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Environmental Effects of Zinc Runoff from Roofing Materials – A New Multidisciplinary Approach

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Abstract: The objective of this work is to study changes in concentration and bioavailability of zinc-containing runoff water, released from roofing materials, upon passage through soil. The experimental approach is based on simulating the interaction between zinc in artificial runoff water and soil in a column system.

The total zinc concentration of runoff was substantially reduced when passing through the soil and suggests a marked zinc retention. During a constant flow and supply of zinc into the soil, equivalent to 3.5 years of precipitation in Stockholm, a zinc retention capacity of approximately 99% was recorded. Not only the total concentration, but also the bioavailable portion of the total zinc concentration was reduced after passage through soil. Most of the retained zinc was located in top 3 cm of the soil core and suggests the total capacity for zinc retention of the investigated soil to be about 140 years per kilogram soil in an isolated system. In real systems, changes of temperature, pH, microbial activity, weathering of minerals and deposition of new organic material must be considered.

The results form part of the effect assessment, preceding future risk assessment of the environmental effects of dispersed zinc.

Keywords: Zinc, atmospheric corrosion, runoff rate, soil, zinc ion, metal retention

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Background

Extensive knowledge of metal dispersion rates, chemical speciation of released metals, environmental interactions and, finally, changes of the retained metal in the environment are crucial parameters to consider when evaluating the potential environmental effects of metal dispersion. The effect of various environmental parameters on the metal concentration in runoff water has recently been studied through extensive field and laboratory investigations [*1-2*]. In addition, the chemical speciation and the bioavailability of metal runoff have been investigated when the runoff water leaves the metal surface [*3*]. However, information on the interaction between metal in the runoff water and the environment is still lacking. Many investigations reported in the literature have focused on the interaction between metals in urban storm water and different soil systems on specific locations [*4-6*]. This is often complicated, since the metal may originate from a number of diffuse sources, which results in complex travelling paths for the water and a large volume to sample ratio.

The aim of this study is to isolate and study the interaction between zinc runoff water from roofing materials through a controlled laboratory set-up using realistic metal concentrations. According to the knowledge of the authors, no investigation has earlier combined metal-containing runoff water with soil column studies to evaluate the zinc retention capacity of soil, changes in chemical speciation and bioavailability during passage through the soil, and the ecotoxicity of the runoff water after soil passage (the so-called percolate). The work forms part of a large European industrial collaboration project with the aim to increase the knowledge on runoff rates, bioavailability and ecotoxicity of metal dispersion from zinc-based construction materials used in the society. The approach combines three interdisciplinary sciences, corrosion science, soil science and environmental toxicology for investigating the interaction between dispersed metals and the environment.

Focus of this paper is to illustrate the structure of the project by describing the most important steps of runoff water after leaving the roof and passing through the soil. By taking zinc as the example, the following key issues will be described in logistic order (see Figure 1).

Before soil passage
- Atmospheric corrosion and zinc runoff
- Concentration and bioavailability of zinc runoff

During soil passage
- Important physico-chemical processes during interaction between metal runoff and soil
- The design of an experimental set-up for percolation studies
- Experimental results on zinc retention

After soil passage
- Experimental results on percolate water and its bioavailability
- Massbalance of the column experiment

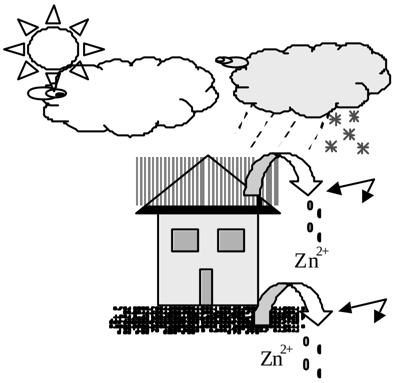

Figure 1- *Study of changes of metal concentration, chemical speciation, bioavailability and ecotoxicity of zinc runoff in contact with a soil system*

Before soil passage

Atmospheric corrosion and zinc runoff

Zinc forms relatively porous and voluminous patina layers, primarily composed of basic zinc carbonate $Zn_5(CO_3)_2(OH)_6$ and basic zinc sulphates $Zn_4SO_4(OH)_6 \times nH_2O$ (n=1-5), during urban atmospheric exposures [*7*]. One of the predominating atmospheric pollutants that governs the corrosion attack of zinc is sulphur dioxide (SO_2). A strong correlation between the zinc corrosion rate and the SO_2 concentration has earlier been demonstrated through a number of dose-response functions [*8*]. As a result of substantial reduction in SO_2 concentration seen during the last decades in urban environments of Europe and North-America, a significant decrease in zinc corrosion rate has been observed. During a rain event, soluble and poorly adhesive phases of the corrosion patina can dissolve and be released from the surface by rain water. Not only the corrosion rate but also the zinc runoff rate has been substantially reduced as a result of lower pollutant levels. A correlation between SO_2 and the runoff rate has recently been presented in the literature [*8*]. The equation can easily be used to transform runoff rate data from present study (with an SO_2-concentration of 3-4 $\mu g/m^3$) to other more polluted urban test sites. Annual zinc runoff rates in the range 2.5 to 3.5 g/m^2 have been determined for zinc sheet of varying age exposed in Stockholm. The runoff rate of zinc has been between 40 and 65% (for SO_2-concentrations higher than 50 $\mu g/m^3$) of the corrosion rate, at least during the first 5 years of exposure [*9*].

