



**KTH Industrial Engineering
and Management**

Corrosion-induced metal runoff from external constructions and its environmental interaction.

**- A combined field and laboratory investigation of
Zn, Cu, Cr and Ni for risk assessment.**

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Doctoral Thesis

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Abstract

The 1990s has seen an increased awareness of possible environmental effects of corrosion-induced metal release from outdoor constructions. Considerable efforts have been initiated to perform critical assessments of possible risks of selected metals. Gaps of knowledge have been identified and research investigations started. This doctoral thesis is the result of an interdisciplinary research effort in which scientific insight into corrosion, soil chemistry and ecotoxicology has been integrated. The work comprises atmospheric exposure of pure metals and commercial materials for outdoor use. The focus is on release of four metals, copper, zinc, chromium and nickel. Their chemical speciation and bioavailable fraction in metal runoff were determined, both at the release moment and after environmental interaction with, e.g., soil and limestone.

Total metal concentrations in runoff are influenced both by material properties (e.g., corrosion product solubility, and specific surface area) and by exposure parameters (e.g., rain volume, intensity, contact time and pollutants). Long-term runoff rates of copper, zinc, chromium and nickel were based on exposures (4-8 years) at standardized conditions (45° inclination facing south) in Stockholm, Sweden. Runoff rates for pure copper range from 1.2 to 1.5 g m⁻² yr⁻¹, depending on year. At the copper release moment the potential environmental effect was evaluated using 72 hours growth inhibition test with the green algae *Raphidocelis subcapitata*. This resulted in a mean value of 15 µg L⁻¹ causing a 50% growth reduction (EC₅₀). Long-term runoff rates for pure zinc range from 1.9 to 2.5 g m⁻² yr⁻¹. A considerable variation in average annual runoff rates (0.07-2.5 mg zinc m²yr⁻¹) was observed between different investigated commercial zinc-based materials. An average 72 hour (EC₅₀) value of 69 µg L⁻¹ towards *Raphidocelis subcapitata* was found for runoff water from zinc-based materials. Long-term runoff rates from stainless steel of grade 304 and 316 range from 0.23 to 0.30 chromium and 0.28 to 0.52 nickel mg m⁻² yr⁻¹, with corresponding concentrations in the runoff at the release moment far below reported ecotoxic concentrations for chromium and nickel.

Two predictive runoff rate models were successfully developed for transforming copper runoff rate data from Stockholm to other exposure sites. One model is based on rain pH, yearly precipitation and building geometry, and the other on average annual SO₂ concentration, yearly precipitation and building geometry.

In addition to total metal concentration, adequate effect assessments also require information on chemical speciation of the released metal and its bioavailability. Metal chemical speciation in runoff was determined experimentally through an ion selective electrode (for copper), and also

modelled with the Windermere Humic Aquatic model (WHAM (V)). Bioavailability assessments were generated through bioassay tests. At the moment of metal release, all methods show that the majority (60-99%) of the metal in runoff exists in its most bioavailable form, the hydrated metal ion. During subsequent environmental entry the metal undergoes major reductions in concentration and bioavailability. This was evidenced by model column studies of the capacity of soil to retain and immobilize the metal in runoff water, and by model and field column studies of the capacity of limestone to retain copper. The retention by soil of all metals investigated is very high (96-99.8%) until each materials retention capacity is reached. Limestone also exhibits a substantial capacity (5-47%) to retain copper. The capacity is significantly increased by increased amount and decreased fraction of limestone particles.

Any outer or inner surface with significant retention ability and with low possibility of subsequent mobilization is an excellent candidate for neutralizing metal release and its potential ecotoxic effects. This was demonstrated through computer modelling (WHAM(V)) and biosensor tests (Biomet™), which showed the most bioavailable and ecotoxic metal species to be reduced during passage through soil and limestone. Predictions based on the computer model HYDRUS-1D suggest a time-period of between 4 and 8000 years, depending on runoff water and soil characteristics, before saturation in soil retention capacity of copper and zinc is reached. A significant fraction of the retained metal is extractable towards the strong complexing agent EDTA, indicating possible future mobilisation. It is also available for plant uptake, as shown by DGT- (Diffuse Gradients in Thin films-) analysis of copper and zinc in soil.

The data generated, presented and discussed are all believed to be important for risk assessment work related to corrosion-induced metal release from outdoor constructions. As evidenced from this doctoral thesis, such work requires a complete set of data on annual runoff rates, concentrations, chemical speciation and bioavailability and its changes during environmental entry, together with knowledge on, e.g., type of material, service life of coating, building geometry, and dewatering system.

Keywords: Atmospheric corrosion, metal runoff, metal dispersion, soil, limestone, retention, immobilisation, bioavailability, chemical speciation, copper, zinc, nickel, chromium, stainless steel, future mobilisation

Preface

This thesis includes the following nine papers, referred to in the text by their roman numerals:

- I *"Release rates of chromium and nickel from 304 and 316 stainless steel during urban atmospheric exposure. - A combined field and laboratory study"*
I. Odnevall Wallinder, J. Lu, S. Bertling and C. Leygraf
Corrosion Science. 44, 2303 (2002)

- II *"Corrosion-induced release and environmental interaction of chromium, nickel and iron from stainless steel"*
I. Odnevall Wallinder, S. Bertling, D. Berggren and C. Leygraf
Submitted to Water, air and soil pollution, October (2004)

- III *"Environmental effects of zinc runoff from roofing materials – A new multidisciplinary approach"*
S. Bertling, I. Odnevall Wallinder, C. Leygraf and D. Berggren
Outdoor and Indoor Atmospheric Corrosion, ASTM STP 1421, p. 200, H.E. Townsend, Ed., American Society for Testing and Materials, West Conshohocken, PA, (2002)

- IV *"Occurrence and environmental fate of corrosion-induced zinc in runoff water from external structures"*
S. Bertling, I. Odnevall Wallinder, D. Berggren Kleja and C. Leygraf
Submitted to the Science of the Total Environment March (2005)

- V *"Immobilization of copper in runoff water from roofing materials by limestone, soil and concrete"*
S. Bertling, I. Odnevall Wallinder, C. Leygraf and D. Berggren
Proceedings, 15th International Corrosion Conference, paper 44, Granada, Spain, (2002)

- VI *"The capacity of limestone to immobilize copper in runoff water. A laboratory investigation"*
S. Bertling, I. Odnevall Wallinder and C. Leygraf
Proceedings, 15th International Corrosion Conference, paper 42, Granada, Spain, (2002)

- VII *“Predictive models of copper runoff from external structures”*
I. Odnevall Wallinder, S. Bertling, X. Zhang, and C. Leygraf
Journal of Environmental Monitoring, 6, 704 (2004)
- VIII *“Long term corrosion induced copper runoff from natural and artificial patina and its environmental fate”*
S. Bertling, I. Odnevall Wallinder, D. Berggren Kleja and C. Leygraf
Submitted in revised form to Environmental Toxicology & Chemistry, March, (2005)
- IX *“Model studies of corrosion induced copper runoff fate in soil”*
S. Bertling, F. Degryse, I. Odnevall Wallinder, E. Smolders and C. Leygraf
Submitted in revised form to Environmental Toxicology & Chemistry, March, (2005)

In addition, several reports and conference proceedings have been completed, but not included in the thesis.

“Release and bioavailability of zinc from roofing materials induced by atmospheric corrosion”
I. Odnevall Wallinder, S. Bertling, and C. Leygraf, Proceedings, Galvanized Steel Sheet Forum – Construction, The Institute of Materials, Minerals and Mining, Carlton House, London, April 12-14, (2003)

“Immobilization of copper in runoff water from roofing materials by limestone, soil and concrete”
S. Bertling, I. Odnevall Wallinder, C. Leygraf and D. Berggren, Proceedings, UN/ECE Convention on long-range transboundary air pollution, Workshop on release of heavy metals due to corrosion of materials, Munich, Germany, May 12-14, (2003)

“Release rates of chromium, nickel and iron from pure samples of the metals and 304 and 316 stainless steel induced by atmospheric corrosion – a combined field and laboratory study”
I. Odnevall Wallinder, S. Bertling, G. Herting and C. Leygraf, Proceedings, UN/ECE Convention on long-range transboundary air pollution, Workshop on release of heavy metals due to corrosion of materials, Munich, Germany, May 12-14, (2003)

“Atmospheric corrosion, runoff and environmental effects of zinc-based materials”
I. Odnevall Wallinder, S. Bertling, and C. Leygraf, Proceedings, UN/ECE Convention on long-range transboundary air pollution, Workshop on release of heavy metals due to corrosion of materials, Munich, Germany, May 12-14, (2003)

“Release of chromium, nickel and iron from stainless steel exposed under atmospheric conditions and the environmental interaction of these materials”

I. Odnevall Wallinder, S. Bertling, G. Herting, C. Leygraf, D. Heijerick, D. Berggren and P. Koundakjian, report 72 pages, www.eurofer.org (2004)

“Environmental interaction of copper and zinc released from building materials as a result of atmospheric corrosion”

I. Odnevall Wallinder, S. Bertling and C. Leygraf
Metall 11 (2004)

”Miljöaspekter på takmaterial: metallavrinning, biotillgänglighet och ekotoxicitet”

S. Bertling, I. Odnevall Wallinder och C. Leygraf
Bygg och Teknik, 2 (2001)

”Korrosion och avrinning av zink från takmaterial”

I. Odnevall Wallinder, S. Bertling och C. Leygraf
Bygg och Teknik, 2 (2003)

”Kan miljöeffekter påvisas från utomhuskonstruktioner i rostfritt stål?”

I. Odnevall Wallinder, S. Bertling och C. Leygraf
Bygg och Teknik, 4 (2004)

”Miljöaspekter vid avrinning från tak”

S. Bertling, I. Odnevall Wallinder och C. Leygraf
Stålbyggnad, ISBN 91 7127 033 7 (2002)

“Vad sker med koppar i avrinningsvatten i kontakt med miljön?”

I. Odnevall Wallinder och S. Bertling
Kopparforum, 15 (2003)

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1.1 Background

External structures of copper, zinc and stainless steel, are used due to aspects related to e.g. durability, possibility to form difficult shapes, beauty and cost effectiveness. The use of alloyed, metal coated and surface treated metals for corrosion protection in building applications, increases the service time considerably. In the last decade, increased awareness of environmental impacts of metals in the society has resulted in critical assessments of possible risk when using metals.

European environmental risk assessments on zinc, copper and nickel are underway and a risk assessment on chromium was initiated in 2004. The risk assessments aim at evaluating at what concentrations, and in what chemical form the metals might cause environmental effects, and to develop tools for environmental protection. Final risk dossiers will be published during 2005, for both copper and zinc. When performing an environmental risk assessment for a metal, a number of considerations need to be taken into account. In addition to metal essentiality for many plants and organisms (copper, zinc, nickel and chromium), the chemical speciation of metals vary, as do their background concentrations. All factors influence the bioavailability (rate and extent of uptake by a plant or organism) and toxicity (damaging action upon an ecosystem) of a metal. Some general conclusions have recently been formulated that should be considered for risk assessment [Landner and Reuther, 2004]:

- "The total concentration of an essential element alone, is not a good predictor of its bioavailability or toxicity."
- "The toxicity of an essential metal will depend on environmental conditions and habitat types, thus risk assessment of the potential effects of these metals on organisms must take into account local environmental conditions."
- "Procedures to prevent toxic levels of essential metals in the environment should not incorporate safety factors that result in recommended concentrations being below natural levels or causing deficiency symptoms."

Predicted No Effect Concentrations (PNEC) of the specific metals will be defined within each risk assessment dossier. Local site-specific background concentrations of the metals, will probably be added to the PNEC value and compared with a Predicted Environmental Concentration (PEC), caused by one or several sources of metals that may expose a recipient (further described in section 1.2). Even though many studies have shown corrosion-induced metal release (runoff) from external constructions to be a minor contributor to total copper and zinc flows in the society, it is important, at some locations, to evaluate the possible environmental impact of a specific building. This evaluation should result in a PEC value based on accurate and scientifically sound data on metal runoff rates, metal concentrations and chemical speciation. It is not a simple task to predict the concentration and chemical speciation of a metal that may expose a recipient. The reason is that metal flows will confluence from different sources. The metal concentration and the chemical speciation are both affected by dilution with water from areas without any metals, and by retention and precipitation processes during environmental entry, and transport towards a recipient (river, ground water, sea, sewage system). Such a cross-disciplinary path emphasises the importance of using site-specific data within its limitations, to keep an open mind, and to critically review data. It is impossible to completely understand a system as complex as the environment, but we can know how accurate our description is and what the limitations of using it are.

