Comparison of in situ trace element concentration of soil water with concentration in aqueous extracts as a background concentration level

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Abstract

This study compares concentrations of trace elements measured in soil water samples with concentrations determined in batch experiments as a background concentration level. One batch experiment was conducted at a liquid/solid (LS) ratio of 5 L/kg with samples specifically adjusted for ionic strength using $Ca(NO_3)_2$ as the background electrolyte. The other is an aqueous extract at a LS ratio of 2 L/kg. Both batch experiments show similar results in their ability to estimate in situ concentrations. The results illustrate that for most trace elements the concentrations, which are determined in extracts, show statistically significant relations (p-value <0.01) with those measured in in situ soil percolation water. The level of fit measured by R^2 increases in the following order Pb, Cr<<As<Cu, Zn, Sb, Mo, V< Cd, Ni, Co. Low concentration levels in situ concentrations were underestimated by both extraction methods and vary about two orders of magnitude around the regression mean.

Key Words

Batch experiment, liquid/ solid ratio 2 L/kg, background electrolyte $Ca(NO_3)_2$, desorption, risk assessment.

Introduction

In the upcoming revision to the German Federal Soil Protection and Contaminated Sites Ordinance (BBodSchV) the aqueous extraction at a liquid/solid (LS) ratio of 2 L/kg according to DIN 19529 is suggested to be the reference standard for contaminant related risk assessment. Another method of contaminant related risk assessment in soil and groundwater protection is the model-based soil prediction of contaminant migration, which employs overall substrate sorption isotherms. These isotherms were derived from data gained by batch experiments at a LS ratio of 5 L/kg using $Ca(NO_3)_2$ as the background electrolyte to adapt the natural ionic strength of each sample to compensate for the wider LS. For both extraction methods the same trigger values apply. In addition the German Working Group on water issues (LAWA, 2004) plans to make the trigger values of the soil-groundwater pathway be those with insignificant thresholds (GFS) installed by the German Working Group on water issues (LAWA 2004). The GFS are up to ten times smaller than the trigger values of the BBodSchV. Bearing in mind the natural heterogeneity of the soil and soil parameters, the following questions arise: (1) Is it possible to compare in situ concentrations of trace elements with those measured in solutions from batch experiments? (2) Are there significant differences in the results of the different batch methods? (3) What is the accuracy with which we can estimate trace element concentrations in the soil water by batch experiments at the concentration level of the GFS?

Methods

The sampling sites were selected to determine regional representative background concentrations of trace elements in soil percolation water. Each pair of samples, liquid and solid phase, has been taken at the transition of the unsaturated to the saturated zone. The sample pairs originate from 37 sites in Northern Germany. The total population consists of 270 sample pairs, where soil sediment and soil water were sampled at exactly the same depth. We took samples from soils of the three major parent material classes of Northern Germany: sand, boulder clay and loess. Within the class of sand we categorized three different groups of land use: arable land, grassland and forest. The samples thus show a wide range of pH values (<3 to >7), particle size distributions and ionic strength (electrical conductivity ranges from <100 $\mu S\ cm^{-1}$ to >3000 $\mu S\ cm^{-1}$). The soil water was taken with sorption free suction cups with an internal sample collector at the transition of the unsaturated to the saturated zone (Duijnisveld *et al.* 2008). Table 1 shows the medians and the 25th and 75th percentiles of the trace element concentrations measured in soil percolation water as well as the GFS. The data show that the trace element concentrations are in the same order of magnitude as the GFS.

Table 1. Median, 25th and 75th percentile of in situ measured trace element concentrations and insignificance thresholds (GFS).

Element	N	25th percentile	Median	75th percentile	GFS
		µg/L			
As	158	0.35	0.50	0.91	10
Ba	197	30.84	44.00	63.27	340
Cd	265	0.03	0.09	0.43	1
Co	270	0.18	0.53	3.41	8
Cr	269	0.29	0.60	1.28	7
Cu	269	1.20	3.00	6.80	14
Mo	258	0.03	0.11	0.39	35
Ni	270	1.10	3.02	8.99	14
Pb	207	0.13	0.32	0.92	7
Sb	270	0.06	0.14	0.33	5
V	265	0.16	0.41	2.18	4
Zn	240	4.13	14.09	70.35	58