Zinc in urban storm water and runoff water originates also from natural deposition by dry and wet deposition. Annual natural deposition rates of zinc in Stockholm are typically 0.02 g Zn/m^2 [*1, 10*]. During entry into the environment, the runoff water from a roof will eventually be mixed with urban storm water from, *e.g.*, roads and sidewalks. This results in dilution of the metal concentration in the runoff water, and in concomitant complexation, sorption, ion exchange and other processes through which the metal can interact with the ambient environment along its way to the recipient.

Concentration and bioavailability of zinc runoff

Information of metal concentration is one of several crucial parameters to consider when evaluating ecotoxicity of metal dispersion. The reason is that a concentrated dose of metal during a short exposure period may be much more harmful for living organisms and plants than the same dose extended over a long period. As can be seen in Figure 2 (left part), the variation in zinc concentration between different samplings within the present study varies from 1 to 14 mgZn/l. The data are based on runoff water from zinc sheet of varying age and based on all sampling periods (including several rain events) during a two-year exposure period in Stockholm [*11*]. Figure 2 (right part) exhibits the distribution of the zinc concentrations and shows that the average zinc concentration in the runoff water is approximately 5 mg/l.

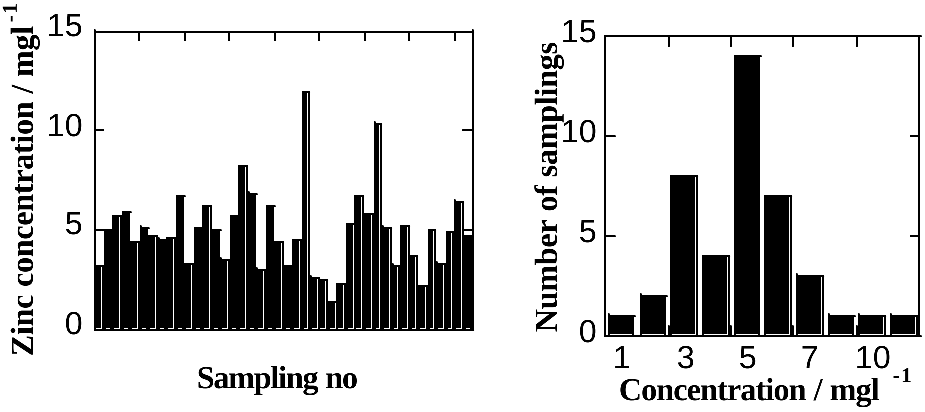

Figure 2 - *Total zinc concentration in all samplings of runoff water during a two-year exposure period in Stockholm (left), and distribution (n=41) of zinc concentration (right) in the same samplings*

The concentrations mentioned so far concern total concentrations of zinc, irrespective of chemical speciation. However, when discussing ecotoxicity it is important to assess the bioavailable fraction of the total zinc concentration. For metals, the most bioavailable form is often the free ion, which is hydrated in water solutions ($Zn(H_2O)_6^{2+}$ in the case of zinc, see ref. 3). In the present study the bioavailability of zinc was evaluated using a metal-specific assay (Biomet®) with the bacteria *Alcaligenes eutrophus*. This is a genetically modified bacteria strain, which produces light in the presence of bioavailable zinc. The procedure of the biosensor test is described in more detail elsewhere [*3*]. The Biomet® test has been verified through ecotoxicity tests of zinc in runoff water by using the internationally recognised standard 72 hour algal growth inhibition test with *Raphidocelis subcapitata* [*3*].

Biosensor test results are presented in Figure 3 from runoff water collected from new zinc sheet and galvanised sheet panels during two sampling periods. The results show that most of the zinc in the investigated runoff waters is bioavailable. The zinc sheet and the galvanized steel sheet show very similar behaviour, although a difference in both total zinc concentration and bioavailable zinc concentration is seen between the two sampling periods. The difference in total zinc concentrations between the two sampling periods is attributed to normal variability caused by different precipitation volumes, dry periods between rain events etc. The difference in the bioavailable zinc fraction is probably due to organic material found on the panels during the August sampling (pollen). This causes organic complexes to form with zinc ions, which results in less bioavailable forms of zinc than the free hydrated zinc ion.

