# Highlighting processes involved in mobility and bioavailability of zinc within contaminated substrates: Multiple approaches

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## Abstract

Zinc is an essential element for plants but excessive uptake can lead to (phyto) toxicity and contamination of the foodweb. Mobility and bioavailability depend on zinc speciation in solid and liquid phases. Considering the importance of solid phase, three contaminated substrates were studied: two soils and a slag heap. The relative amounts of exchangeable zinc were estimated by $MgCl_2$ extraction. We investigated chemical composition of solution collected *in situ* using zero-tension lysimeters. Furthermore, in order to complete the description of the substrate-plant system, zinc concentrations were measured in plants growing in the field. Zinc mobilization was determined by substrate-solution equilibrium and thus exchange processes. Importance of exchange processes was confirmed by the positive correlation between proportion of zinc leached and proportion of exchangeable zinc. Finally, zinc in solution and exchangeable zinc were positively correlated with plant uptake and transfer coefficient. As a general conclusion, exchange processes played a crucial role in mobility and bioavailability.

## Key Words

Exchangeable zinc, substrate-solution equilibrium, divalent competition, ph, predictive equation, chemical assessment.

## Introduction

Due to the past metallurgical industry in Belgium, zinc is one of the country's main inorganic pollutants. Potential contamination of foodweb or hydrological system by heavy metals motivated researchers to study their mobility and bioavailability (e.g. Marseille *et al.* 2000; Sterckeman *et al.* 2000; Chaignon and Hinsinger, 2003; Impellitteri *et al.* 2002; Ettler *et al.* 2007; Schwab *et al.* 2007). It is well-known that solid phase and soil parameters such as pH, redox conditions and ligands or competitive cations concentrations impact on mobility and availability of heavy metals. Therefore, in addition to total concentrations, solid and liquid phases have to be characterized to predict the mobility or the bioavailability of zinc and, consequently, potential risks.

Numerous methods have been developed to describe zinc bound to solid phase. Chemical methods such as single or sequential extractions give information about fractionation of zinc between bearing-phases. The latter can be identified by X-ray diffraction, electronic microscopy with microprobe and other physical methods. Previous studies have shown that exchangeable zinc was the most important labile form and its determination was useful to predict zinc mobility and bioavailability (e.g. Ettler *et al.* 2007; Menzies *et al.* 2007; Burgos *et al.* 2008). In the field, zero-tension lysimeters are the easiest and cheapest device to collect gravity water.

The aim of this study is to highlight processes controlling zinc mobility in order to identify the essential parameters to predict its mobility and availability. Considering the importance of solid phase, we choose three contrasted substrates – two soils contaminated by aerial fallout and a slag heap – presenting different characteristics.

## Materials and methods

### *Substrates characterization*

Two soils contaminated by aerial fallout (Prayon, Belgium) – a calcareous soil (CaS) and a shale-derived soil (ShS) – and a slag heap (SH) (Angleur, Belgium) were chosen (Table 1). Depending on the cover type, three stations were identified on the slag heap: bare (BSH), under *Armeria maritima* (ASH) and under the grass *Agrostis tenuis* (GSH). In slag heap, organic-horizons were identified thanks to visual and textural characteristics and organic matter contents. Sampling of organic horizon (designate as O or 0 in soils and slag heap respectively) of all substrates and organo-mineral horizon Ah1 (A) of soils only was performed in November and December 2005. Organo-mineral horizon samples (A) were air-dried and organic horizon samples (O and 0) were stored at 4°C after removing roots without drying . Fine earth fraction was obtained by dry sieving (< 2 mm).

**Table 1. Substrates characterization.**

| Substrates | Horizons | Depth | $C_{org}$[1] | pH-$H_2O$[2] | Exchangeable bases $_{(exch)}$[3] | | | | | CEC (pH 7)[3] | $Zn_{tot}$[4] |
|---|---|---|---|---|---|---|---|---|---|---|---|
| | | | | | Ca | K | Mg | Na | Zn | | |
| | | cm | % | | ---------- cmol$_c$/kg ---------- | | | | | cmol$_c$/kg | mg/kg |
| Ca-S | O | 0-7 | 11.05 | 6.40 | 4.65 | 0.32 | 0.25 | 0.18 | 24.32 | 22.65 | 74800 |
| | A | 7-17 | 2.46 | 7.05 | 11.30 | 0.50 | 0.39 | 0.03 | 6.16 | 18.21 | 9700 |
| Sh-S | O | 0-6 | 21.65 | 4.78 | 16.77 | 0.45 | 1.38 | 0.12 | 3.37 | 37.96 | 7400 |
| | A | 6-12 | 2.66 | 5.35 | 3.20 | 0.24 | 0.27 | 0.03 | 1.12 | 13.41 | 2200 |
| BSH | 0 | 0-7 | 4.05 | 7.34 | 5.72 | 0.17 | 0.22 | 0.01 | 6.76 | 11.43 | 54800 |
| ASH | 0 | 0-7 | 14.91 | 6.72 | 9.51 | 1.81 | 1.36 | 0.11 | 48.92 | 44.72 | 52900 |
| GSH | 0 | 0-7 | 8.53 | 6.55 | 6.30 | 0.20 | 0.35 | 0.08 | 20.67 | 29.61 | 65600 |