Trace element concentrations were analysed using inductively coupled plasma mass spectrometry (ICP-MS). The properties pH and electrical conductivity (EC) were analysed on site for the liquid samples. The pH of the soil sample was measured both in H_2O and $CaCl_2$, and EC was measured in an aqueous (LS ratio 5 L/kg) extract (results not shown). The aqueous extraction at a LS ratio of 2 L/kg was conducted according to DIN 19529 with an equilibrium time of 24 h. The mixtures were shaken in an end-over-end shaker at 4-5 rpm. For the extraction at a LS ratio of 5 L/kg the EC of the liquid reagent was adjusted using $Ca(NO_3)_2$ as the background electrolyte and it was adjusted to the EC measured in the corresponding soil water sample. The mixture was shaken for 48 h at 20 rpm (Heidkamp, 2005; Utermann *et al.* 2005). Both kinds of extracts were centrifuged before filtration and being stabilized by acidifying the filtrate with 1% HNO_3 for trace element analysis in the ICP-MS. In the remaining supernatant we measured pH and EC of each sample. Due to the $\log_{10}$-normal distribution of the data, regression analysis has been calculated with $\log_{10}$-transformed data.

Results

For most elements regression analysis showed statistically significant, and more or less distinct relationships, between trace element concentrations measured in soil water and in extracts. Table 2 shows the regression coefficients of both comparisons. Only Pb concentrations in the LS ratio 2 L/kg extract showed no statistically significant relationship to its in situ response. Pb is known to be hardly soluble in aqueous solutions. Also the coefficient of determination for the relationship in situ vs. LS 5 L/kg of $R^2 = 0.37$ does not allow inference at a higher level of accuracy. Even poorer results, although statistically significant, were calculated for Cr.

The R^2 increased in the following order for comparison of in situ vs. LS 2 L/kg: Pb, Cr<<As<Cu, Ni, Zn, Co, Sb, Mo, V< Cd. The order slightly changes for the relation between trace elements determined in situ and in LS 5 L/kg extracts: Cr<< Sb, As, Pb< Cu, Mo < Zn, V, Cd < Ni, Co. These results are in good agreement with the order of mobility of the trace elements (Brümmer *et al.* 1986). The highest regression coefficients show that no more than 60-70% of response variation of the in situ determined trace element concentration can be "explained" by the concentrations measured in the extracts (Table 2). Table 2 also shows that the R^2 in the regressions with the trace element concentrations measured in LS 5 L/kg are slightly higher. This may be mainly due to methodological artefacts, such as the well fitted ionic strength (EC R^2=0.99), different velocities of end-over-end shaking or the longer equilibrium time of 48 h instead of 24 h.

Table 2. Adjusted regression coefficients with p-value<0.01 for the relationship between pH, EC or trace element concentrations measured in situ and in extracts of LS ratios of either 2 L/kg or 5 L/kg.

		pH	EC	As	Cd	Co	Cr	Cu	Mo	Ni	Pb	Sb	V	Zn
R^2 adj	in situ~ LS 2 L/kg	0.67	0.36	0.34	0.5	0.45	0.04	0.4	0.46	0.43	-	0.46	0.46	0.45
R^2 adj	in situ ~ LS 5 L/kg	0.73	0.99	0.37	0.58	0.63	0.18	0.42	0.47	0.62	0.37	0.36	0.59	0.57

Figure 1 shows that the variance of the data is about one order of magnitude higher or lower than the regression mean. This variation can be caused by various effects. Soil as a part of the natural environment is exposed to several influences while developing, and, therefore, is a heterogeneous compartment. Drying and re-moistening the soil samples may influence the solubility of the trace elements, as well as aging effects due to different storing times (Strawn, 1999 in Selim, 1999; Jones and Edwards, 1993). The variation between the pH-value in situ measured and in extracts, which is also apparent in the moderate R² (Table 1), may also contribute to a varying solubility.