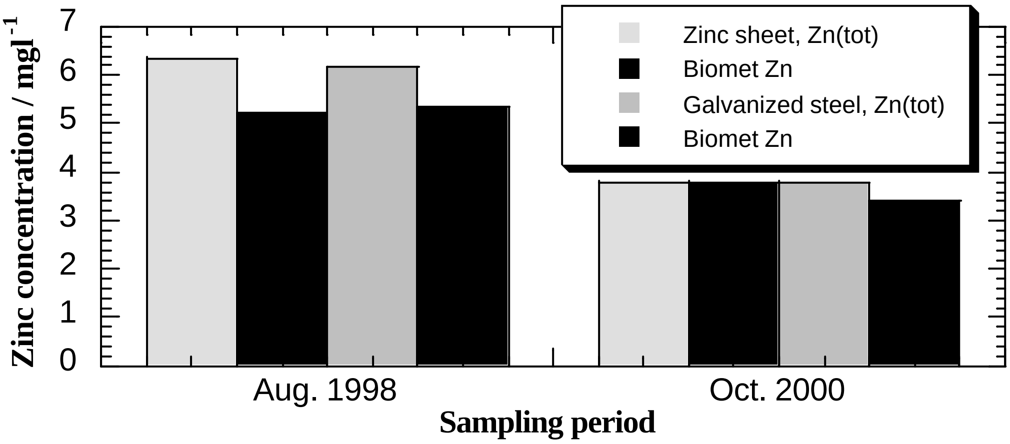

Figure 3- *Total (dashed) and bioavailable (black) zinc concentration for zinc sheet and galvanized steel in runoff waters collected during two sampling periods.*

At this point it seems appropriate to compare measured zinc concentrations in runoff water with selected concentrations reported for ecotoxicity effects. For water a defined deficiency boundary has been set to be less than 1 µg Zn/l, and an ecotoxicity boundary at zinc concentrations higher than 1000 µg Zn/l [*10*]. Ecotoxicity tests with the algae *Raphidocelis subcapitata* show EC_{50} values (*i.e.*, the concentration of zinc where the growth rate of the algae is reduced with 50%) from 30 to 60 µg/l Zn^{2+} [*3*]. For the crustaceans *Daphnia Magna*, the acute LC_{50} value (*i.e.*, lethal concentration causing 50% mortality) have been found ranging from 5 to 2300 µg Zn/l, depending on various test conditions, abiotic (nonbiological) factors and the circumstance that different life stages of the species have been used. For the rainbow trout *Oncorhynchus Mykiss* the acute LC_{50} values vary from 90 to 7200 µg Zn/l, due to the same factors as mentioned above [*12*]. These large variations in results stress the importance of choosing a test that is sensitive, relevant and with species that are not influenced by too many uncontrolled parameters. This requirement is achieved with the algae *Raphidocelis subcapitata.*

During soil passage

Important physico-chemical processes during interaction between metal runoff and soil

Soil, as used in this context, consists of a thin layer of loose earth materials composed of weathered minerals (oxides and layer silicates) and decaying organic matter (humus), with all solid phases and water in close contact. Due to its complex composition, the soil can interact with metals through a variety of physico-chemical processes, as briefly discussed below [*13*]. Irrespective of process, the resulting ecotoxicity of the retained metal is often reduced in comparison to the free, hydrated, metal ion.

The solid phase (clay or humus) carries in most cases an excess of negative charge. This leads to a surface potential which determines the distribution of cations, including metal ions, and anions in the liquid phase. Two opposing forces, electrical attraction and diffusion back into the bulk solution, act on cations, which have to counterbalance the negative surface charge. In addition to the electrostatic attraction, ions might bond to the solid phase by chemisorption processes. The latter type of bonding is much stronger.

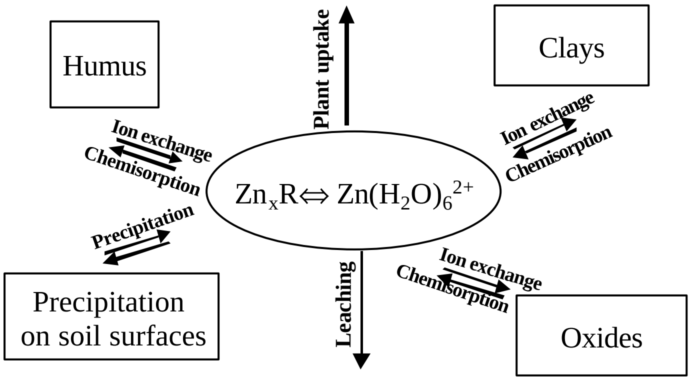

Figure 4- *Interactive processes determining retention and bioavailability of zinc*

Figure 4 is a principal figure that shows the main processes for metal retention in the soil and complexation in solution, as well as showing that these processes determine the bioavailability of zinc. Metal retention processes in soil can be divided into the following main groups:

- chemisorption
- cation exchange, and
- precipitation of secondary minerals.