This thesis work comprises collaboration between scientists in three main scientific areas, corrosion science, ecotoxicology, and soil chemistry. Each of these disciplines incorporates several areas of expertise, including e.g. chemistry, physics, medicine and hydrology. The collaboration is schematically summarized in Fig. 1.

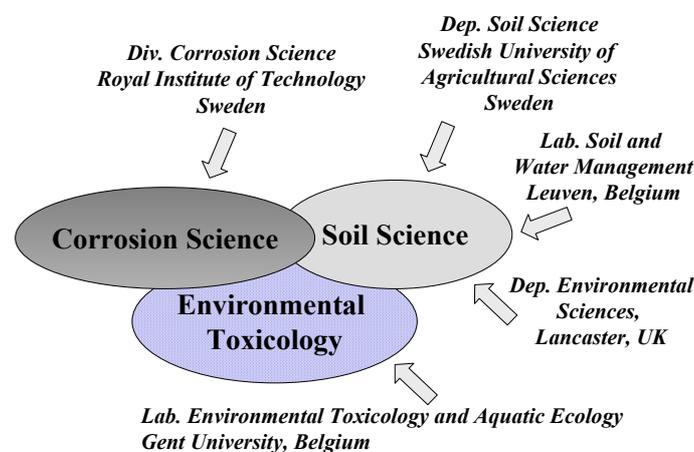


Figure 1. Cross-disciplinary research activities and collaborating partners.

This work is the third thesis in a row that has been generated within an extensive cross-disciplinary research project at the Division of Corrosion Science, KTH, with the aim to understand the metal runoff process, and to elucidate the environmental fate of corrosion-induced metal runoff from external constructions. Key-parameters investigated within the research project are; runoff rates, total metal concentrations, metal chemical speciation, bioavailability, ecotoxicity, and environmental fate of released copper, zinc, chromium, nickel and iron (only runoff rates).

The first thesis, [He, 2002], combines field and laboratory investigations. The work includes a thorough evaluation of differences in runoff rates and corrosion rates, and investigates the importance of environmental and surface parameters on the runoff rate of naturally patinated copper and zinc. The second thesis, [Karlén, 2001a], presents annual runoff rates of commercially available copper (naturally and artificially patinated), and zinc-based (bare, zinc-aluminium coated steel and surface treated) roofing materials, determined during 3 years at an urban field exposure site of Stockholm, Sweden. The work focuses on total copper and zinc concentrations and their chemical speciation, bioavailability, and ecotoxicity towards algae, at the immediate release situation.

In total, 21 peer-reviewed papers, 13 conference proceedings, and 11 popular papers, have been completed (including papers within this thesis) that describe the corrosion-induced metal runoff process and its environmental interaction. A detailed list of references is available at the following web page: www.corrosionscience.se.

One additional paper, relevant for the context of this thesis, has recently been published that elucidates differences in runoff rates of alloy constituents from stainless steel alloys and its pure metals [Herting et. al, 2005].

1.2 Methodology for performing a risk assessment of an external source

The objective of a risk assessment is to evaluate whether or not a substance released from a source imposes a potential threat to the environment. Such an assessment requires adequate data and understanding of parameters determining release of the substance, and its environmental fate combined with environmental effect data. A general methodology for such an assessment is schematically described in Fig. 2. The risk assessment involves an exposure and an effect assessment, often performed in parallel, followed by a risk characterisation, estimating the risk for adverse effects of an ecosystem. In essence, the highest concentration in the environmental compartment (Predicted Environmental Concentration, PEC),

determined in the exposure assessment, is compared with the concentration below which no unacceptable effects on organisms will occur (Predicted No Effect Concentration, PNEC), derived from the effect assessment. The PEC value is derived from available monitoring data, and/or model calculations, adding up metal concentrations from different sources that may expose a recipient. The PNEC value is derived on the basis of a species-sensitivity distribution of available ecotoxicity data, with a criterion at a specific protection level (often 95% of the species) [Van Straalen and Van Leeuwen, 2001]. This PNEC value should be added to the site-specific background concentration, in order to avoid deficiency levels, and account for natural variations of metals in the environment. Data are usually presented as the dissolved metal fraction, *i.e.* smaller than 0.45 μm , thereby excluding metal particles. Due to the artificial nature of laboratory elaborated data, and their lack of connection with the higher levels of ecosystem organization, a large variation of ecotoxicity values are found for one single substance (e.g. a metal). This variability can be significantly decreased if species sensitivity (SS) values (ecotoxicity data), expressed as dissolved metal concentrations, are translated to a concentration of actual metal species that causes an ecotoxic response, e.g. predominantly the free metal ion. Main parameters for this translation are water pH, hardness, and amount of dissolved organic carbon (DOC). In a similar way, $\text{Me}_{\text{dissolved}}$ values (environmental concentrations) should be transformed to involve the bioavailable metal species, before added to the total metal concentration that may expose the recipient ($\text{PEC}_{\text{free metal}}$), and compared with corresponding PNEC value ($\text{PNEC}_{\text{free metal}}$) within the step of the risk characterisation.

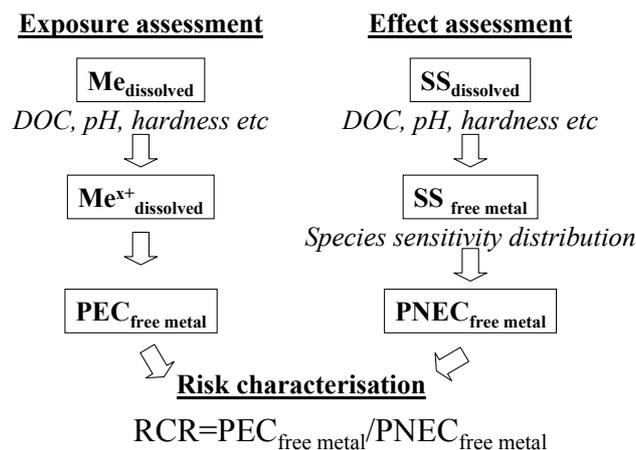


Figure 2. General methodology for performing an environmental risk assessment for the water compartment. RCR denotes Risk Characterisation Ratio, and SS species sensitivity.

In practice, an **exposure assessment** includes site-specific information of the total amount, concentration, chemical speciation and bioavailability of a metal exposing a recipient, for which a risk assessment is made. Site-determined metal runoff rates would of course be preferable, but are time-consuming to monitor. Empirical models are available for runoff rate predictions of zinc and copper [Odnevall Wallinder et. al, 2000; Verbiest et. al, 1999; Paper VII]. The models include environmental data and aspects related to building geometries. Environmental data, such as atmospheric pollutant concentrations, precipitation quantities, etc. can either be monitored or obtained from existing data-bases and reports [www.nilu.no/050317, www.slb.nu/050317, Henriksen et. al, 2001]. These data, together with information regarding e.g. type of material, area of exposed metal, orientation, inclination, etc. are crucial input values to accurately determine the amount of released metal at a specific site. Substantially reduced SO₂ emissions in Europe [Henriksen et. al, 2001] during the last decade have resulted in decreased runoff rates. It is therefore of considerable importance to use recent runoff rates for risk assessment. The total metal concentration in runoff water at the immediate release situation, is initially measured or predicted. If this concentration is below known effect concentrations for the system being protected, the assessment can be finalized at this stage. If not, dilution factors and changes in chemical speciation upon environmental entry need to be evaluated [Boulangier et. al, 2003]. For zinc and copper based materials, concentrations between 1 and 24 mg L⁻¹ (median concentration: 5.5 (Zn) and 3.0 (Cu) mg L⁻¹) [Karlén et. al, 2001a; Jouen et. al, 2003; Paper IV, VIII], have been detected at the immediate release situation. Concentrations of chromium and nickel at the immediate release situation vary between 0.1 and 11 (often around 0.2-0.5) µg L⁻¹ (Paper I, II). Variations in concentration depend on environmental parameters and corrosion product properties [He et. al, 2000; He et. al, 2001]. Copper and zinc concentrations are high enough to cause effects on some organisms, and it is therefore important to evaluate how dilution with urban storm water, and different retention processes onto surfaces in the near vicinity of the building site change the concentration and speciation before a recipient is reached. A number of analytical techniques (e.g. voltametry, Donnan Membrane, Diffuse Gradients in Thin films) and computer models (e.g. MinteqA2, WHAM (V, VI), PHREEQC) are today available for speciation analysis and predictions [Kozelka et. al, 1998; Temminghoff et. al, 2000; Zhang et. al, 1995; Allison et. al, 1991; Tipping, 1998; Parkhurst, 1995]. Different bioassays, using e.g. bacteria, can also be used to evaluate the bioavailable metal fraction [Heijerick et. al, 2002a]. The recently developed Biotic Ligand Model (BLM), evaluates metal interactions both with chemical ligands, as the above-mentioned models, and with biotic ligands, treated within the

same system for predictions of copper, zinc and chromium toxicity in natural waters with different chemical composition [Paquin et. al, 2002; Janssen et. al, 2003]. Although this model has greatly improved the understanding of the effect of variation in water chemistry on the toxicity of metals to aquatic systems, it is important to remember the assumption made within the model [Hassler et. al, 2004].

The lowest metal concentration causing adverse effects on the protected ecosystem (PNEC) is determined or predicted within the **effect assessment**, with species-specific ecotoxic data, usually by distribution-based extrapolation methods [Van Straalen and Van Leeuwen, 2001]. To achieve the best predictability, the PNEC values should, as previously discussed, reflect the chemical speciation of the metal, resulting in a $PNEC_{\text{free metal}}$ value. A proposal within the on-going European risk assessment is currently to add the PNEC concentration to the site-specific natural background concentration, in order to avoid PNEC values below the natural background concentration.

Within **the risk characterisation**, the PEC-concentration of bioavailable metal is compared with the PNEC concentration to which natural background concentrations potentially are added. If the PEC/PNEC ratio is less than 1, (i.e. $PEC < PNEC$), no adverse effects are anticipated. A quotient above 1 means that adverse effects are likely to occur, and a risk management procedure may be initiated.

1.3 No observed effect concentrations in aquatic and soil systems

Metals are naturally present in our atmospheric, aquatic and terrestrial environment at concentrations that depend on geological and environmental conditions. Background concentrations of Cu, Zn, Cr and Ni in fresh water and soil range from 0.5 to 40 $\mu\text{g L}^{-1}$, and from 10-300 mg kg^{-1} , respectively [Landner et. al, 1998; Landner and Reuther, 2004, Van Assche et. al, 1996; Merian, 1991]. Large variations in background concentrations of metals in water and soil are primarily attributed to regional variations due to differences in weathered minerals at different sites. This emphasizes the necessity to relate effect concentrations for organisms and plants to prevailing background concentrations at the site of interest, when performing a risk assessment.

The uptake of most metals by organisms and plants is predominantly from the aqueous phase. It is thereby the metal concentration in fresh waters, or in the case of soil, in the solution phase, together with the soils solid:liquid distribution coefficient (determining the re-supply of metals to the aqueous phase) that determine the potential uptake of metals. The concentration causing growth inhibition or lethality, depends on type of organism, uptake route, and on the chemical speciation of the metal [Merian, 1991]. Laboratory derived ecotoxicity data often overestimates toxicity levels. The reason is that such investigations often are performed with spiked soils, for which equilibrium for slow reactions seldom has time enough to occur, and the type and concentration of constituents seldom are comparable to field conditions [Smoulders et. al, 2003]. Laboratory derived total no effect concentrations (NOEC), or effect concentrations (EC_{50} ; concentration causing 50% growth reduction), of Cu, Zn, Cr and Ni are compiled in Table 1 for different aquatic organisms and soil living organisms. The large variation in effect concentrations indicates that the total concentration of a metal is a poor predictor of effects on organisms.

