to environmental consequences the question of plant uptake or leaching into the groundwater has also to be raised.

2. TOTAL CONTENTS OF INORGANIC POLLUTANTS

The use of nitric acid gives an approximation of the total content of heavy metals

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Table 2 The losses of soil materials (%) after extraction with 2 M HNO_3 of Swiss soils. From Hu Aitang and Häni[4]

Soil samples no.	*The losses of soil samples (% based on soil)*				*The losses of humus (% based on soil humus)*				*The losses of inorganic[a] part (% based on inorg. matter)*			
	100 °C	*70 °C*	*40 °C*	*18 °C*	*100 °C*	*70 °C*	*40 °C*	*18 °C*	*100 °C*	*70 °C*	*40 °C*	*18 °C*
1	23.1	17.6	11.8	9.5	67.8	39.3	30.8	21.3	18.1	15.2	9.7	8.2
2	20.8	13.7	7.1	5.4	83.6	57.0	29.8	17.5	16.2	10.5	5.4	4.5
3	13.8	12.1	5.4	4.5	83.2	57.6	29.1	28.2	8.8	8.8	3.7	2.8
4	14.3	10.2	5.7	4.3	77.9	46.1	29.0	8.7	11.2	8.5	4.6	4.1
5	15.7	10.5	6.2	6.0	79.1	48.1	25.7	3.4	12.1	8.4	5.1	6.1
6	30.8	24.9	20.5	17.3	78.8	47.6	24.1	15.9	26.5	22.8	20.2	17.4
7	8.2	5.2	3.3	3.3	76.7	45.7	34.7	8.7	6.7	4.3	2.6	3.2
8	30.8	26.1	19.5	18.6	77.2	48.8	26.4	20.6	26.0	23.8	18.3	18.4
9	40.7	31.9	21.2	19.4	62.8	44.1	13.4	17.7	32.4	27.4	24.1	20.0
10	20.6	16.8	12.0	11.3	73.5	46.3	30.1	18.4	17.7	15.2	11.0	10.9
11	7.8	5.3	2.3	2.5	68.4	46.0	55.3	28.9	7.3	5.0	1.9	2.3
Average	20.6	15.8	10.5	9.3	75.1	47.9	29.9	17.2	16.6	13.6	9.7	8.7

[a] By calculating

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in soil. The method is easy, reproducible and free of interferences in flameless atomic absorption (graphite furnace technique) which may be stressed as an important advantage compared to hydrochloric acid containing extracts.

Table 2 contains the results of the losses of soil materials (%) after extraction of 11 Swiss soils with 2 M HNO_3 at different temperatures. As can be seen from this table the overall average values of the losses of soil samples at 100 °C range from 8–40%. From most of the samples 10–20% were lost. In general the higher values, i.e., more than 20%, are found from soils containing $CaCO_3$ or a higher content of oxalate-soluble iron and aluminium. It can also be shown that almost 80% of the total humus was removed from the soils at 100 °C.

The percentage of free iron oxides and of oxalate-soluble iron and aluminium dissolved during the acid treatment were calculated on the base of their total content in the soils. The results are given in Table 3.

Ninety percent of oxalate-soluble iron and aluminium can be removed from the soil, while nearly 70% of free iron oxides dissolved in the range from 55 to 85%, with one exception, where only 11% of the total iron oxide is dissolved. In this sample the presence of goethite was recognized by X-ray diffraction analyses.

X-ray diffraction and infrared spectroscopy analyses on clay and silt fractions of the 11 soils showed the removal of amorphous materials (more intense X-ray lines) and the decomposition of chlorite after the treatment with 2 M HNO_3 at 100 °C. The other clay minerals like illite, montmorillonite and muscovite remained unchanged.