Electrostatic sorption in soil is controlled by either fixed charge constituents (*e.g.*, clay minerals such as hydrous silicates that develop negative charge as a result of lattice substitutions) or variable charge constituents (*e.g.*, the surface charge of humus and iron-, manganese-, aluminium- or titanium oxides that varies with pH of soil water). At a soil pH lower than 7, clay minerals adsorb far smaller quantities than other main sorbents of the soil, *e.g.* humus.

Cation exchange is governed by the number of ions exchangeable (cation exchange capacity, $CEC_{relative}$) to zinc ions. Silicates, oxides and humus all contribute to the CEC. In the top soil layer, humus is the main contributor to CEC, whereas in deeper soil layers, mineral is the main contributor to CEC together with humus. The overall exchange process is diffusion controlled, and equilibrium is often attained within an hour.

Cations bound to the surface of minerals can diffuse into the interior of the solid phase. The relative diffusion rate depends, among others, on the ionic diameter of the cations. In the interior, these cations can neutralize negative charges and remain fixed in appropriate positions. The processes are described as irreversible and cause metals to become immobilized.

Other processes, such as microbial activity and CO_2 –dissolution, may influence soil pH to some extent, and thereby indirectly influence the metal retention capacity. To summarize, Figure 5 displays different zinc retention mechanisms as a function of reaction time and solubility of the adsorbate. The figure shows that surface precipitation (of, *e.g.*, hardly soluble sulfides, carbonates, phosphates or oxides) only occur at very high metal concentrations, in fact, far higher than those usually found in runoff water. For this reason, precipitation is not regarded as an important retention processes within this context.

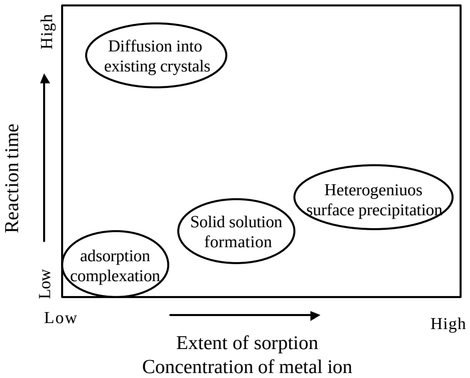

Figure 5- *Possible fates of ionic adsorbates in soil as a function of reaction time and metal concentration*

Having discussed conditions of the metal runoff and possible processes that govern the interaction between metal runoff and soil, we next discuss a possible design of an experimental set-up for soil percolation studies.

The design of an experimental set-up for percolation studies

Runoff water- In order to obtain a well-defined runoff water for the percolation study, artificial rain was used with a composition that resembles precipitation in the central and southern part of Sweden, see Table 1 [*14-15*]. The use of artificial rain for simulating runoff water has been verified elsewhere [*2*].

Table 1 - *Composition of artificial rain used in the percolation study*

SO_4-S (mg/l)	Cl^- (mg/l)	NO_3-N (mg/l)	NH_4-N (mg/l)	Na^+ (mg/l)	K^+ (mg/l)	Mg^{2+} (mg/l)	Ca^{2+} (mg/l)	pH
1.17	0.36	0.56	0.56	0.23	0.12	0.12	0.20	4.3

pH of the artificial rain was adjusted to 6.2 with NaOH, in agreement with runoff water collected from zinc roofs [*1*]. Earlier results from the present field exposure program and the biosensor tests [*1*] suggest that between 90 and 99% of zinc in the runoff is present in a bioavailable form at this pH. Based on these results, the zinc content in the artificial rain was added as $Zn(NO_3)_2 \bullet 6\ H_2O$ (quality purum) with a zinc concentration of 5 mg/l. As discussed before, see Figure 2, this concentration is representative of field data obtained within the present exposure program.

The rain intensity, finally, was arbitrarily set at 2 mm/h, representative of a medium or light rain intensity in Stockholm, Sweden. [*2*].

Soil- The soil material used in this study was sampled one year prior to the experiment from a depth of 0-20 cm in Kalmthout, Belgium. This soil represents one out of five evaluated soils within the European collaboration project. Despite different soil characteristics, all soils exhibit similar tendency towards zinc retention during the simulated 3.5 years. Soil samples were sieved (< 2 mm) under ambient moisture conditions, dried at 20°C, homogenised and stored at room temperature prior to investigation. The pH was measured in a water extract at 8°C with a combined glass electrode (Radiometer GK2401C 291-3-065). Total content of organic carbon (C_{org}) was determined using a LECO CHN-932 analyser. The cation exchange capacity (CEC) was calculated from the Ca, Mg, Na and K content of the soil (determined by extraction with 0.1 M $BaCl_2$ and analysed with atomic absorption spectroscopy, Analyst 300 Perkin Elmer). The natural zinc concentration in the Kalmthout soil was determined as: the exchangeable concentration of zinc, defined as zinc extractable using the complexing agent EDTA (disodiumsalt), and the total concentration of zinc, obtained through extraction with 7 M HNO_3. All extractions were performed for 24 hours. The results of soil characteristics are found in Table 2.