[1] Organic carbon content (Corg) was determined using the Walkley and Black method.

[2] pH was measured in solid:water suspension (1:5).

[3] Exchangeable cations (Ca, K, Mg, Na and Zn) concentrations and cation exchangeable capacity pH 7 (CEC) were determined according to the Metson method ($NH_4AcO$).

[4] Zinc concentration was measured by ICP-AES (Thermo Jarrell Ash Iris Advantage) after calcination at 450°C and tri-acid digestion ($HNO_{3conc}$, $HF_{conc}$ and $HClO_{4conc}$).

*Exchangeable zinc*

1 g of substrate (fraction < 2 mm) was agitated with 8 ml of $MgCl_2$ 1N for one hour. Extractions were replicated two or three times on each sample. Zinc concentration was measured by ICP-AES after centrifugation (10 000 rpm) and filtration (0.45 µm).

*Collect and analysis of substrate solutions*

*In situ* gravity solutions were collected using zero-tension lysimeters (adapted from Titeux 2005) buried in triplicates under organic horizon of each substrate and under organo-mineral horizon of soils only. After filtration (0.45 µm), we determined cations (ICP-AES), anions (HPLC-Dionex) and dissolved organic carbon (DOC) (Dohrman DC-180) concentrations. Four collecting campaigns were performed under 0 horizon of slag heap and 8 under O and A horizons of soils.

*Shoot sampling and analysis*

Shoots of plants growing on the different substrates were randomly sampled and zinc concentrations were measured by ICP-AES after tri-acid digestion (3ml $HNO_{3conc}$, 5ml $HF_{conc}$ and 5ml $HClO_{4conc}$).

## Results and discussion

*Zinc in solution*

In soils, after passing through A horizon, release of zinc ($Zn_{liq}$), calcium ($Ca_{liq}$) and DOC (Table 2) decreases because substrates and solutions equilibrated. Adsorption processes occurred in A horizons while in O horizons zinc and calcium were desorbed, processes involving weakly bound elements, probably exchangeable zinc.

According to Ettler *et al.* (2007), mobile zinc could be evaluated by exchangeable zinc extraction with $CaCl_2$. Percentage of leached zinc (Table 2), defined as the ratio between quantity of leached zinc and quantity of zinc in horizons above lysimeter, is well-correlated with percentage of zinc extracted with $MgCl_2$ under agitation ($Zn_{MgCl2}$) ($r^2$=0.64, n=7) and with pH of substrates ($r^2$=0.78, n=7). These results confirmed both the importance of exchangeable zinc, and thus exchange processes in mobilization of zinc but highlighted also a pH effect. The highest mobility of zinc in ShS could be explained by its larger proportion of exchangeable zinc and its lower pH.

Moreover, $Zn_{liq}$ is positively correlated with $Ca_{liq}$ ($r^2=0.77$, n=124) and with DOC ($r^2=0.60$, n=124), as well as $Ca_{liq}$ with DOC ($r^2=0.84$, n=124). These results indicated that zinc and calcium had the same behaviour during substrate-solution equilibration and complexation with DOC. So, competition between divalent cations for adsorption, desorption and complexation with DOC played a key role in zinc mobilization.