These findings illustrate that the extraction efficiency of 2 M HNO_3 varies remarkably from soil to soil. Especially a wide range in extractability, from 20–90% of the total, was found in the case of copper. For zinc the release percentages between soils vary from 50–80% and for nickel from 25–70%. The average

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Table 3 The percentages[a] of sesquioxides dissolved during the procedure with 2 M HNO_3 of Swiss soils[4]

Soil samples no.	*Free ironoxide*				*Oxalate-soluble (at 100°C)*	
	100°C	*70°C*	*40°C*	*40°C/100°C*	*Fe*	*Al*
1	86.2	77.7	60.9	70.7	92.7	84.8
2	67.9	37.5	25.3	37.2	87.2	94.7
3	77.9	57.8	32.9	42.3	93.0	94.8
4	67.8	50.0	31.4	46.3	89.2	88.2
5	63.8	46.3	39.0	61.2	88.0	96.1
6	11.0	3.7	1.9	17.5	77.2	83.0
7	60.7	47.0	36.3	59.9	86.2	91.7
8	73.1	51.9	36.8	50.3	91.7	91.7
9	78.1	63.4	52.0	66.7	90.7	94.5
10	55.9	30.4	22.6	40.4	86.5	86.8
11	61.1	33.0	15.2	24.8	87.1	88.9
Average	64.0	45.3	32.2	—	88.1	90.5
Average excluded No. 6	69.3	49.5	35.2			

[a] Based on their total content in soils.

Table 4 Dithionite soluble copper, lead, zinc and nickel of Swiss soils

Soil samples No.	*Amounts in µg/g*				*% based on total content*			
	Cu	*Pb*	*Zn*	*Ni*	*Cu*	*Pb*	*Zn*	*Ni*
1	0.8	0.6	9.4	0.4	1.8	2.3	9.6	0.9
2	1.2	1.3	46.5	1.5	3.2	3.2	27.9	1.1
3	0.5	0.8	28.9	0.7	1.3	3.0	34.5	2.1
4	0.7	0.9	19.4	0.7	1.8	2.2	19.7	1.4
5	1.2	1.2	19.5	0.9	3.6	5.7	30.7	4.0
6	0.5	1.3	69.0	1.7	1.8	4.5	49.5	3.7
7	0.6	0.6	6.1	0	2.4	3.7	11.1	0
8	0.8	1.3	32.9	0.2	2.3	3.9	34.2	0.7
9	1.4	1.0	9.6	0.2	3.4	5.1	15.8	0.5
10	0.6	1.5	49.0	0.5	1.7	3.6	40.2	0.8
11	0.5	0.9	17.7	0.9	1.2	6.7	24.7	1.9
Average	0.8	1.0	28.0	0.7	2.2	4.0	27.1	1.6

percentages of copper, zinc and nickel resulted in 59, 68 and 58% of the total, respectively.

The difference between the HNO_3- and total content may be mainly explained by the fraction bound in primary and clay minerals. With regard to environmental research these fractions are of minor significance. However, the iron oxides which are incompletely dissolved in 2 M HNO_3 and which are of prime importance in soil formation processes merit a special interest.

According to Table 4 only zinc has a dominant amount tied up with iron oxides. It accounts for nearly one third of the total zinc in soils over a range from 10–40%, and in one sample up to 50% of the total. The amounts of copper, lead and nickel held by iron oxide are quite small, only 1–5% of the total content. It

Table 5 The percentage of lead, cadmium, copper and zinc dissolved from Swiss soils in 2 M HNO_3 compared to aqua regia (= 100%)

Soil depth (cm)	*% lead*	*% cadmium*	*% copper*	*% zinc*
0–20	97	121	94	64
0–20	105	96	100	73
0–20	105	100	94	75
20–40	118	38	104	61
20–40	127	58	75	59
20–40	118	43	77	62
20–40	108	52	86	52
40–60	125	75	79	47
40–60	110	50	71	40
60–80	129	115	67	46
>80	69	47	69	36
Average	110	72	80	56

would therefore be interesting to look at the solubility of zinc in an iron oxide dissolving solvent like aqua regia.

From Table 5 the important difference in the solubility of zinc in these two solvents can be seen. The other elements lead, cadmium and copper show much smaller differences. This may indicate that primary and clay minerals are not much more attacked by aqua regia than by 2 M HNO_3.

The differences are most pronounced in deeper soil horizons. This special behaviour is also expressed by the strong temperature dependence of the solubility (Figure 1). These findings have to be considered in environmental studies. The higher solubility of metals in aqua regia compared to HNO_3 is mainly due to oxide forms of very low solubility (zinc occluded in iron oxides or chromium as component of chromium oxide).