Table 1. No effect concentrations (NOEC), or effect concentrations (EC₅₀, EC₁₀), for some laboratory exposed organisms to Cu(II), Zn(II), Cr(III) and Ni(II).

| | Fresh water µg L ⁻¹ | Organism | Reference |
|---------|-----------------------------------|---|--|
| Cu(II) | 2-338 | 21 species, chronic | Landner and Reuther, 2004 |
| Zn(II) | 4.8-610 ¹ | green algae, <i>Raphidocelis Subcapitata</i> , chronic | Landner and Reuther, 2004 |
| Cr(III) | 40-110 ² | crustaceans, <i>Daphnids</i> , chronic | www.risk.lsd.ornl.gov/cgi-bin/eco/bench |
| Ni(II) | 50-750 ² | green algae, <i>Raphidocelis Subcapitata</i> | NiDi, 2000 |
| | Soil mg kg ⁻¹ | Organism | Reference |
| Cu(II) | 8.4-1450 | invertebrates | Van Sprang et. al, 2005 |
| Zn(II) | 56-1800 | invertebrates, <i>F. candida</i> , acute | Landner and Reuther, 2004 |
| Cr(III) | 604-892 ³ | invertebrates, <i>E. fetida</i> , <i>F. candida</i> , <i>E. albidus</i> , chronic | Koen et. al, 2002a |
| Ni(II) | 275-476 ³ | invertebrates, <i>E. fetida</i> , <i>F. candida</i> , <i>E. albidus</i> , chronic | Koen et. al, 2002b |

¹ EC₁₀ ²72-h EC₅₀, ³28-42 days EC₅₀

Toxicity results vary in the order of a magnitude when related to total metal concentrations. This depends primarily on differences in water characteristics (hardness, pH, dissolved organic carbon), or soil characteristics (Cation exchange capacity, pH, organic matter content). This variability can be significantly decreased if ecotoxicity values are, instead, expressed as dissolved metal concentrations and translated to a concentration of actual metal species that causes the ecotoxic response, e.g. often the free metal ions. Expressing 72-h effect concentrations (*R. subcapitata*), as free ion copper activities, the variability decreased by a factor of 10 (from 20 to 2) [De Schamphelaere et. al, 2003]. Normalization of NOEC values to the 5th percentile of pH, water hardness and DOC, by using the chronic BLM-model, resulted in a normalised PNEC-value of 8 µg Cu L⁻¹ (dissolved copper) [Landner and Reuter, 2004]. PNEC_{dissolved} values between 15 and 25 µg Zn L⁻¹ have recently been reported for aquatic ecosystem of Europe [Landner and Reuter, 2004], with 95% of all endpoints protected at a zinc concentration of 25 µg L⁻¹. A PNEC_{dissolved} value for zinc of 17.2 µg L⁻¹, with a safety factor of two is currently discussed and proposed for Europe within the on-going European risk assessment on zinc, [<http://chimie.ineris.fr/en/LesPDF/MetodExpChron/zinc.pdf>].

In conclusion, since total metal concentrations in fresh water and soil are poor predictors of toxicity, metal bioavailability should be considered for improved understanding of potential environmental effects. Metals introduced at field conditions often result in less toxic effects compared to laboratory spiked soils, in which metals often are introduced in an accelerated

manner and in an available form to a simplified system. This leaves a short time-period for immobilisation reactions, such as occlusion and inward diffusion. NOEC values should be related to background concentrations and prevailing water and/or soil characteristic for the specific site.

1.4 Thesis outline

This work aims at exploring long-term runoff rates of metals from commercially available copper, zinc and stainless steel materials in urban atmospheres, and to elucidate how the released metal concentrations, chemical speciation, bioavailable fraction and ecotoxicity change from the immediate release situation and upon environmental entry. A schematic representation of the thesis outline and questions addressed is given in Fig. 3.

Can corrosion-induced release of Cu, Zn, Cr and Ni from external constructions at urban sites cause environmental effects?

Long-term runoff rates of
Cu, Zn, Cr and Ni
from outdoor constructions



The interaction between
Cu, Zn, Cr and Ni in runoff water
with soil and limestone

Chapter 3

Chapter 4

Laboratory exposure

Laboratory exposure: soil and limestone

- Does rain intensity and pH influence the release rate of Cr and Ni from stainless steel used for outdoor applications?

*- What capacities have soils of various characteristics, and limestone systems, to retain metals in runoff water?
- In what way is the retention capacity of metals influenced by soil characteristics, including cation exchange capacity (CEC), soil pH, fraction of organic matter and clay?
- Are the total metal concentration and the chemical speciation, bioavailability and ecotoxicity of metals in runoff water changed during soil and limestone interaction?
- Can retained metals become mobilised in the future?
- Are retained metals in soil available for plant uptake?
- Can laboratory derived data be used to understand real scenarios at field conditions?*

Field exposure

*- At what rates and quantities are Cu, Zn, Cr and Ni released from external constructions on a long-term perspective?
- Are metal runoff rates lower for alloys, metal coated and surface treated materials compared to bare sheet?
- Can metal runoff rates be predicted for sites of different environmental characteristics?
- In what concentrations and chemical forms exist metals in runoff water at the immediate release situation?
- Can metal containing runoff water cause a detrimental effect on the environment?*

Field exposure: limestone

- What is the retention capacity of released copper by limestone?

Figure 3. Schematic representation of the thesis outline and questions addressed (in italic).

The content of this thesis is schematically illustrated in Fig. 4. The work comprises field data on annual runoff rates of chromium, nickel and iron (4 years) from stainless steels (grade 304 and 316) (Papers I and II), long-term runoff rates of copper from naturally and artificially patinated copper (8 years) (Paper VIII), long-term data on zinc from 14 different zinc-based materials (5 years) (Paper IV), and data to elucidate the environmental fate of these metals, Fig. 4. Laboratory simulations of the effect of rain pH and intensity were performed for chromium and nickel release from stainless steel, in complement to the field exposure (Paper I). Predictive runoff rates models for copper were deduced, one based on the average annual SO₂ concentration and the other on rain pH, combined with annual precipitation quantities (Paper VII). The fate of released metals upon environmental entry was exemplified with laboratory column studies exposing soil (Cu (Papers V, VI, VIII, IX), Zn (Papers III, IV), Cr, Ni (Paper II)) and limestone (Cu (Papers V, VI)) to artificial runoff water. The change in total metal concentration (Cu, Zn, Cr, Ni), chemical speciation (Cu, Zn, Cr, Ni) and ecotoxicity (Zn) was determined upon environmental entry (Cu (Papers V, VI, VIII), Zn (Papers III, IV), Cr and Ni (Paper II)). The possibility to understand real field scenarios from small soil column exposures was evaluated by transport modelling, using the software HYDRUS-1D (Paper IX). The potential for future mobilisation of metals retained in soil, was evaluated with sequential extractions (Cu, Zn, Cr, Ni) and a newly developed technique, Diffuse Gradients in Thin films (DGT), which mimics plant uptake (Cu (Bertling, unpublished data), Zn (Paper IV)).

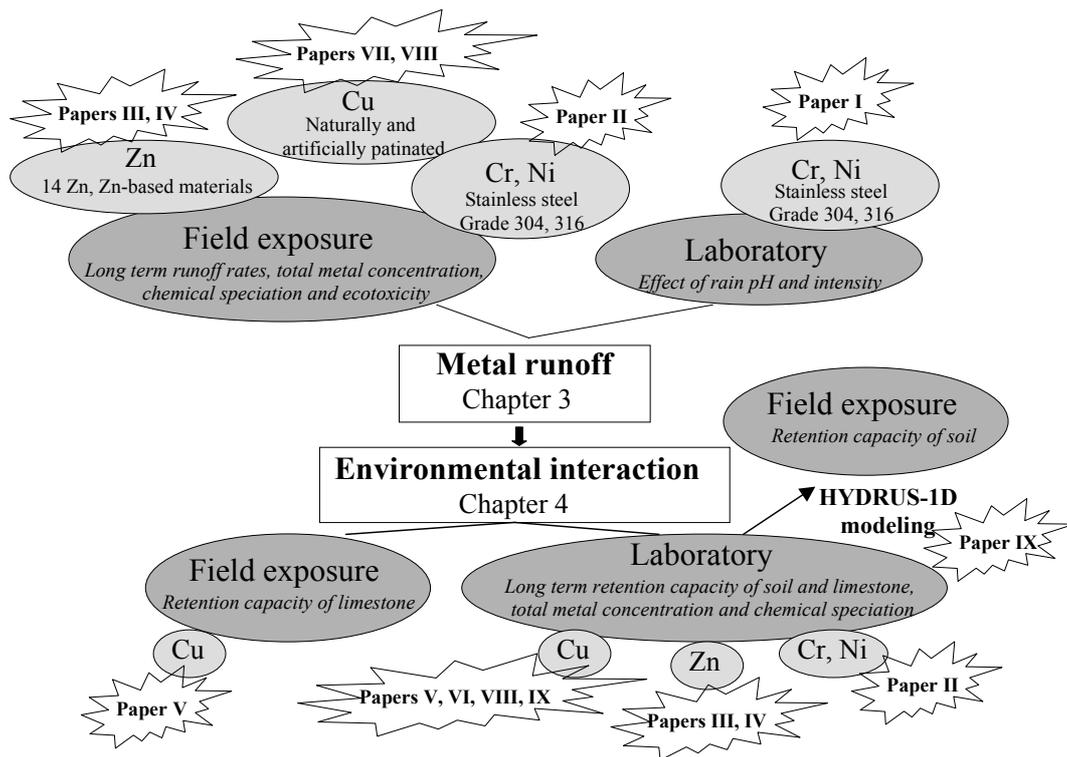


Figure 4. Compilation of investigations performed within the scope of this thesis and corresponding Papers.

In all, this thesis compiles current state-of-knowledge on the corrosion-induced metal runoff process, including long-term runoff rates, predictive runoff rate models, total metal concentrations, chemical speciation and bioavailable metal fractions at the immediate release situation and after environmental interaction. The work provides scientific data to be used within exposure assessments of corrosion-induced metal release from external constructions.

The thesis work comprises both field and laboratory investigations. A description of key information and investigating tools used within this thesis is schematically compiled in Fig. 5.

A more thorough description of experimental set-ups, analytical methods, computer modelling and bioassay tests are given in Papers I-IX.

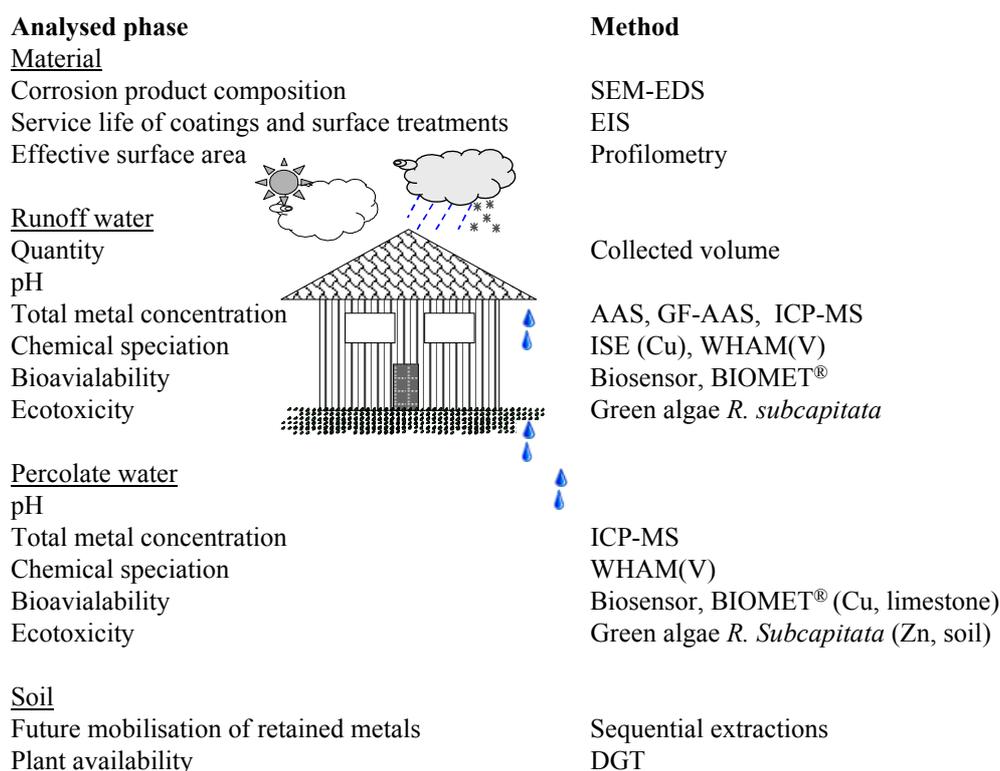


Figure 5. Schematic illustration of key information and investigating tools for; *i*) exposed metal surface, *ii*) runoff water (collected at the immediate release situation), *iii*) the percolate water (runoff water after soil or limestone interaction), and *iv*) metals retained in soil.