Table 2 - *Characteristics of Kalmthout soil used for the percolation studies*

Soil Data	Clay (%)	C_{org} (% dry weight)	pH $_{H_2O\ 8°C}$	CEC (cmol/kg)	Ca $_{BaCl2}$ (mg/100g)	Mg$_{BaCl2}$ (mg/kg)	Na $_{BaCl2}$ (mg/kg)	K_{BaCl2} (mg/kg)	Zn_{EDTA} (mg/kg)	$Zn_{7M\ HNO3}$ (mg/kg)
	1	4.1	4.93	2.6	38.2	44.2	4.1	132.7	18.6	30.2

Kalmthout soil is regarded as a low retention soil for zinc, characterized by a clay content of only 1% (compared to typically 10-20%), a medium fraction of organic material, 4.1% (typically 2-10%), low pH 4.9 (typically 6-7), and low amount of CEC 2.6 cmol/kg (typically 10). As the soil pH is below 6-7 the soil oxides will have a positive charge and thereby will not contribute to the CEC. Average concentrations of total zinc content in some soils from Western Europe are found in Table 3. Such data, however, can vary widely from site to site.

Table 3 - *Mean concentrations of total zinc content in unpolluted soils from Western Europe*

Country	*Belgium*[16]	*Germany*[16]	*Sweden*[10]
mg Zn/kg	*57*	*83*	*55*

Soil column design and analysis

Changes in bioavailability and ecotoxicity when zinc runoff enters the Kalmthout soil were evaluated with soil column experiments, Figure 6. A similar set-up has earlier been used for clay soils [*17-18*]. The diameter of each glass column is 32 mm and the height is 140 mm. In order to avoid contamination, all columns, preparation and storage vessels were immersed in 10% HNO_3 for at least 1 day, rinsed 3-4 times with ultra-pure water (<18 $M\Omega cm^{-1}$) and sealed before use. The soil had an initial water holding capacity of ~15% and was packed in each column by gravity. Each soil core was about 7 cm in height, corresponding to a mass of 55g soil. A sintered glass-filter disc (Duran P4; pore size diameter 9-15 µm), a 0.2 µm filter (Gelman Supor), and a glass-fibre filter (Gelman A/E 1.0 µm) were placed between the bottom cover of the column and the soil core.

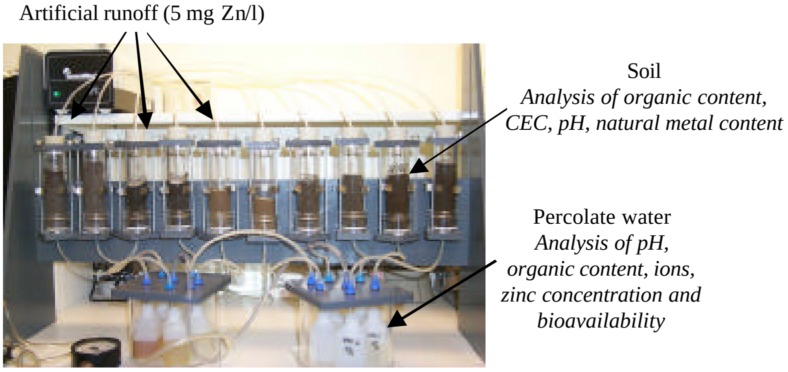

Figure 6 - *Experimental set-up showing the soil cores, collecting vessels and the pump providing artificial rain to the soil cores*

The artificial runoff water entered each soil core through a glass filter ensuring a uniform wetting of the whole soil core surface. A peristaltic pump was used to keep a constant rain intensity of 2 mm/h (equivalent to a supply of 1.5 ml/h for this column size). Duplicate control tests were performed which resulted in excellent agreement. The result suggests that no preferred routes for the runoff water were created during the percolation experiments.

The investigations were performed at +8°C with aerobic conditions (achieved by a permanent vacuum of –100 mbar at the outlet of the columns) in a dark room. Samples were collected once a day and pH and total zinc concentration, determined by ICP-AES (inductively coupled plasma-atomic emission spectroscopy, ARL ICP 3520B) were analysed for each sample. Prior to total zinc concentration measurements the samples were acidified with HNO_3 to reach a pH of approximately 2. Total organic content (TOC) and bioavailability were evaluated for some of the percolate water samples. TOC was determined with a TOC-5000A Shimadzu analyser. In-between analysis the samples were stored at +8°C.

The column experiments were conducted for about one month. The total volume of added artificial runoff was 1200 ml corresponding to 1600 mm of rain and a total quantity of 6.1 mg zinc. This volume is equivalent to 3.5 years of rain in Stockholm.