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3. SOLUBLE CONTENTS OF INORGANIC POLLUTANTS

In Figure 2 the cadmium content of rye grass grown on three different soils in a pot experiment is compared with the total (2 M HNO_3) and the soluble (0.1 M $NaNO_3$) soil content. As can be seen from this figure three straight lines, the slope of which depends on the soil properties (pH, CEC etc.), are obtained in case of total soil content whereas one more or less straight line results in case of soluble content. This means that the cadmium content of a given test plant grown on different soils can be assessed by just one soil value. Similar results are obtained for zinc, copper and nickel.

In these pot experiments the heavy metals were added in form of their salts to the soils. An approach which comes nearer to practice is achieved by realizing pot experiments with soils from polluted areas. Figure 3 shows an example of radish tubers grown in soils contaminated by zinc from a zinc coating plant (1), a motorway (2), compost (3) and sewage sludge (4). Again, the plant content corresponds with the soluble (0.1 M $NaNO_3$) and not with the total content.

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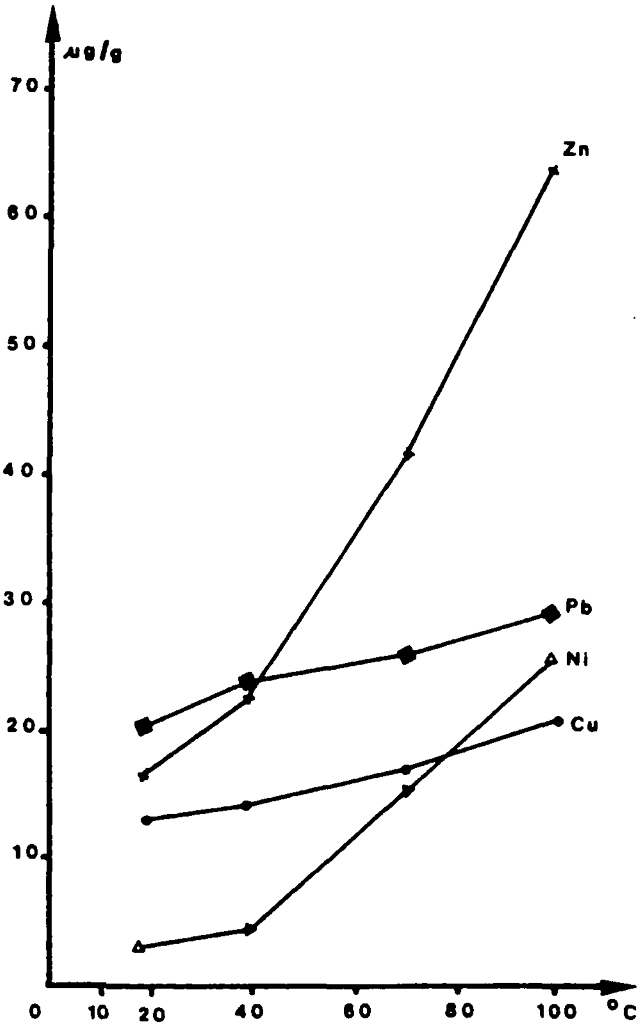

Figure 1 Dissolved amounts of copper, lead, zinc and nickel by 2 M HNO_3 at different temperatures (overall average of 11 top soils).[4]

Vineyard soils are mainly contaminated by copper. Although total contents often exceed the critical value considerably, the soluble soil concentrations remain within the tolerated range. This harmonizes with the analysis of vine leaves, because the measured contents of 11.3–17.9 ppm are still below the phytotoxic threshold of 20 ppm.

Figure 4 is a presentation of a field study. In this field the growth of maize and beetroots was seriously disturbed or even reduced to nil. By only considering the total contents of copper and zinc one would not expect such pronounced toxic effects. These are explained by the high soluble contents which in case of zinc exceeds the indicative value in the Swiss Ordinance on Content of Pollutants in the Soil by more than 20. Zinc belongs under acid conditions (pH 5 in the layer