Abbreviations; SEM: Scanning Electron Microscopy, EDS: Energy Dispersive Spectroscopy, EIS: Electrochemical Impedance Spectroscopy, AAS: Atomic Absorption Spectroscopy (with and without graphite furnace), ICP-MS: Inductively Coupled Plasma Mass Spectroscopy, ISE: Ion Selective Electrode, WHAM: Windermere Humic Aquatic Model, DGT: Diffuse Gradients in Thin Films.

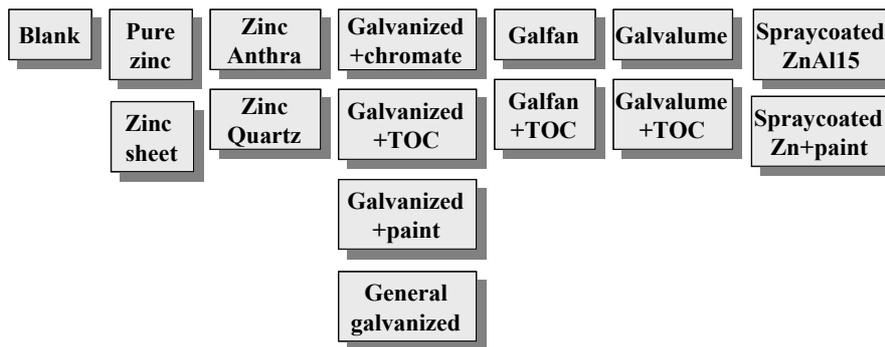
2.1 Field exposures (Papers I, II, III, IV, V, VIII)

The thesis includes data from a long-term field exposure of 14 different zinc-based materials (up to 5 years), 5 copper-based materials (8 years) and 2 grades of stainless steel (4 years). The exposure was performed on a building within the campus area of KTH [Karlén et. al, 2001a]. All panels were exposed at standardized exposure conditions (45° inclination facing south) in Stockholm, Sweden, Fig. 1. Average annual concentrations of $2.8 \mu\text{g m}^{-3} \text{SO}_2$, $43 \mu\text{g m}^{-3} \text{NO}_2$, $51 \mu\text{g m}^{-3} \text{O}_3$, $18 \mu\text{g m}^{-3} \text{PM}_{10}$, and annual precipitation quantities between 450 to 800 mm yr^{-1} , characterize the test site during the total period of exposure (1996-2004). Detailed information is provided in Paper III, IV for the exposure of zinc-based materials, in Paper VIII for copper, and in Paper I, II for stainless steel. A schematic compilation of investigated materials is given in Fig. 6.

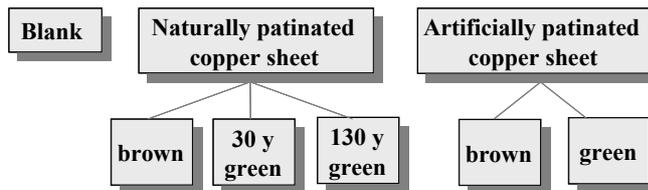


Figure 6. Test site for metal runoff studies (field exposure).

Zinc-based Materials: Paper IV



Copper-based Materials: Paper VIII



Stainless steel: Papers I, II



Figure 7. Investigated materials.

The thesis also includes data from a separate field exposure (1.5 years) to study the interaction of copper runoff water and limestone (Paper V). The exposure was performed on a copper roof of a summerhouse at Älgö, in the archipelago of Stockholm, Sweden, Fig. 8. Runoff water was collected from two sections of the roof (inclined 23° from horizon, facing south), each 2 m², after passage through down-pipes. One pipe was filled with limestone and the other pipe used as a reference. The most important experimental details are given in Fig. 8 (right). More details are given in Paper V.



| Parameter | Value |
|------------------------------|-------|
| Fraction of limestone/mm | 4-8 |
| Density / g*cm ⁻³ | 2.70 |
| Amount of limestone / kg | 1 |
| Diameter / cm | 4.2 |
| Height / cm | 27 |
| Duration / years | 1.5 |

Figure 8. Test site for studies of the interaction of copper containing runoff water and limestone (left) and important experimental details (right).

2.2 Laboratory investigations

Three different laboratory investigations were performed within the scope of this thesis, *i*) artificial rain simulations to investigate the effect of rain characteristics on the release rate of chromium and nickel from stainless steel (Paper I), *ii*) simulations of the interaction between metal containing runoff water and soil (columns), (Papers II, III, IV, V, VIII), and *iii*) simulations of the interaction between copper containing runoff water and limestone (Paper VI).

Simulations of realistic rain events of varying intensity and pH were performed in a rain chamber, previously shown to successfully mimic outdoor conditions [He, 2002]. Experimental details are given in Paper I.

Simulations of the interaction between metal containing runoff water and soil were made by continuously introducing metal containing artificial runoff water to soils of different characteristics. The experimental set-up is illustrated in Fig. 9 and a compilation of characteristics for each soil investigated given in Table. 2. The chemical composition of runoff water resembles rain in the central and southern part of Sweden, and a pH and a metal concentration representative of runoff water from each group of material in the urban field exposure (Paper II-VIII). The metal concentrations represent the immediate release situation, without any dilution of rainwater from non metal-covered areas, i.e. a worst-case scenario. The laboratory simulation mimics an outdoor exposure period between 18 and 34 years (assuming an infiltration rate of 400 mm yr^{-1}). Experimental details are given in Papers II, III, IV, V, VIII.

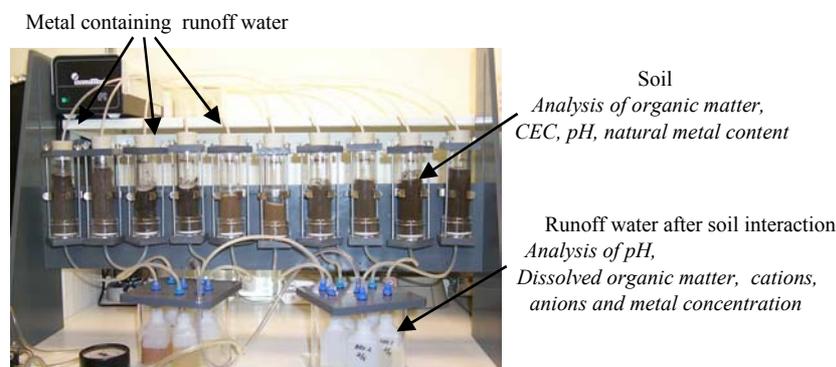


Figure 9. Experimental setup for simulations of the interaction between metal containing runoff water and soil.

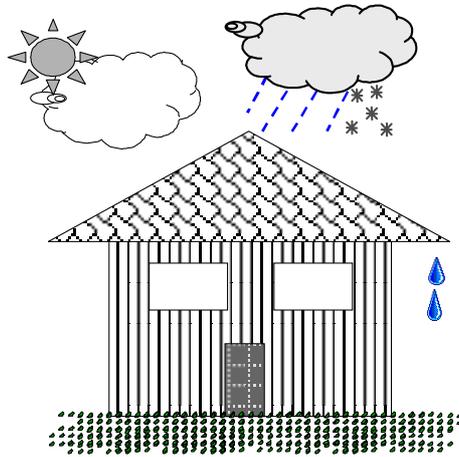
Table 2 Characteristics of investigated soils.

| <i>Soil</i> | Clay (% D.W.) | C _{org} (% D.W.) | pH H ₂ O, 8°C | CEC (cmol kg ⁻¹) | Me _{EDTA} (mg kg ⁻¹) | | | | Me _{7M HNO₃} (mg kg ⁻¹) | | | | Paper |
|-------------------------|------------------|------------------------------|-----------------------------|---------------------------------|--|------|-----|------|--|------------------|------|------|---------------|
| | | | | | Zn | Cu | Cr | Ni | Zn | Cu | Cr | Ni | |
| OECD | 20 | 8.6 | 6.49 | 13.4 | 0.9 | 0.3 | 0.0 | 0.01 | 3.0 | 1.2 | 1.0 | 1.8 | II, V |
| Kalmthout | 1 | 4.1 | 4.93 | 2.6 | 18.6 | 1.8 | 4.1 | 3.7 | 30.2 | 7 ^a | 8.1 | 2.9 | III, IV, VIII |
| Ter Munck | 17 | 1.5 | 7.95 | 12.4 | 11.0 | 5.4 | 3.1 | 8.5 | 48.2 | 12.4 | 18.7 | 8.7 | IV |
| Högbytorp | 20-40 | 5.1 | 5.95 | 13.4 | 1.3 | 3.0 | 2.3 | 9.0 | 73.5 | 13 ^a | 29.5 | 14.6 | IV, V, VIII |
| Kövlinge | 7 | 5.6 | 5.65 | 6 | N.A | 1.7 | N.A | N.A | N.A | 6.6 ^a | N.A | N.A | VIII |
| Kövlinge _{Bw1} | 4 | 2 | 5.30 | 1.6 | N.A | 0.1 | N.A | N.A | N.A | 1.8 ^a | N.A | N.A | VIII |
| Rosenlund | 7 | 3.8 | 4.09 | 0.7 | 1.0 | 21.0 | 0.1 | 0.2 | 47.5 | 36.0 | 4.0 | 1.7 | II, V |

N.A = not analysed, D.W. = Dry weight, ^a aq-regia

In complement to the soil column exposures, batch experiments were conducted to evaluate distribution coefficients of zinc in the Kalmthout, the Högbytorp and the Ter Munck soil (results presented in section 4.1). The measurements were performed with 0.2 mmole Ca(NO₃)₂ of varying zinc concentration (Högbytorp 30, 60, 120 mg Zn L⁻¹, Kalmthout 10, 20, 40 mg Zn L⁻¹, Ter Munck 20, 40, 80 mg Zn L⁻¹). After zinc introduction, the pH was adjusted to each soil pH by adding either NaOH or HNO₃. 2 grams of each soil, were separately introduced to 20 mL solution in polypropylene centrifugation tubes. The suspension was shaken, end over, for one day, centrifuged (20 min, 3000 rpm), filtered (0.45 µm) and analysed for zinc (AAS) in the solution phase. The results from the batch experiments are presented in the thesis summary.

Laboratory exposures of limestone to copper containing runoff water were performed to optimise copper retention. The effect of copper concentration, flow rate of runoff water, amount and specific surface area of limestone was investigated. Evaluated copper concentrations and runoff pH were based on data from field exposures of copper (Paper VIII), and data on flow rates of runoff water and amount of limestone from the field exposure (Paper V). More details are given in Paper VI.