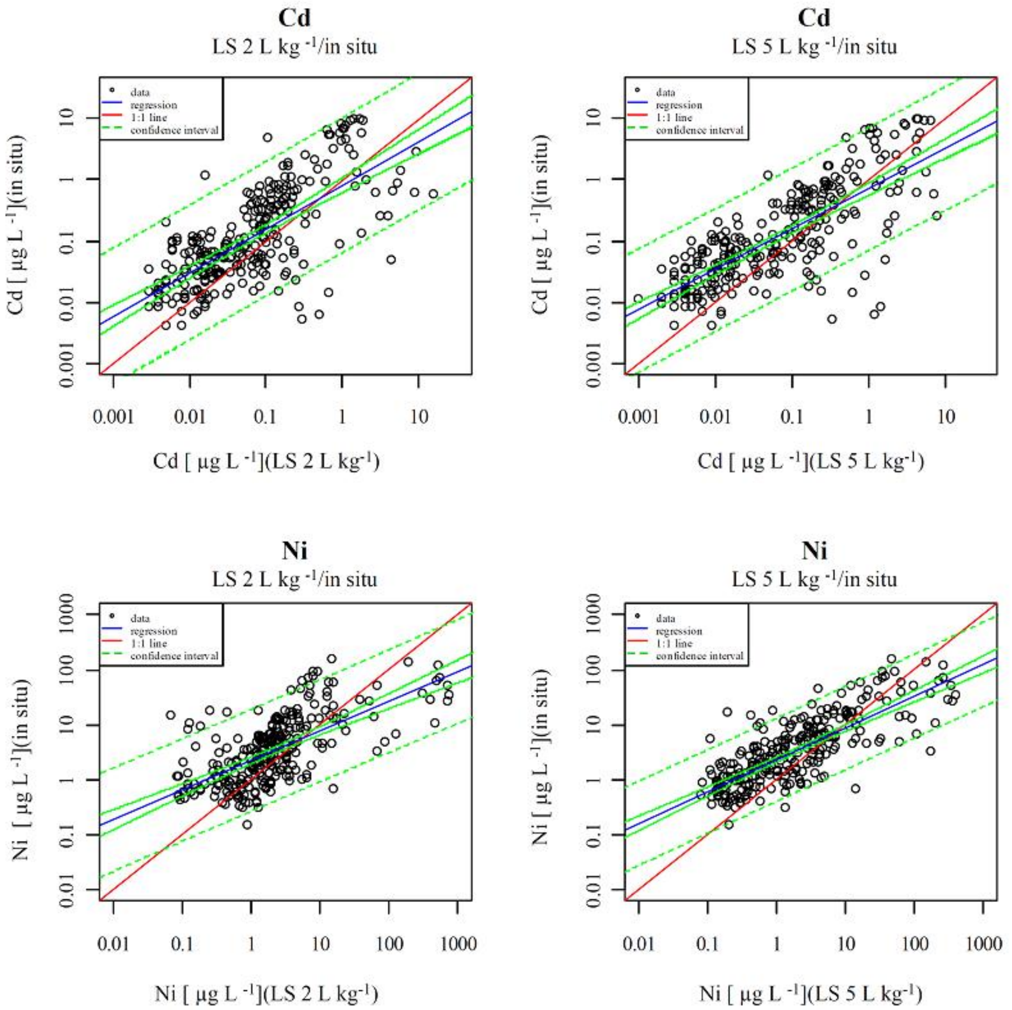

Figure 1. Regression plots of Cd and Ni concentrations in extracts related to corresponding in situ concentrations in soil percolation water (○ = data, red line = 1:1 line, blue line =regression, dashed green lines = confidence interval).

As expected, especially at lower concentration levels, the in situ trace element concentrations are underestimated by the concentration measured in the extracts. This causes the regression line to deviate from the 1:1 line. The dilution effect is due to the wider LS range than in situ. However, both extracts underestimate the concentrations at a similar level, which shows the effect of ionic strength adjustment.

Conclusion

The study shows, in principle, that both batch methods, aqueous extracts with LS ratio 2 L/kg and extracts with adjusted ionic strength at a wider LS ratio of 5 L/kg using $Ca(NO_3)_2$ as a background electrolyte, are equally applicable to estimate in situ concentrations. Both methods of aqueous extraction show similar results. However, the results also show that data gained by batch experiments should primarily be used for exploratory in opposition to detailed risk assessment. Especially at the critical low concentration levels (of GFS), in situ concentrations are underestimated. Thus, the relation between in situ measured concentrations and concentrations measured in extracts is not one-to-one. Additionally, the data from batch experiments exhibit a variance of about two orders of magnitude. In order to confirm statistically exceeded thresholds, in situ concentrations must be at least one order of magnitude higher than the GFS.

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