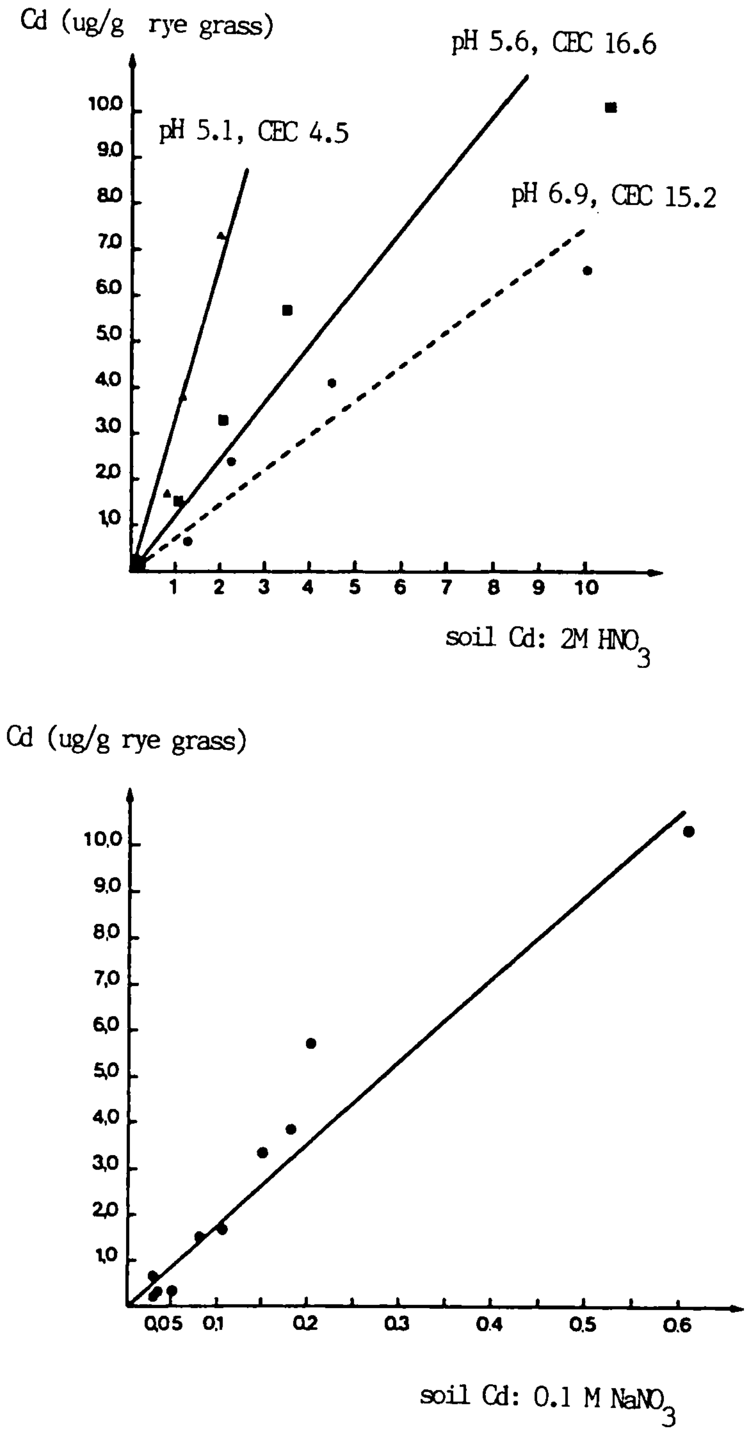

Figure 2 Cadmium content in rye grass as function of 2 M HNO_3- and 0.1 M HNO_3-soluble cadmium in three different soils.[5]

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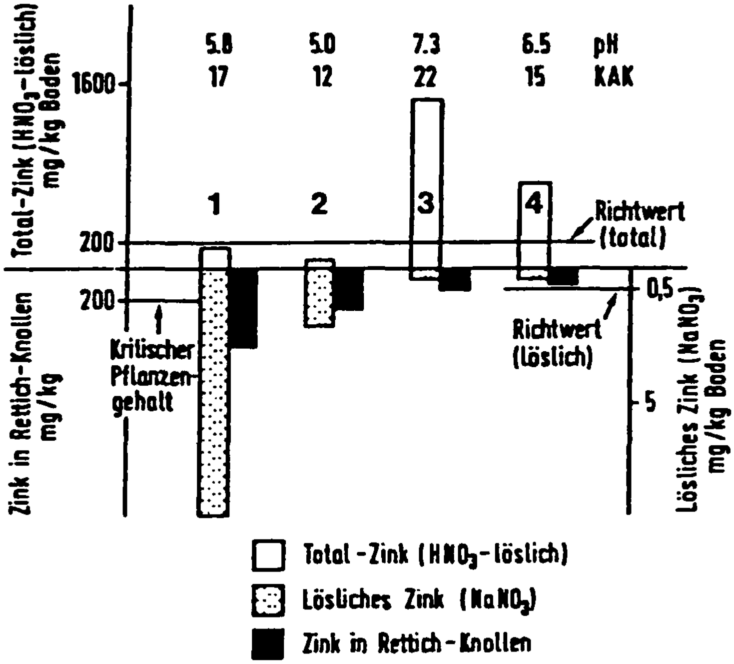