Issues addressed within this chapter:

- *Does rain intensity and pH affect the release rate of Cr and Ni from stainless steel used for outdoor applications?*
- *At what rates and quantities are Cu, Zn, Cr and Ni released from external constructions on a long-term perspective?*
- *Are metal runoff rates lower for alloys, metal coated and surface treated materials compared to bare sheet?*
- *Can metal runoff rates be predicted for sites of different environmental characteristics?*
- *In what concentrations and chemical forms exist metals in runoff water at the immediate release situation?*
- *Can metal containing runoff water cause a detrimental effect on the environment?*

3.1 Atmospheric corrosion

A large number of different metals; pure, alloyed and/or coated, are used for external building applications. As a result, the constructions are exposed to the atmosphere and will corrode to some extent, forming a surface layer of corrosion products. The corrosion process forms part of a natural cycle in which the metal is striving, through spontaneous reactions, to reach its most stable condition in the ambient environment, *i.e.* as a mineral, from which it was once refined. Therefore, the composition and protective characteristics of the corrosion products depend primarily on the type of material, prevailing environmental conditions and ambient pollutant concentrations. The ambition to reach a state of “no corrosion” is an impossible mission, and not always desirable, since the corrosion process often results in corrosion products that protect the surface from further corrosion. However by, decreasing atmospheric pollutants and select the right material for a specific exposure situation, the extent of the atmospheric corrosion can be minimized. Corrosive pollutants are deposited either from direct transfer of gases and particles to the surface from the atmosphere (dry deposition), or from indirect transfer by precipitation (wet deposition). Generalized schemes, describing corrosion product formation during sheltered and unsheltered atmospheric exposure, have been elaborated for zinc (Fig. 10) and copper (Fig. 11) [Odnevall and Leygraf, 1995; Leygraf et. al, 2000; Krätschmer et. al, 2002]. An unsheltered condition involves both dry and wet deposition of corrosive species, and direct exposures to precipitation, whereas sheltered outdoor conditions comprise dry deposition without any precipitation. Urban (cities with SO₂ as main atmospheric constituent) and rural (low polluted atmospheres) atmospheric exposure of bare zinc results in the formation of relatively porous and voluminous corrosion products, primarily composed of a 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) [Odnevall, 1995].

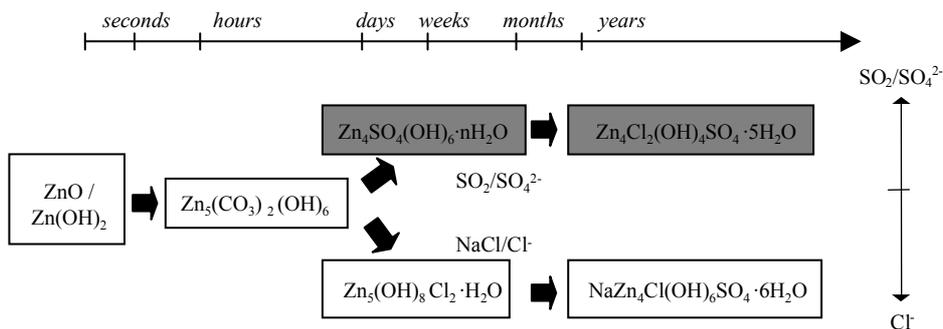


Figure 10. Reaction scheme for corrosion product formation of bare zinc sheet exposed to different sheltered and unsheltered atmospheric conditions. The time scale indicates approximately the shortest exposure time after which a certain compound is observed. Grayish fields denote compounds primarily detected in sheltered conditions [Odnevall and Leygraf, 1995]. Reprinted with permission from Odnevall and Leygraf 2005.

Copper forms, similar to zinc, relatively porous and voluminous layers of corrosion products during urban atmospheric exposures. An inner layer of cuprite (Cu_2O), and an outer layer primarily composed of posnjakite ($\text{Cu}_4\text{SO}_4(\text{OH})_6\text{H}_2\text{O}$) and brochantite $\text{Cu}_4\text{SO}_4(\text{OH})_6$, are the main constituents of the corrosion product layer on unsheltered copper in urban environments [Cramer et. al, 2001; Krätschmer et. al, 2002; Graedel, 1987a, b]. A general scheme for corrosion product formation on copper in urban and rural environments is presented in Fig. 11.

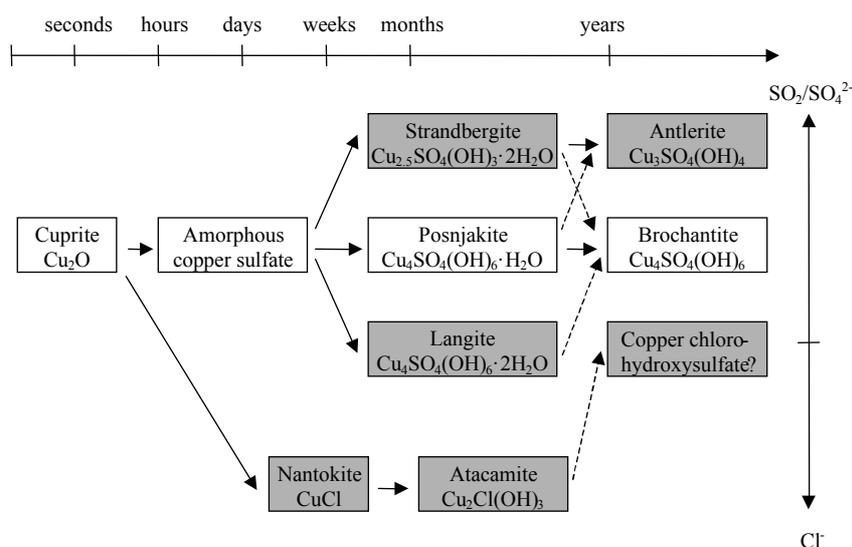


Figure 11. Reaction scheme for corrosion product formation on unsheltered copper in urban and rural atmospheric environments. The time scale indicates approximately the shortest exposure time after which a certain compound is observed. Greyish fields denote compounds primarily detected in sheltered conditions [Leygraf and Graedel, 2000]. Reprinted with permission from Leygraf 2005.

Stainless steels are corrosion resistant alloys of iron that contain a minimum of 11wt% chromium. Chromium is the essential alloying element for the formation and stabilization of the passive film. Other alloying elements (e.g. Ni, Mo, Cu, S, C, Si) may be added, singly or in various combinations and concentrations, in order to vary the properties of the stainless steel (e.g. mechanical properties, corrosion resistance). The term passive film refers to the presence of a very thin (nm, 10^{-9} m) and protective surface oxide on stainless steel, significantly different from the relatively thick (μm , 10^{-6} m) and porous nature of the corrosion product layer formed on copper and zinc. A surface alloy layer enriched in Ni and Mo (e.g. grade 316) is present adjacent to the passive film, with a thickness in the same order as the passive film. Alloying improves the corrosion resistance by influencing the efficiency of chromium to form and/or maintain the passive film (e.g. Ni promotes re-passivation, especially in reducing environments; and Mo stabilizes the passive film in the presence of chlorides). The stability of the passive film is significantly improved by increasing the Cr content to 17 to 20 wt%. Essentially, Cr reacts with oxygen and moisture in the environment to form a protective, adherent, coherent and self-healing surface layer that envelops the entire surface, and confers the corrosion resistance. The passive film is described to consist of an

inner barrier composed of Fe and Cr oxides and an outer layer of Cr hydroxides [Clayton et. al, 2002; Wegrelius, 1995]. The chemical composition and thickness vary with a number of different parameters such as electrochemical potential, exposure condition and time [Olsson, 1994].

The rate at which the metal/alloy corrodes is known as the corrosion rate and is defined as the amount of metal that is oxidized per unit area in a given time (commonly expressed as the loss of weight or thickness per unit area and unit time). As the corrosion product layer gradually is built up, the corrosion rate decreases as a result of a reduced possibility for corrosive species to diffuse towards the interface between the bulk metal and the corrosion product and oxidize the metal surface [Graedel, 1987b; Odnevall Wallinder and Leygraf, 2001]. Attempts have been made to link the corrosion rate of a metal to causative agents in various field exposure programs, i.e. UN/ECE International Cooperative Program of Effects on Materials [<http://www.corr-institute.se/ICP-Materials/050317>]. Dose response functions are available that describe the relation between the corrosion rate (response) and various environmental parameters (type and dose). Such relations are useful tools for material selection at specific environmental and exposure situations. Numerous dose-response functions are available in the literature. Functions for corrosion rates of unsheltered copper [eq. 1] and zinc [eq. 2] have recently been derived, based on long-term (8 years) data from 39 sites in Europe and North America, [http://www.corr-institute.se/ICP-Materials/html/dose_response.html/050317]:

$$\text{Cu (g m}^{-2}\text{)} = 0.0027[\text{SO}_2]^{0.32}[\text{O}_3]^{0.79}\text{RHexp}(f(T))t^{0.78} + 0.05\text{Rain}[\text{H}^+]t^{0.89} \quad [\text{eq. 1}]$$

$$\text{Zn (g m}^{-2}\text{)} = 1.4[\text{SO}_2]^{0.22}\text{exp}(0.018\text{RH}+f(T))t^{0.85} + 0.029\text{Rain}[\text{H}^+]t \quad [\text{eq. 2}]$$

where $[\text{SO}_2]$ and $[\text{O}_3]$ are atmospheric gas concentrations ($\mu\text{g m}^{-3}$), RH the relative humidity (%), Rain the total rainfall quantity (mm), $[\text{H}^+]$ the hydrogen ion concentration in rain water (mg L^{-1}), T the temperature ($^{\circ}\text{C}$) and t, the time of exposure (years). The temperature dependent function $f(T)$, is described by $0.062(T-10)$ when $T < 10^{\circ}\text{C}$, otherwise $-0.021(T-10)$ in case of zinc and $0.083(T-10)$ when $T < 10^{\circ}\text{C}$, otherwise $-0.032(T-10)$ in case of copper.

Dose-response relations show a strong correlation between the corrosion rate of zinc and the SO₂ concentration [Tidblad et. al, 1999; Odnevall Wallinder et. al, 1998]. The relation for copper is more complex and depends on an interactive effect of SO₂ and O₃, the annual rain quantity and acidity, and prevailing environmental parameters. Reported corrosion rates of unsheltered copper and zinc exposed in urban and industrial environments vary between 8.91-22.3 g m⁻² yr⁻¹ and 14.3-114.2 g m⁻² yr⁻¹, respectively [Leygraf, 1995]. Quantitative data on corrosion rates of stainless steels in atmospheric conditions are rare, even though the corrosion resistance of stainless steels is well studied. Corrosion rates in the range between 0.02 and 0.9 mg m⁻² yr⁻¹, and between <0.025 and 0.3 mg m⁻² yr⁻¹, have been reported for 304 and 316 stainless steels, respectively, exposed in different marine and polluted locations, [Johnson and Pavlik, 1982; Heidersbach, 1987; Baker and Lee, 1990]. Environments of low pollution (rural and most urban sites) result in lower corrosion rates; 0.2-0.5 mg m⁻² yr⁻¹ and 0.1 mg m⁻² yr⁻¹, for grades 304 and 316, respectively [Leygraf and Graedel, 2000]. Substantial reductions in SO₂ concentrations during the last decades in Europe have resulted in significantly reduced corrosion and runoff rates of zinc [Korenromp and Hollander, 1999].

In conclusion, depending on type of material and exposure situation, a variety of corrosion products can form on a metal surface. With time, the corrosion rate decreases as the overall process is diffusion controlled and a layer of corrosion products is formed. Dose response functions are available that relate environmental parameters to corrosion rates, and are hence useful tools for site predictions and material selection.

3.2 The runoff process

During precipitation events, phases of the corrosion product layer (copper and zinc), or metals from a combination of the passive film and the surface alloy layer (stainless steels), will dissolve and be released from the surface. The metal release rate, or runoff rate, is the amount of metal that is released per unit of surface area in a given time. Whereas the corrosion process takes place at the interface between the metal substrate and the corrosion product layer, the runoff process occurs at the interface between the atmosphere and the corrosion products, see Fig. 12 in the case of copper and zinc. The situation is somewhat different for stainless steels. Due to the very thin passive film, metal release occurs both at the interface between the atmosphere and the passive layer, and at the interface between the passive layer and the metal.

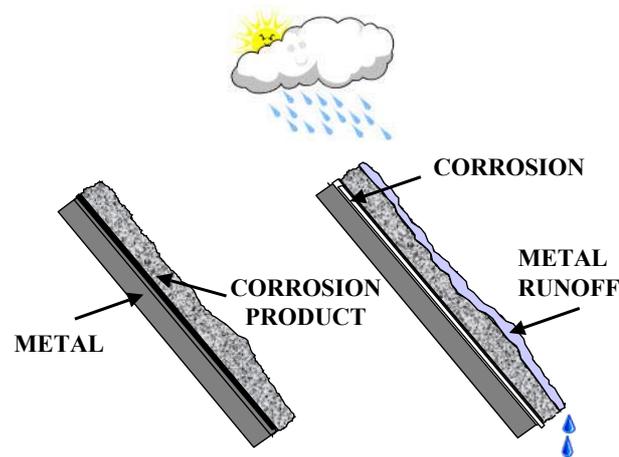


Figure 12. Schematic illustration on differences between the corrosion- and the runoff process for copper and zinc.