Experimental results on zinc retention

Figure 7 displays the zinc retention capacity of Kalmthout soil, *i.e.*, the ability to retain zinc within the soil core. The results of this figure are presented as a function of rain amount percolating through the soil. Figure 7 is based on data of zinc concentration of the percolated water, which is further discussed in a subsequent section (Figure 10, right). The data includes a natural leaching of zinc from the soil. Apart from the initially low zinc retention capacity during the first 200 mm of rain, a capacity of 99% is observed throughout the remaining exposure of up to 1400 mm of continuous rain (corresponding to about 3.5 years of natural rain in Stockholm).

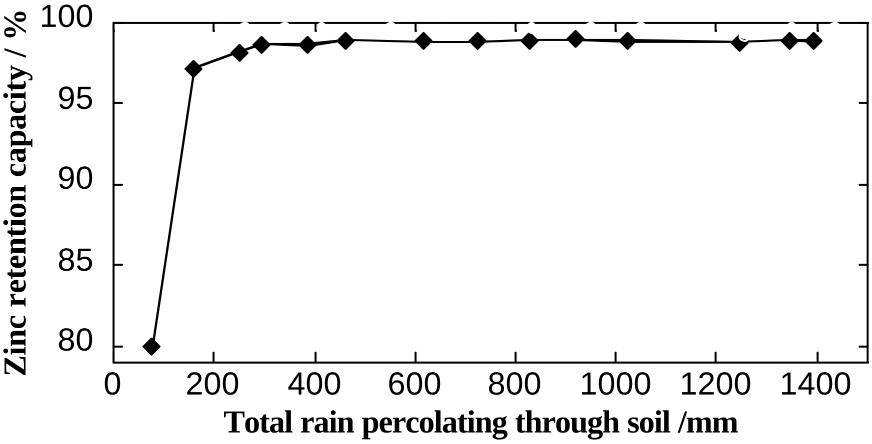

Figure 7 - *Zinc retention capacity of the Kalmthout soil*

The observed zinc retention is due to one or several of the previously discussed physico-chemical processes, which operate during zinc interaction with the soil, probably a combination of ion exchange and chemisorption. As stated before, the formation of metal-organic complexes is a most plausible process at low zinc concentrations. A hint for possible causes of the initially low zinc retention is given in Figure 8, which displays the total organic content (TOC) in the percolate water as a function of rain amount. The behaviour of TOC follows the zinc concentration in the percolate water (see Figure 10, left), exhibiting a high value during the first 200 mm of rain, which drops to lower values with extended rain up to 1500 mm. This implies that complexation between zinc and mobile organic ligands are formed, thereby mobilizing zinc which is transported through the soil to the percolate water.

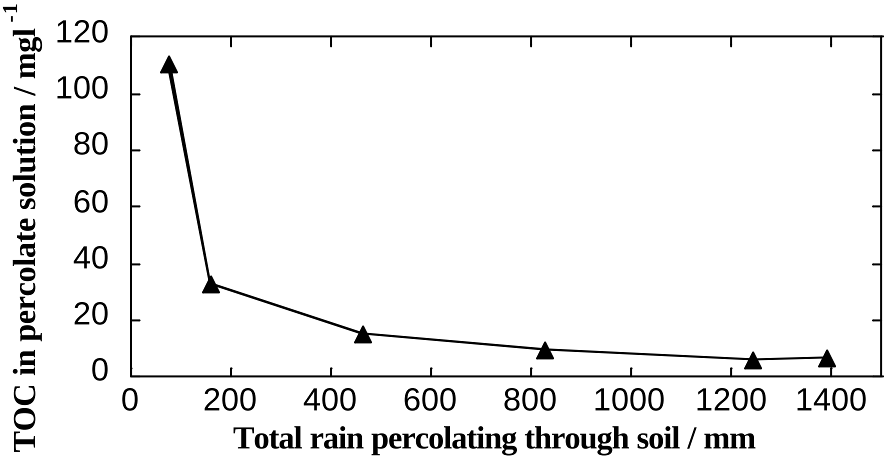

Figure 8 -*TOC concentration in percolate solutions*

With prolonged exposure, the soil obviously exhibits very strong active sites for zinc uptake, as judged from the increasing zinc retention. Through changes in, *e.g.*, temperature, pH, microbial activity and dry depositon of organic substance, the soil system is constantly altering its TOC and, hence, new zinc-complexing abilities are formed.

An obvious issue when discussing zinc retention in soils is the possible mobilization of retained zinc, for instance during increase in concentration of hydrogen ions or other ions with high affinity towards inorganic or organic compounds. One way of illustrating this issue is by studying zinc mobilization from a soil with retained zinc, which is exposed to extracts of varying strength. Figure 9 summarizes results from three different layers, each 1 cm thick, of the column soil after completed exposure to artificial runoff with added zinc. The layers represent the topsoil layer (0-1 cm), middle layer (3-4 cm) and bottom layer (6-7 cm).