Figure 3 Effect of total (2 M HNO_3) and soluble (0.1 M HNO_3) zinc contents in polluted soils on the zinc content in radish tubers.[6]

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0–20 cm) to the most mobile elements which can be seen from the fact that it is, contrary to copper, leached to a depth of 60 cm within the soil profile.

More examples of plant damages which could be explained by increased soluble contents of heavy metals (mainly zinc and copper) exist from the advisory work of our research station.

4. ORGANIC POLLUTANTS

A field investigation was carried out to obtain a better insight into the fate of residues of detergent-derived organic pollutants and PCBs in sludge amended soil. The detergent-derived chemicals are LAS (linear alkylbenzene sulphonates) and NP (Nonylphenol, a highly toxic de-etoxylation intermediate of nonylphenol-polyethoxylates).

In a one-year study (May 1986 to April 1987) samples of sludge amended soils were collected from an experimental plot at Liebefeld research station. Since 1976, this plot had received a total of 142 tons (d.w.) per ha of digested sewage sludge (average application rate 13.5 tons per ha and year, which is approximately six times the normal application rate in Switzerland).

Figure 5 shows the concentration versus time profiles of LAS, NP and PCBs.[7] It appears that all contaminants undergo a disappearance, presumably due to biodegradation. However, all of the studied chemicals demonstrated some level of

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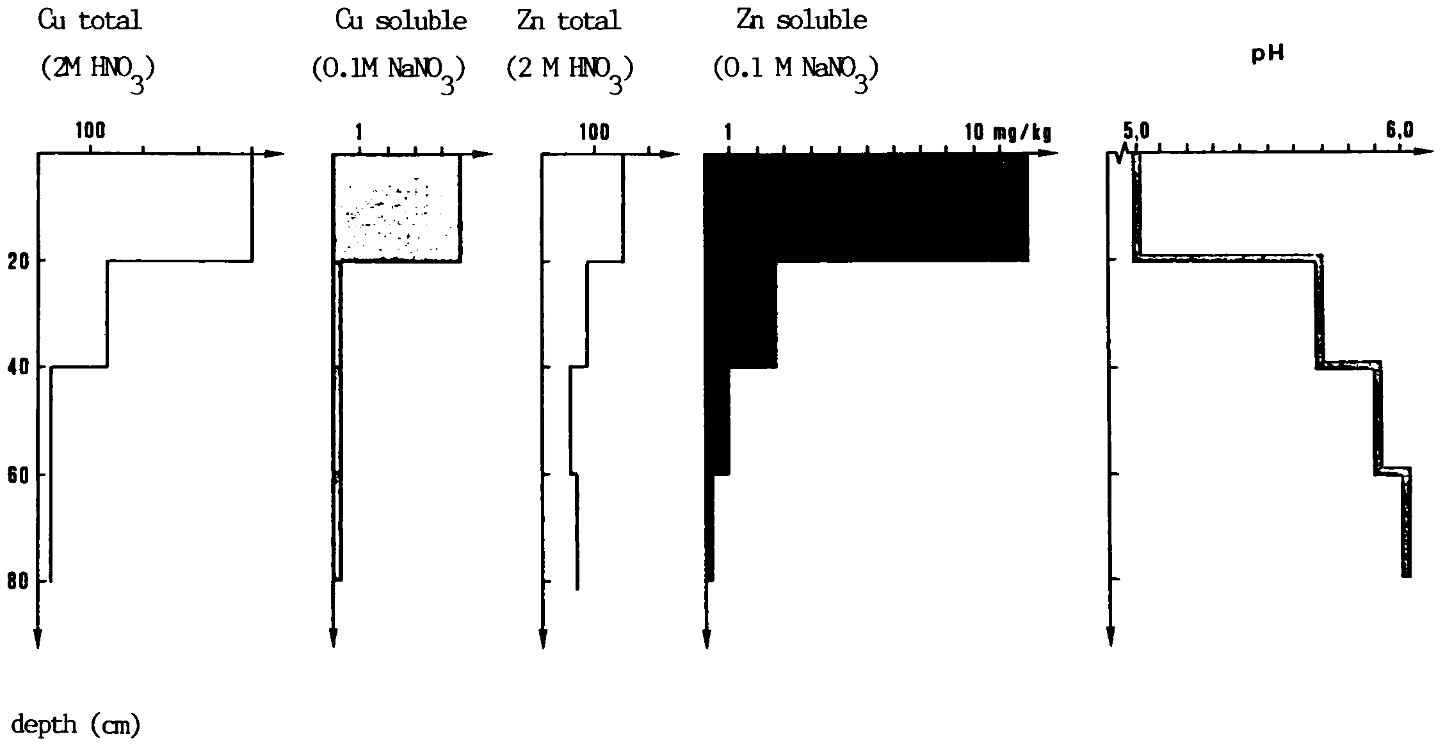