Corrosion and runoff are generally ruled by different physical, chemical and electrochemical processes, and therefore governed by different atmospheric exposure parameters. Hence, it follows that corrosion and runoff proceed at rates that are not necessarily equal or even proportional [He, 2002; Odnevall Wallinder et. al, 2000; Odnevall et. al, 1998; Cramer et. al, 1988]. This is exemplified in Fig. 13 showing the runoff rate (7 years) and the corrosion rate (1 year) of bare zinc sheet, exposed at unsheltered conditions in Stockholm, Sweden. The runoff rate is significantly lower than the corresponding corrosion rate during this time-period [He, 2002]. With time, the rates might become equal when steady-state conditions are reached with a constant thickness of the corrosion layer.

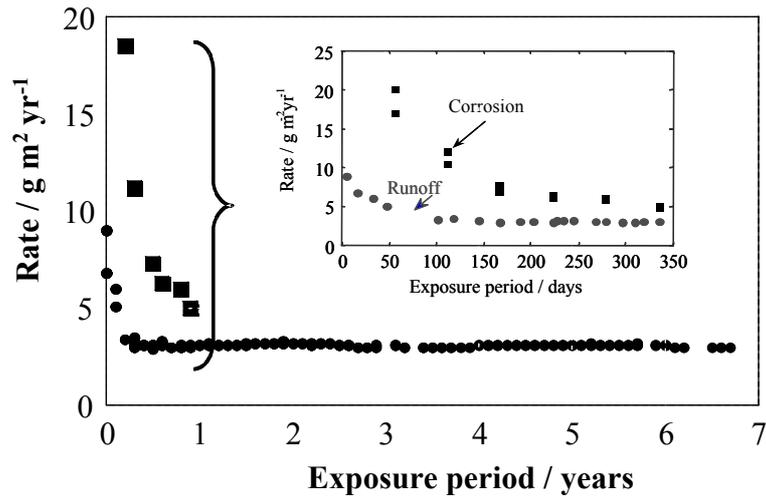


Figure 13. The corrosion rate (1 year) [He, 2002] and corresponding runoff rate (7 years) of zinc from bare zinc sheet during unsheltered exposure (1996-2003) in Stockholm, Sweden. The inserted diagram displays data for the first year of exposure. More details are given in (Paper IV).

Runoff rates of copper and zinc from a large variety of roofing materials have been shown to depend on a combination of environmental and material parameters, including e.g. precipitation and pollutant levels, wind direction, corrosion product characteristics and building geometry [Odnevall Wallinder et. al, 2000; Odnevall et. al, 1998; He, 2002]. A compilation of parameters determining the runoff rate is given in Fig. 14.

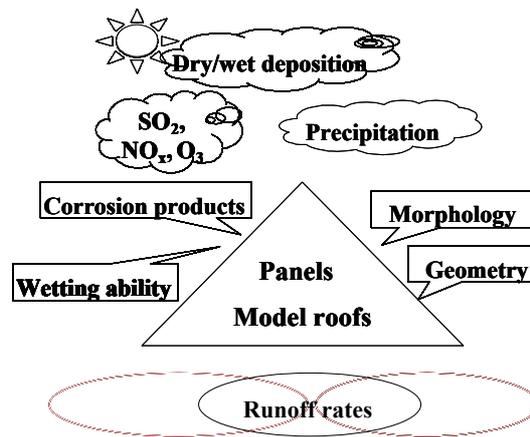


Figure 14. Compilation of parameters determining the metal runoff rate (Paper VII).

Pollutants (dry and wet deposition of SO₂, NO_x etc) are important since they influence both corrosion product formation (primarily copper and zinc) and rainwater characteristics, e.g. pH and ionic composition. The amount, intensity and duration of a rain event influence the

effective time period (contact time) for dissolution and transport of easily soluble phases within the corrosion product layer. The contact time is influenced by the building geometry, where a steep inclination from the horizontal results in a smaller rainfall quantity impinging the surface, and a shorter contact time for dissolution and runoff, compared to a more horizontally orientated surface. Type of material, and ambient environmental conditions and atmospheric pollutant concentrations determine the composition of the corrosion product layer, its thickness and morphology, parameters that are all time-dependent. However, since unsheltered exposure conditions (the only exposure situation resulting in metal runoff), results in a limited number of phases within the corrosion product layer (Figs. 1-2), and the time to reach an equilibrium state for the outermost corrosion product layer seems to be less than one year, are runoff rates of copper and zinc relatively constant on a long-term perspective (exemplified for zinc in Fig. 13). The same situation is valid for stainless steels, experiencing an even shorter time-period to reach an equilibrium state for the passive film [Herting et. al, 2005].

3.2.1 Effect of environmental (rain volume, intensity and pollutants) parameters on the metal runoff rate.

On a short time scale, corresponding to a single rain event, the runoff rate exhibits a clear time-dependence. The runoff rate is initially high, during which easily soluble species are washed off the surface (the so-called “first flush”). Prolonged exposure results in a gradual decrease of the runoff rate that, with time, becomes relatively constant (Fig. 15 left) [He et. al, 2002a; He et. al, 2000; Herting et. al, 2005]. When runoff water is collected e.g. once every week, the runoff rate can, even at comparable rain volumes, vary significantly depending on if the sampling period includes a few precipitation events of long duration or many events of short duration (Fig. 15, middle). However, on a yearly perspective, most environmental parameters are fairly constant at a specific site, with only minor variations of the annual runoff rate as a result. Such data can be used for long-term predictions of expected metal runoff rates from external constructions (Fig. 15 right and Fig. 13).

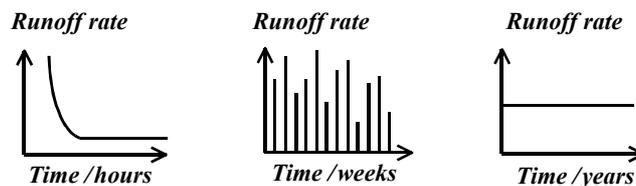


Figure 15. Variation in metal runoff rates during short and long-term exposures (More details are given in Paper II, VII).

As previously discussed, the rain intensity determines the contact time for dissolution. Larger runoff quantities are obtained at lower rain intensities for a given total rain volume compared to higher intensities. Higher copper and zinc concentrations in the runoff water are therefore detected in runoff water after several rain episodes of low intensity compared to few events of high intensity [He et. al, 2001]. However, this observation is not very pronounced after long periods of continuous wet conditions, since the contribution of first flush with soluble corrosion products, hence are low. This is clearly seen for stainless steel, possessing a low contribution of first flush due to the thin and compact passive film of relatively low solubility, where the release of chromium and nickel from grades 304 and 316, are independent of rain intensity. More details are given in Paper II.

Rain contains a large number of chemical constituents, e.g. inorganic and organic ions, radicals and molecules. The acidity (concentration of protons, H^+) varies between and during rain events, and reflects indirectly the prevailing pollutant level of e.g. SO_2 and NO_x dissolved and transformed to acids in rain droplets. The acidity is commonly highest during the initial portion of a rain event with decreasing levels in subsequent rain portions [Graedel, 1986]. No simple relations exist to transform “easily” monitored atmospheric pollutant concentration levels of e.g. SO_2 , NO_x , O_3 , to reflect rain concentrations of SO_4^{2-} , H^+ , NO_3^- . Scarce data exist in the literature that relates metal runoff rates to rain constituents [He, 2002]. An attempt was therefore made to evaluate the individual and interacting effect of the most common chemical rain constituents on the runoff rate of copper (Paper VII) and zinc (Bertling unpublished data). The investigation was planned with a two level fractional factorial design by the software program Modde6[®], with sulphate (SO_4^{2-}), nitrate (NO_3^-), chloride (Cl^-) and rain pH as the main parameters. A minimum and maximum value was

selected for each parameter, based on an extensive data-set representing different rain conditions in 37 different European sites during 1987 to 1995 (Paper VII). The results clearly show rain pH to be of major importance for the dissolution of copper (Fig. 16, left) and zinc (Fig. 16, right). The concentration of SO_4^{2-} in rainwater has a larger effect on the dissolution of zinc compared to copper. NO_3^- shows an inhibiting effect on the dissolution and is commonly used for corrosion inhibition. The results indicate that relations for predictions of runoff rates should include rain pH and the chemical constituents that have an effect on rain pH.

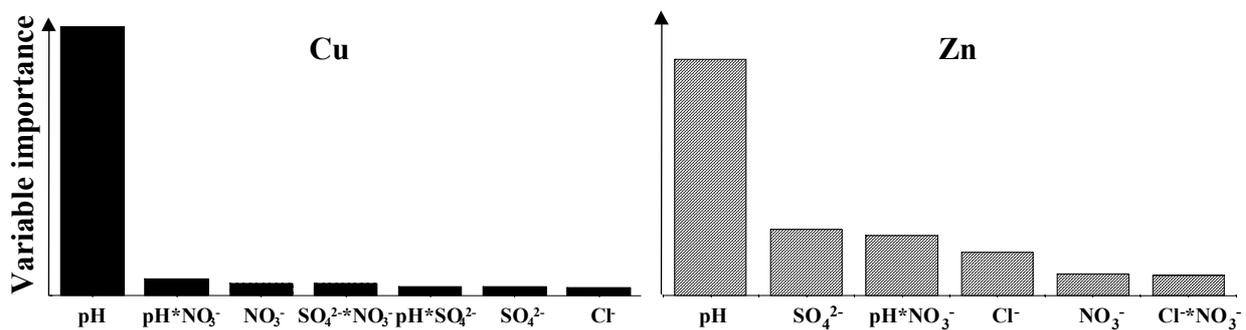


Figure 16. Relative importance of rain constituents on the dissolution of naturally brown-patinated copper sheet (left) and bare zinc sheet (right) (Paper VII).

The effect of rain pH, intensity and dry deposition on the runoff rate of copper and zinc is illustrated in Fig. 17, [He, 2002]. The figure shows that dry deposition of pollutants influence the metal concentration during the initial runoff volume, whereas rain pH and intensity also are important for the copper and zinc concentration during steady state conditions of a rain event.

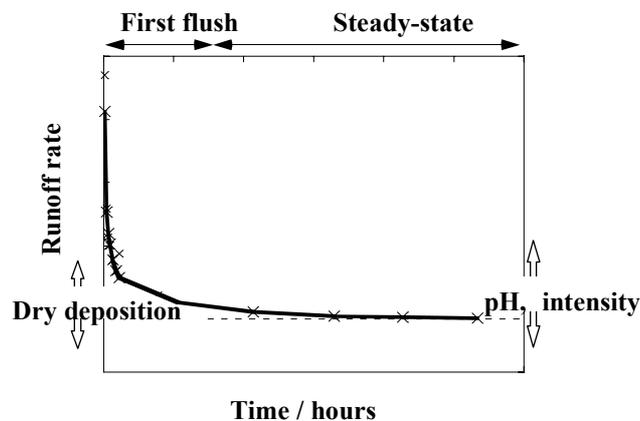


Figure 17. Summary of environmental parameters affecting the runoff rate of copper and zinc [He, 2002]. Reprinted with permission from He 2005.

Similar investigations on stainless steel grades 304 and 316 showed rain pH to be of major importance on the runoff rate. The effect of pH was further evaluated in rain exposure experiments for grade 304 (Paper I) at a given rain intensity and duration, Fig. 18. The runoff rate of chromium was approximately 10 times lower at pH 5.7 and approximately 3 times higher at pH 3.5 compared to the rate obtained at pH 4.3 (most common rain pH in Stockholm, Sweden), and further increased at pH 2.5. The runoff rate of nickel was 3 to 4 times lower at pH 5.7 and 2-3 times higher at pH 3.5.

The runoff rate of nickel was higher compared to chromium. More details are given in Paper I.