**Table 2. Exchangeable zinc ($Zn_{MgCl2}$) and characterization of substrate solutions (±*SD*).**

| | | $Zn_{MgCl2}$ | Characterization of solutions | | | | |
|---|---|---|---|---|---|---|---|
| | | | $Zn_{liq}$ | $Ca_{liq}$ | DOC | $pH_{liq}$ | $Zn_{liq\%}$ |
| | | % | µ$mol_c$/kg | | mg/kg | | % |
| CaS | O *(n=24)* | 3.93 ± *0.14* | 268.4 ± *101.3* | 312.8 ± *103.7* | 12.89 ± *4.64* | 6.97 ± *0.33* | 0.0117 ± *0.0044* |
| | A *(n=24)* | 10.23 ± *0.18* | 42.8 ± *18.8* | 170.1 ± *75.2* | 3.30 ± *2.71* | 7.13 ± *0.40* | 0.0050 ± *0.063* |
| ShS | O *(n=16)* | 18.65 ± *0.22* | 413.3 ± *251.7* | 978.6 ± *492.4* | 51.70 ± *18.59* | 5.85 ± *0.30* | 0.1855 ± *0.1111* |
| | A *(n=24)* | 10.31 ± *0.10* | 54.3 ± *24.2* | 146.1 ± *62.4* | 9.27 ± *2.53* | 5.71 ± *0.38* | 0.0567 ± *0.0359* |
| BSH | 0 *(n=12)* | 1.69 ± *0.03* | 17.2 ± *7.1* | 15.4 ± *4.5* | 0.74 ± *0.45* | 6.89 ± *0.48* | 0.0010 ± *0.0004* |
| ASH | 0 *(n=12)* | 11.16 ± *0.09* | 1.5 ± *0.7* | 8.7 ± *4.7* | 0.48 ± *0.32* | 7.11 ± *0.37* | 0.0001 ± *0.0001* |
| GSH | 0 *(n=12)* | 4.98 ± *0.11* | 92.7 ± *48.4* | 67.6 ± *34.7* | 1.65 ± *1.13* | 7.06 ± *0.16* | 0.0046 ± *0.0024* |

*Zinc in plants*

Zinc concentrations in shoots ($Zn_{sh}$ in Table 3) do not follow the same trend that total zinc concentration in substrates. On one hand, uptake mechanisms of plant species could explain this difference. On the other hand exchangeable zinc should be a better indicator than total concentration since it is easily mobilized and thus immediately available for plant uptake. Indeed, our results show that zinc concentration in shoots is positively correlated with the quantity of zinc extracted from O/0 horizon sample with $MgCl_2$ under agitation [mg/kg](data not shown) ($r^2=0.97$, n=4) and $Zn_{liq}$ ($r^2=0.72$, n=4). This corroborates the study of Burgos *et al.* (2008).

**Table 3. Zinc in shoots (n=3).**

| Substrates | Species | $Zn_{sh}$ mg/$kg_{DM}$ | Transfer % |
|---|---|---|---|
| CaS | *Viola calaminaria* | 1390 ± *228* | 1.85 ± *0.30* |
| ShS | *Agrostis tenuis* | 450 ± *68* | 6.08 ± *0.11* |
| ASH | *Armeria maritima* | 4760 ± *59* | 8.99 ± *0.92* |
| GSH | *Agrostis tenuis* | 1600 ± *68* | 2.44 ± *0.10* |

*Prediction of zinc in substrate solutions*

In the view of the importance of exchangeable zinc and zinc competition with calcium, a multiple regression was developed to predict zinc leached (µ$mol_c.kg^{-1}$) from parameters generally involved in exchange processes: $Zn_{tot}$ (mg/kg), $Ca_{exch}$ ($cmol_c$/kg), pH and Corg (%) ($r^2=0.83$, n=7, p=0.05 (Figure 2)). This last parameter was integrated instead of CEC because, in the chosen substrates, it is the main component of CEC.

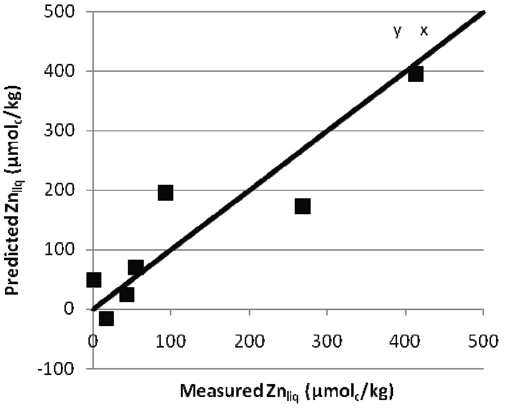

**Figure 2. Prediction of zinc leached using a multiple regression involving values of $Zn_{tot}$ (mg/kg), $Ca_{exch}$ ($cmol_c$/kg), pH and Corg (%).**

## Conclusions

Determination of exchangeable zinc proportions by $MgCl_2$ extraction allows a good assessment of zinc mobility and phytoavailability. Moreover, values of parameters usually and easily measured for soil samples (pH, organic carbon content, exchangeable calcium and total concentration in zinc) could be used to predict leached zinc and thus zinc uptake since uptake is correlated with zinc in solution. Predicting regression should be improved by comparison with other substrates but it highlighted, once again, the crucial importance of exchange processes in mobilization of zinc.

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