Figure 4 Distribution of total and soluble metals (copper, zinc) within the profile of a polluted acid soil.

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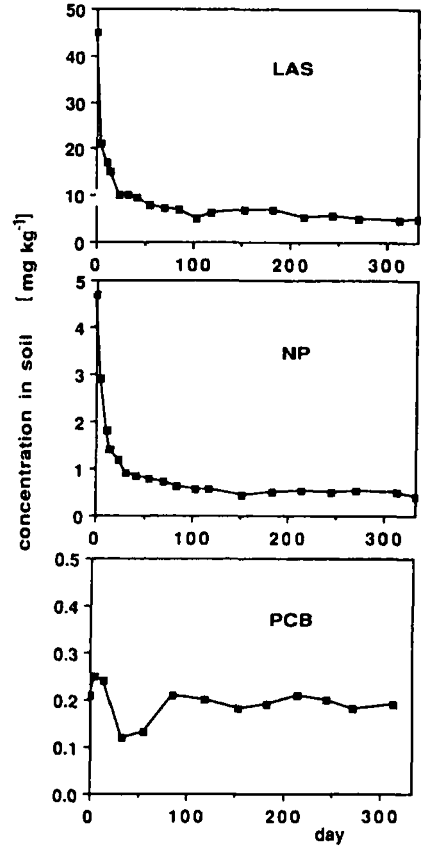

Figure 5 Concentrations of linear alkyl-benzene sulphonates (LAS), nonylphenol (NP) and polychlorinated biphenyls (PCB) in sludge-amended soil. The results were measured during the course of one year after the last sludge application.

persistance over the study period (330 days). Residual mean soil concentrations for LAS and NP were 5 and 0.5 mg.kg^{-1}, respectively. The observations can possibly be explained by the competition between biodegradation and sorption on and into soil particles. Based on the behaviour of these chemicals in a sewage treatment plant, it can be inferred that biodegradation occurs in the aqueous phase and/or on particle surfaces.[8] Immediately following the application of the sludge to the soil, the examined detergent-derived chemicals disappear quickly (initial period) because they are readily available to the soil microorganisms. The residues are slowly incorporated into the soil particles and/or more strongly bound to the soil organic fraction making them less available (transition period) or unavailable (final period) to biodegradation.

The PCBs comprised mainly the more chlorinated compounds (4, 5, 6, 7 and 8 chlorines/molecule) and showed little, if any, degradation.

It is presumed that the residual concentrations would only slowly decrease over the following years. Further investigations are needed to evaluate the environmental risk of such residues. Entrance into and behaviour in the food chain through

Table 6 Indicative values in the Swiss Ordinance on content of pollutants in the soil (1986)[a]

Pollutant	*mg/kg dry soil*	
	Total content (*2 M HNO$_3$*)	*Soluble content* (*0.1 M NaNO$_3$*)
Pb	50	1.0
Cd	0.8	0.003
Cr	75	—
Co	25	—
F	400[b]	25[c]
Cu	50	0.7
Mo	5	—
Ni	50	0.2
Hg	0.8	—
Tl	1	—
Zn	200	0.5

[a]The methods are described in an annexed instruction.
[b]NaOH-fusion.
[c]Water-soluble.