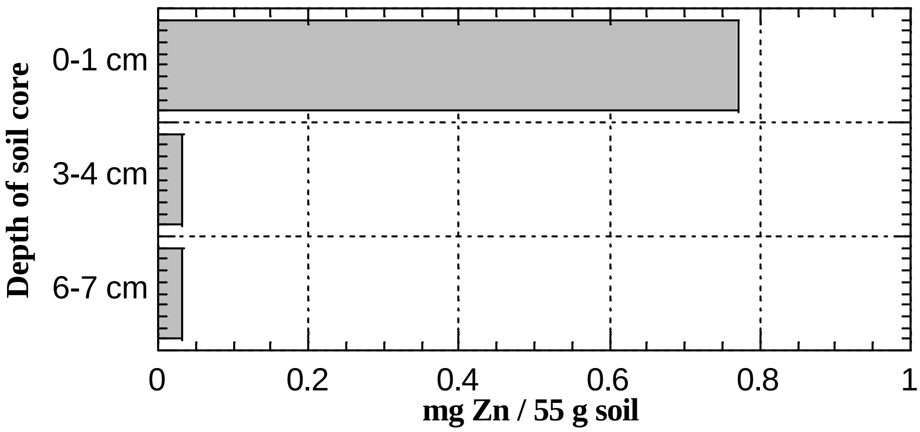

Figure 9 - *Zinc mobilized from column soil by extraction with artificial rain at pH 4.3*

When each soil layer was extracted with artificial rain (5 g soil mixed with 40 ml artificial rain, after 24 hours shaked for 1 hour, centrifuged and analysed), the results reveal that 0.77 mg zinc per 55 g soil was extracted from the top layer and 0.033 mg from the other layers. As will be shown in a subsequent section (Massbalance of Kalmthout soil) 55 g soil has retained totally 5.9 mg zinc (7.6 mg subtracted with the natural zinc content of 1.7 mg). 0.77 mg zinc then corresponds to 13% of the totally retained zinc for the top layer and 0.5% for the middle and bottom layer. Leaching experiments have shown that 0.06 mg zinc per 55 g soil leaches naturally from Kalmthout soil. This is similar to the amount found at a depth of more than 3 cm in the soil core. Therefor the conclusion can be drawn that zinc from the runoff water has been retained in the first 3 cm of the soil core, at the most. If we assume that this top 3 cm layer has reached the breakthrough capacity for zinc retention, 24 g of soil (equals to 3 cm) would result in a breakthrough capacity of 3.5 years. A worst-case scenario for breakthrough of a kilogram of Kalmthout soil would then be about 140 years.

To conclude: after passage of zinc-containing artificial runoff, equivalent to 3.5 years of rain in Stockholm, more than 80% of the zinc is immobilized by various processes and retained in a top soil layer with a thickness of less than 3 cm.

After soil passage

Experimental results on percolate water and its bioavailability

As previously discussed, the zinc retention capacity of the soil proved to be between 80 and 99%, hence allowing only a small portion of introduced zinc in the rain or the natural zinc content of the soil to pass through the soil core during a continuous rain event. This is illustrated in Figure 10 (left) showing a significant decrease in zinc concentration (~80%) already in the first sampling (from 5000 µg/l to about 1000 µg/l) after which the zinc concentration in the percolating water becomes even lower (50-140 µg/l) during subsequent sampling periods.

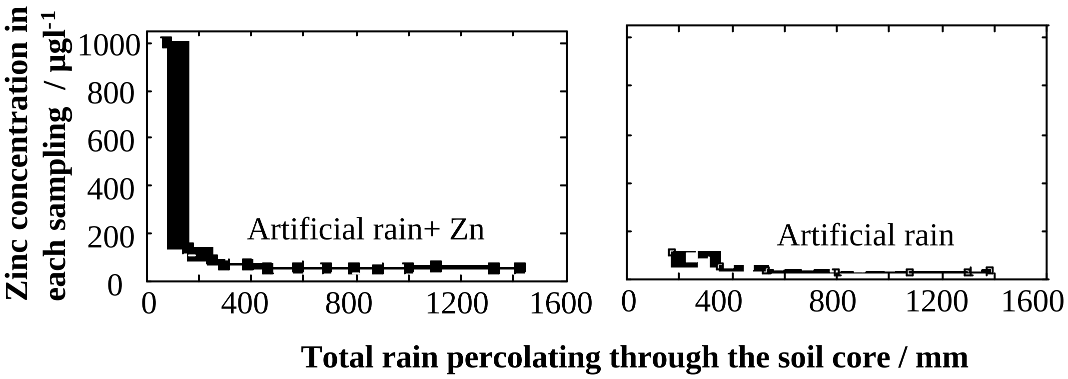

Figure 10 - *Zinc concentration in percolated water samples during a continuous rain event with (left) and without (right) zinc added to the artificial runoff*

However, a continuous rain event without any zinc addition, showed a natural, and relatively constant leakage (30-100 µg/l) of zinc from the soil core itself, Figure 10 (left).