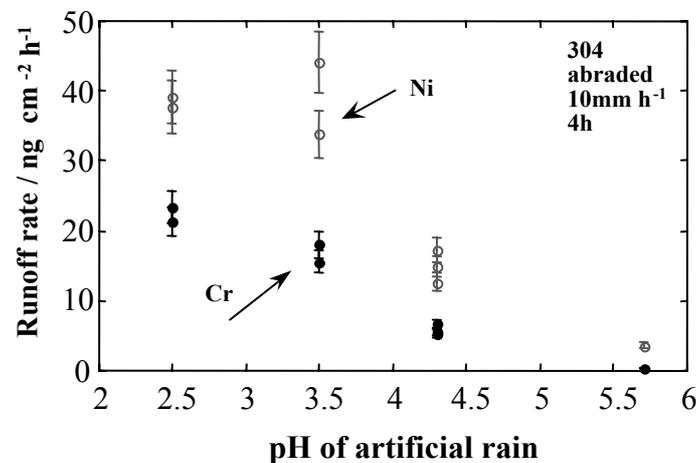


Figure 18. Runoff rates of Cr and Ni from abraded 304 stainless steel during single artificial rain events of intensity 10 mm h⁻¹ and varying pH (Paper I).

It can be concluded that the rain intensity under present conditions has no direct influence on the runoff rate of chromium and nickel, but increases the runoff rate somewhat for copper and zinc. The metal runoff rate is volume and time dependent, with an initially high rate (first flush effect) followed by a more constant rate during subsequent rain. Dissolution of copper, zinc and chromium and nickel from stainless steel was primarily influenced by the rain pH. This suggests that rain pH and/or pH-affecting parameters should be included in predictive runoff rate considerations.

3.2.2 *Effect of material parameters (corrosion products and effective surface area) and building geometry on the metal runoff rate.*

The effective surface area exposed to rainwater, determined by the thickness and morphology of the formed corrosion products, as well as the solubility of the corrosion products, are all influenced by the type of material.

The runoff rate is usually somewhat higher for materials with thick and porous corrosion products, compared to materials with thin well-adherent surface oxides. This is primarily related to larger effective surface areas with higher ability to attract corrosive pollutants and moisture. Such morphologies enable dissolution of phases within the corrosion product layer in-between rain events. Dissolved species are washed from the surface during subsequent rain episodes. This behavior is e.g. seen for naturally green-patinated copper sheet, with thicker and more porous corrosion products, compared to naturally brown-patinated copper (section 3.3.1). However, such differences in runoff rates are negligible when determining metal flows from external constructions and from a risk assessment perspective.

The building geometry has a large effect on the runoff rate since surfaces of varying inclination and orientation, results in differences in amount and contact time of impinging rainwater. As previously discussed, the contact time for dissolution is influenced by a number of different parameters, including e.g. inclination, rain intensity and rain volume. A low inclination from the horizontal and, hence, a slow flow rate of rain water over the surface, induces high runoff rates by increasing both the contact time for dissolution of corrosion products, and the precipitation volume impinging on the surface. As an example, a 7° inclination from the horizontal resulted in a runoff rate of 6.7 g Zn m⁻² yr⁻¹ compared to 2.3 g Zn m⁻² yr⁻¹ for a 90° inclination from the horizontal for zinc sheet exposed at an industrial site in Belgium [Odnevall Wallinder et. al, 2000; He, 2002]. The volume of rainwater impinging the surface, and consequently the runoff rate, is influenced by the prevailing wind direction [He, 2002].

In conclusion, the morphology and solubility of phases within the corrosion product layer and the degree of inclination of the surface area have a significant influence on the runoff rate.

3.3 Runoff rates of Cu, Zn, Cr, Ni and Fe from construction materials during long-term urban exposures in Stockholm, Sweden (Papers II, IV, VIII)

As previously discussed, the runoff process is intimately related to environmental characteristics such as rain volume, pH, intensity, pollutant levels, and to material and surface characteristics including e.g. corrosion products, surface inclination and degree of sheltering [He et. al, 2000; 2001]. The material dependence is a consequence of the formation of different corrosion products of varying properties and morphology. In the forthcoming section, long-term runoff rates of Cu, Zn, Cr, Ni and Fe from copper (8 years), zinc (5 years) and stainless steel (4 years) are presented. All materials have been exposed at 45° from the horizontal, facing south, at an urban site in Stockholm, Sweden. Annual runoff rates are calculated based on the sum of runoff rates for individual sampling periods during each year of exposure and normalized in relation to the exposed surface area.

3.3.1 Long-term runoff rates of copper (Papers VIII)

Average annual runoff rates of copper from naturally brown and green patinated copper sheet are compiled in Fig. 19 (left) for an 8-year urban exposure. The variations between different years of exposure are primarily a result of differences in annual rainfall quantities (460-790 mm yr⁻¹), Fig. 19 (right). Naturally brown patinated copper and green patinated copper (brown: 1.2±0.3 gm⁻² yr⁻¹, green: 1.5±0.3 gm⁻² yr⁻¹) exhibit somewhat different runoff rates as a result of differences in patina (corrosion product) composition, thickness and morphology. Green patinated copper surfaces (inner layer: mainly Cu₂O and outer green layer of mainly Cu₄SO₄(OH)₆, 14-70 μm) show slightly higher runoff rates compared to brown-patinated copper (mainly Cu₂O, 5-12 μm). The discrepancy between brown and green patinated copper is primarily related to differences in runoff rates during the initial rainfall portion (first flush) as a result of differences in patina thickness and porosity [Zhang et. al, 2002]. The green patina has a high ability to retain corrosive species and humidity, hence increasing the possibility for copper to be dissolved from the patina. However, no significant difference in runoff rate is observed between brown and green patina during prolonged rainfall quantities (steady-state) (Paper VII). However, within the framework of risk assessment and risk management, these small differences are negligible when estimating flows of copper from external constructions. The natural background deposition of copper was measured to approximately 0.02 g m⁻² yr⁻¹.

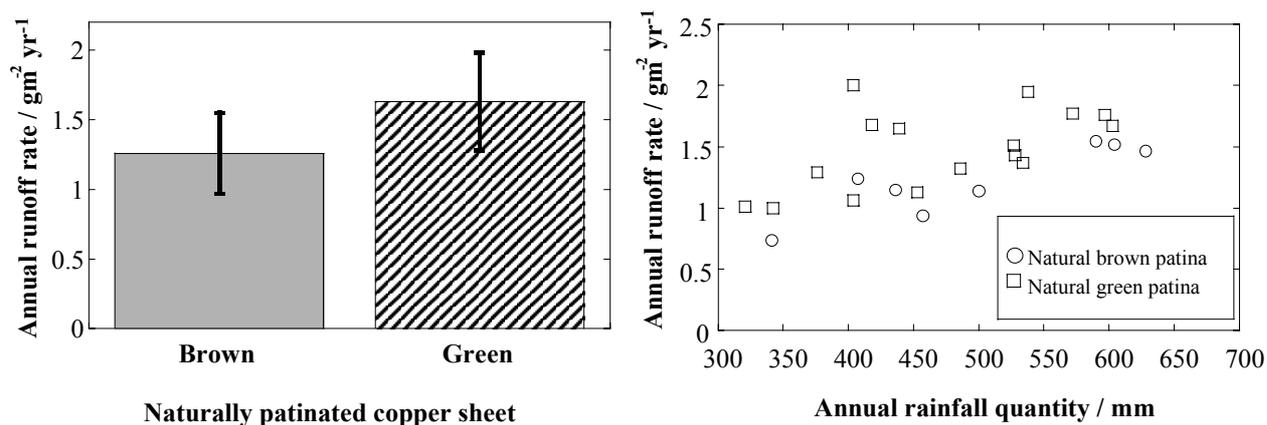


Figure 19. Mean annual runoff rates of copper from naturally patinated copper sheet exposed unsheltered during an eight-year exposure in the urban environment of Stockholm, Sweden (left), and correlation between the annual rainfall quantity and the annual runoff rate for naturally patinated copper sheet (right) (Paper VIII).

Measured runoff rates are in accordance with published runoff rates from urban sites (1.2-3.1 $\text{gm}^{-2} \text{yr}^{-1}$). More details are given in Paper VIII.

In conclusion, average annual runoff rates of copper from naturally patinated copper sheet during an eight-year urban exposure in Stockholm, Sweden range between 1.2 and 1.5 $\text{g m}^{-2} \text{yr}^{-1}$ for naturally brown and green patinated copper, respectively. The data are valid for annual precipitation quantities between 460-790 mm yr^{-1} and for an inclination of 45° from the horizontal. The runoff rate of green patinated copper is somewhat higher due to a more porous and thicker patina, enabling more moisture and corrosive species to be present in the patina between precipitation events, and extending the dissolution process. More details are given in Paper (VIII).

3.3.2 Long-term runoff rates of zinc (Paper IV)

Average annual runoff rates of zinc from zinc sheet and general galvanized steel (1.9 and 2.5 $\text{g Zn m}^{-2} \text{yr}^{-1}$) are presented in Fig. 20 (left) for a 5-year exposure. A small amount of zinc in runoff water originates also from natural dry and wet deposition measured on an inert surface (0.02 $\text{g m}^{-2} \text{yr}^{-1}$). No unambiguous correlation was observed between the annual rainfall

quantity (470-790 mm yr⁻¹) and the runoff rate. This indicates the importance of other environmental and/or material parameters, Fig. 20 (right).

Since zinc sheet is a rolled product, and general galvanized steel produced by hot dipping, the materials possess different surface structures (morphologies and grain size). The difference in morphology might result in slightly different effective surface areas and oxide phases exposed to the atmosphere, and hence explain differences in runoff rates. However, profilometry measurements (Paper IV), showed very similar surface areas for both materials. Observed differences in annual runoff rates between the materials are most probably related to the combined effect of changes in surface properties, in terms of slightly different phases formed on general galvanized compared to rolled products, and preferential zinc release from grain boundaries. However, within the framework of risk assessment and risk management, these small differences are negligible, when estimating flows of zinc from external constructions.

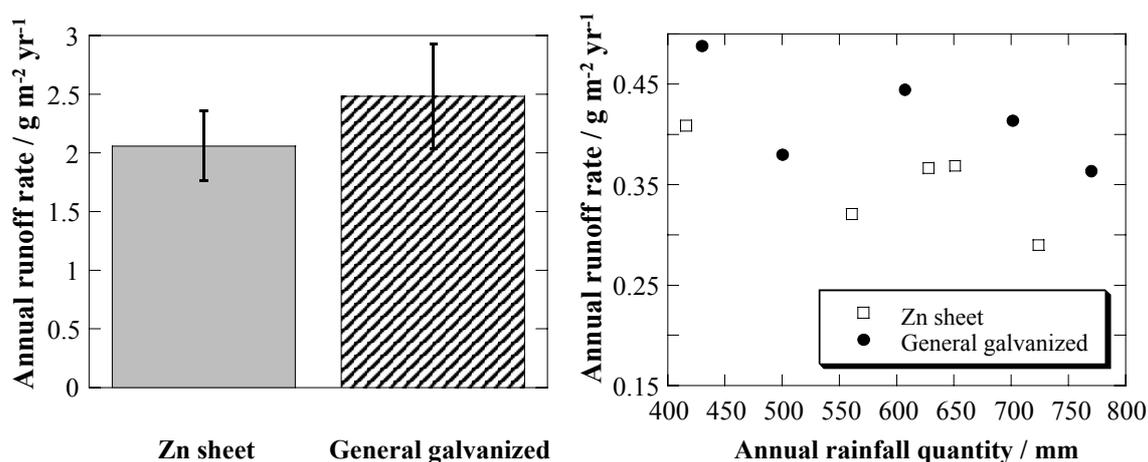


Figure 20. Mean annual runoff rates of zinc from zinc sheet (CuTi) and general galvanized steel exposed unsheltered during 5 years in the urban environment of Stockholm, Sweden (left), and correlation between annual rainfall quantities and corresponding annual runoff rates for the same samples (right) (Paper IV).

Compositional measurements of corrosion products on zinc sheet and general galvanized steel using EDS, combined with knowledge from previous investigations on corrosion product formation on zinc sheet at the same test site [Odnevall, 1996], suggest the formation of basic zinc carbonates as main constituent in the layer of corrosion products on both materials. Observed annual runoff rates of bare zinc sheet (2.1 ± 0.3 gm⁻² yr⁻¹) are somewhat lower compared to literature findings from different test sites (few urban sites) of Europe and the

U.S., primarily as a result of low SO₂-concentrations in Stockholm. Runoff rates between 4.4 and 13.1 g m² yr⁻¹ have been reported for bare zinc sheet at sites (urban + urban-industrial) with SO₂-concentrations between 5 and 70 µg m⁻³ and annual precipitation quantities up to 958 mm yr⁻¹ [Faller et. al, 1999; Cramer et. al, 2000; Odnevall Wallinder et. al, 1998; Odnevall Wallinder et. al, 1999].