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soil ingestion by animals and leaching into the groundwater are examples of such concerns.

In another study it was investigated if PCBs, polycyclic aromatic hydrocarbons (PAH) and phtalates are taken up by test plants through their root systems.[9] As test plants rye grass and rape were used in sand cultures and pot experiments. The results clearly show that the most important accumulation of the micropollutants finds place in the roots (ad- or absorption?). However, a transport to aerial parts inside the plant can be excluded.

5. SWISS ORDINANCE ON CONTENT OF POLLUTANTS IN THE SOIL

In this Ordinance indicative values for 10 heavy metals and fluorine are contained (Table 6). In the introduction it was stated that the indicative values base on total and soluble contents. Because of not yet existing experiments soluble indicative values for chromium, cobalt, molybdenum, mercury and thallium are still missing.

Further, it was also mentioned in the introduction that one has to distinguish between phyto- and zootoxicity. For the five heavy metals with existing soluble values only in case of cadmium the criterion of zootoxicity has been used.

Figure 6 shows the influence of the soluble heavy metal content on the carbon mineralisation as an example of a soil microbiological parameter.[10] It appears that cadmium, nickel and zinc are safe in relation to this microbiological parameter, whereas the soluble copper content should lie below 0.3 ppm because 0.5 ppm already caused an inhibition of soil respiration of 20%.

As a concluding remark one has to be aware that indicative values in soil can never be an absolute measure. Their interpretation is made difficult by the fact that it is not easy to choose from the many plants and microbiological processes

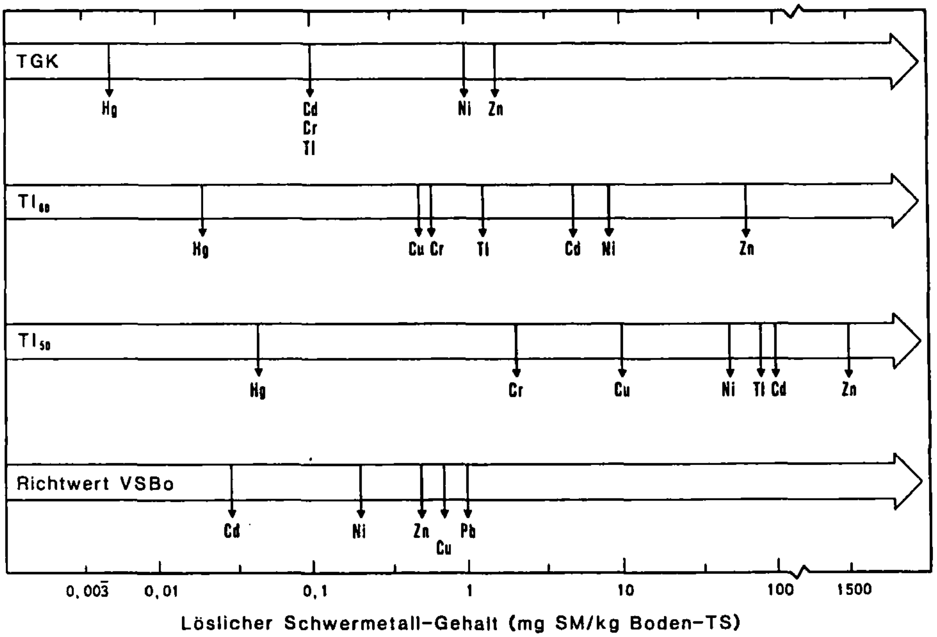

Figure 6 Comparison between the indicative values of soluble heavy metals (0.1 M $NaNO_3$) in the Swiss Ordinance on Content of Pollutants in the Soil and the critical values of influence on soil respiration (TGK: start of inhibition; Tl 80: inhibition of 20%; Tl 50: inhibition of 50%).

the ones which are of most ecological importance. However, soil contents close to the indicative values may be an indication of a situation which is different from a natural one. It has to be looked at for the reasons of this anomaly.

It remains the question of missing indicative values for organic pollutants. The opinion in Switzerland is that these pollutants which contrary to heavy metals do not occur naturally in soil cannot be regulated by indicative values. The elimination of these substances at the source is even more important than for the heavy metals.

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