The bioavailability of zinc in the percolate water was evaluated using the metal-specific assay (Biomet®), previously described. The bioavailable fraction of zinc in the introduced runoff was approximately 100%. Since the detection limit of the test is approximately 200 µg Zn/l, tests could only be performed on the first sampling volume percolating the soil core (see Figure 10). The results for this sampling period are presented in Figure 11, showing 34% of the total zinc concentration (1000 µg/l) to be bioavailable. The difference between total and bioavailable zinc concentration as well as the relatively high zinc concentration during the first sampling volume (< 77 mm) is probably explained by mobile organic ligands from the soil acting as complexing agents for zinc. It is then assumed that the zinc-organic complexes are less bioavailable than the free hydrated zinc ion. Computer model calculations with WHAM (Windermere Humic Aqueous Model) will be performed in order to verify these results.

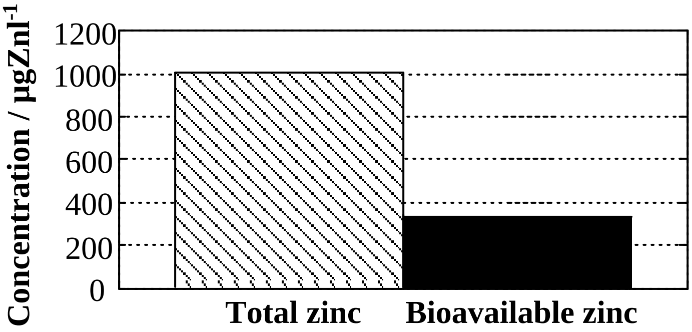

Figure 11 - *Comparison between the total and the bioavailable zinc concentration in percolate water after 77 mm of continuous rain*

Massbalance of Kalmthout soil from the column experiment

In order to verify that all zinc in the system is considered during the experiment a massbalance calculation was performed, the results are presented in figure 12.

55 g of the Kalmthout soil has a natural zinc content of 1.7 mg (figure 12, left, Table 2) of which 1.0 mg zinc is exchangeable.

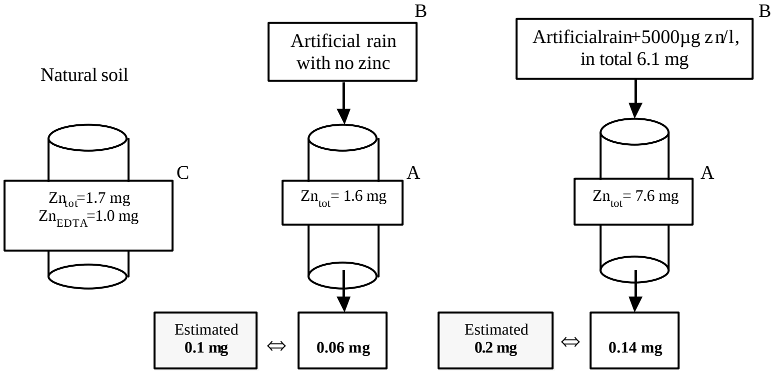

Figure 12 - *Massbalance of 55 g soil exposed to artificial rain (middle) and artificial rain with 5mg Zn/l (right).* Zn_{tot} *= extraction with 7 M* HNO_3. Zn_{EDTA}*= exchangeble fraction of Zn measured by EDTA extraction of the soil*

Input data for the massbalance are the zinc content measured after extraction of the soil core after percolation (A) and introduced amount of zinc to the soil (B). This difference is then compared with the natural content of zinc in the soil (C). The discrepancy is an estimate of the amount of zinc that should have passed the soil core and be present in the percolate water. This value is then compared with the actual measurements of zinc in the percolate water. The results are in excellent agreement for both tests.

Conclusions

The experimental set up used in the study works very well for simulating interactions between runoff water and soil. The following main conclusions can be drawn:

- When artificial runoff water with a total concentration of 5000 µg/l zinc percolate through a soil core of 55g Kalmthout soil, the percolate water shows zinc concentrations of approximately 60 µg/l. This zinc concentration also includes naturally leached zinc from the soil.
- The zinc retention capacity of the Kalmthout soil, which is regarded as a low retention soil is 99 % and continued to be so even after 3.5 years of constant exposure.

- Initially high total zinc concentrations in the percolate water are explained by mobile organic ligands in the soil functioning as complexing agents for zinc ions and thereby mobilizing zinc.
- The fraction of bioavailable zinc in percolate water is significantly lower compared to runoff water.
- 13% of zinc retained in the top 1-cm layer of the soil was mobilised when extractions with artificial rain were performed. In the centre and bottom layers of the core only 0.5% the zinc was mobilised.
- Retained zinc is still after 3.5 years of continuous rainfall not found deeper than 3 cm of the soil core, indicating that a breakthrough of the zinc retention capacity would take about 140 years per kilogram soil.

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