In conclusion, average annual runoff rates of zinc from zinc sheet and general galvanized steel during a five-year urban exposure in Stockholm, Sweden range from 1.9 to 2.5 g m⁻² yr⁻¹, when exposed at 45° from the horizontal facing south, and with an annual precipitation quantity between 470 and 790 mm yr⁻¹. More details are given in Paper IV.

3.3.3 *Long-term runoff rates of Cr, Ni and Fe from stainless steel (Paper II)*

Due to the presence of the passive film, the exposure of stainless steels in the relatively low-polluted urban environment of Stockholm results in low metal runoff rates. 4-year annual runoff rates of chromium, nickel and iron from stainless steel grades 304 and 316 are compiled in Fig. 21. No measurements of iron were made during the first year of exposure. It should be noted that the annual runoff rates of nickel and iron from stainless steel grades 304 and 316 are orders of magnitude lower than for the corresponding pure metals, further discussed in section 3.4.1. Runoff rates of chromium from pure chromium sheet are similar to those from the alloy (stainless steel), as a result of the presence of a passive film enriched in chromium on both surfaces [Herting et. al, 2005]. Average annual runoff rates for chromium, nickel and iron during the four-year exposure are 0.23, 0.28, 65 mg m⁻² yr⁻¹ for grade 304, and 0.30, 0.52, 85 mg m⁻² yr⁻¹ for grade 316 (Paper II). For comparison, estimated values of the annual deposition of chromium and nickel in non-polluted rainwater in Sweden are 0.05 and 0.08 mg m⁻² yr⁻¹, respectively [Walterson, 1998].

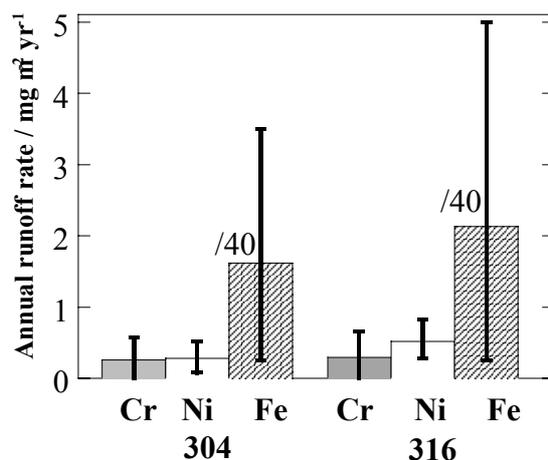


Figure 21. Mean annual runoff rates of chromium, nickel and iron from stainless steel grades 304 and 316 exposed unsheltered during a four-year exposure in the urban environment of Stockholm, Sweden (Paper II). The bars represents minimum and maximum values.

Somewhat higher runoff rates of chromium, nickel and iron from stainless steel grade 316 compared to 304 were measured during the exposure period (Paper II). The results show that grade 316 is not superior to grade 304 in low-chloride, non-aggressive atmospheric environments for simple constructions such as flat surfaces. This is consistent with previous findings, comparing the electrochemical behavior of grades 304 and 316 in bulk rainwater (Paper I). Variations in annual total metal runoff rates (Cr+Ni+Fe) from both stainless steel grades (year 4 >> year 2 > year 3) could not directly be correlated to variations in annual rain quantities impinging the surfaces (year 4 ≥ year 3 >> year 2), (Paper II). Similar conclusions were drawn when examining individual sampling periods. Previous investigations have emphasized the importance of prevailing environmental conditions and rainfall characteristics on the metal runoff process for copper and zinc [He, 2002]. A closer examination of individual sampling periods during the four-year exposure clearly shows higher runoff rates of chromium and nickel to be a result of continuously wet surfaces induced by small amounts of rain at frequent intervals, high humidity and deposition of corrosive species, since the “washing” of the surfaces by larger amounts of rain will not occur (Paper II).

The runoff rate of iron is significantly higher compared to chromium and nickel for both grades. Similar findings were observed in recent laboratory exposures in artificial rain [Herting et. al, 2005]. Selective dissolution of iron has previously been reported during anodic

dissolution and during passivation as a result of chromium enrichment in the passive film and nickel and iron enrichment in the alloy surface layer [Olefjord et. al, 1985; Olefjord and Wegrelius, 1996]. Since nickel and iron are released, despite being primarily present in the alloy surface layer below the passive film, it suggests either the presence of defects in the passive film or a selective dissolution of the different elements. During a precipitation event, part of the chromium-rich passive layer is dissolved. As this layer decreases in thickness, the driving force for potentially driven transport of other elements such as nickel and iron through the passive film might be exceeded. Similar release rates of chromium from stainless steel grades 304 and 316, suggest no large differences with respect to chromium enrichment of the passive films.

In conclusion, measured average annual runoff rates of alloy constituents from stainless steel exposed at 45° from the horizontal, facing south, during four years in Stockholm, Sweden, show somewhat higher rates from grade 316 (0.30, 0.52 and 85 mg Cr, Ni, Fe m⁻² yr⁻¹) compared to grade 304 (0.23, 0.28 and 65 mg Cr, Ni, Fe m⁻² yr⁻¹). Iron was preferentially released from both grades. The annual precipitation quantity varied during the exposure period between 585 and 790 mm yr⁻¹. More details are given in Paper II.

3.4 Runoff rates from alloyed-, coated- and surface treated metals

Metallic construction materials are rarely composed of a single metal, but are more commonly mixtures of different metals (alloys) used in a homogeneous form or as a coating. The alloy can either be used in its metallic form, or further surface treated in order to achieve a desired performance. This proposes a difficulty when predicting runoff rates, since the metal bulk composition of alloys seldom reflects the surface composition for a material. It has been proposed that runoff rates of metals from alloys could be predicted by multiplying runoff rates from the pure metals with the nominal bulk alloy composition. This would simplify the risk assessment of the high number of available alloys. This hypothesis has been evaluated and shown to be erroneous for zinc, in which aluminium has been the main alloy component [Karlén et. al, 2001b; Paper IV] and recently for stainless steel, in which chromium and nickel are the main alloy constituents [Herting et. al, 2005]. In the following section, the effect on the runoff rate by alloying (stainless steel), metal coating (zinc-aluminium coated steel) and/or different surface treatments (including chromate layer, and organic (TOC) coatings, a two component paint system and pre-oxidized/artificially patinated copper sheet) are discussed.

All investigated alloys, metal coatings and surface treatments are commercially used, either for preventing corrosion during transport and storage or for increased durability or aesthetic reasons.

3.4.1 Alloys (Stainless steel)

The difference in runoff rates of chromium, nickel and iron from stainless steel alloys (grades 304 and 316) and pure metals, have been evaluated at identical exposure conditions [Herting et. al, 2005] in order to elucidate the effect of alloying. A comparison between metal runoff rates from stainless steel (presented as the average rate from as-received 304 and 316 alloys) and pure metals was made after eight hours of continuous rain, Fig. 22. The runoff rates of nickel and iron from the stainless steel alloys are several orders of magnitude lower compared to runoff rates from the pure metals. This is connected to the presence of a chromium-rich passive film on stainless steel that successfully reduces runoff rates of nickel and iron compared to surface films formed on the pure metals. The main effect of alloying is related to the ability of the alloying elements to change the properties of the corrosion product layer and/or passive film, thereby altering the ability for release of different metals.

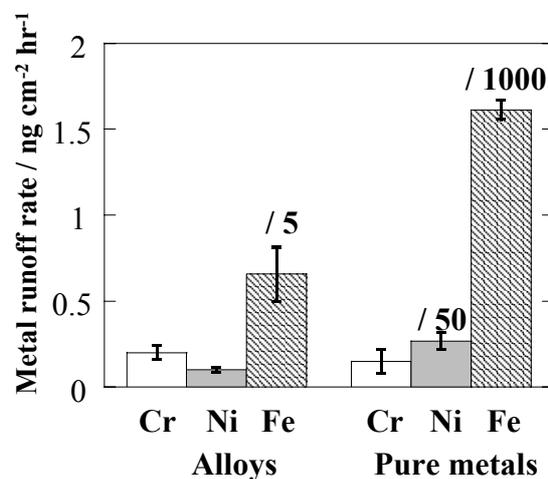


Figure 22. Metal runoff rates of Cr, Ni and Fe from as-received stainless steel (average value of grades 304 and 316) and the pure metals after 8 hours of continuous rain (pH 4.3, rain intensity 4 mm h⁻¹) [Herting et. al, 2005]. Reprinted with permission from Herting 2005.

Annual runoff rates and mass balance calculations show iron to be predominantly released and the release of chromium and nickel to be considerably lower than the corresponding nominal alloy composition. This is schematically illustrated for grade 304 in Fig. 23. It is evident that runoff rates of individual alloy constituents cannot be calculated from the nominal alloy composition.

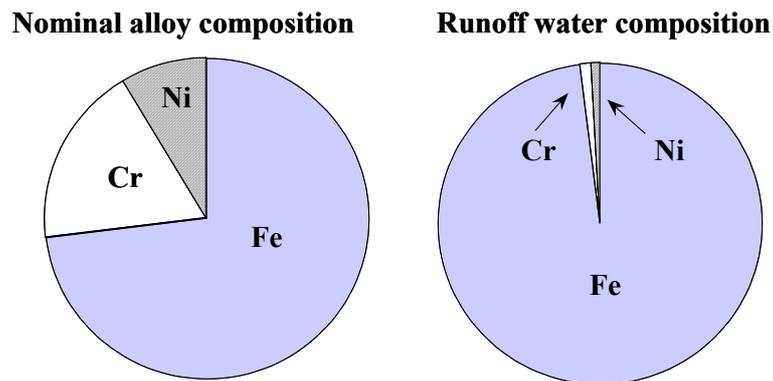


Figure 23. A comparison between the nominal alloy composition and average annual release concentrations of chromium, nickel and iron in runoff water from stainless steel, exemplified for grade 304, (Paper II).

In conclusion, by alloying iron with at least 13%wt chromium, a protective corrosion product layer, referred to as the passive film, decreases the runoff rate of alloy constituents (mainly Ni and Fe). Individual runoff rates of individual alloy constituents cannot be predicted from runoff rates from the pure metals.

3.4.2 Zinc-aluminium coated steel (Paper IV)

Alloying zinc with aluminium results in lower runoff rates of zinc compared to pure zinc sheet, primarily as a result of a smaller area of exposed zinc and different aluminium rich phases acting as barriers for zinc runoff, Fig. 24 (Paper IV). Higher zinc runoff rates were observed for Galfan (95% Zn) compared to Galvalume (45% Zn). For Galfan ($1.1 \pm 0.2 \text{ g m}^{-2} \text{ yr}^{-1}$, 470-790 mm yr⁻¹), the literature suggests zinc runoff to be a result of the dissolution of primary zinc rich phases that penetrate the surface at depressed eutectic cell boundaries [Elvins et. al, 2003], whereas dissolution of zinc rich phases of interdendritic areas is the main origin of released zinc for Galvalume ($0.5 \pm 0.2 \text{ g m}^{-2} \text{ yr}^{-1}$, 470-790 mm yr⁻¹). The spray-coated

3.4.3 Artificially patinated copper (Paper VIII)

Naturally patinated copper can exhibit different colours as a consequence of differences in corrosion products within the patina. However, decreasing concentrations of air pollutants in the western part of Europe during the last decades, have substantially reduced the time-period for greenish corrosion products to form (see section 3.1). Due to aesthetic architectural considerations, with the possibility to select materials of varying colour, and maintenance aspects of existing constructions, e.g. reparations of already green-patinated surfaces without achieving stained areas, have resulted in newly developed materials of pre-oxidised copper surfaces (artificial patina). Since these pre-oxidized surfaces are formed artificially, the stability of phases within the surface layer may be different from naturally grown surface films. With time, artificial patina shows similar corrosion products as naturally patinated copper. Copper runoff rates of artificially patinated brown and green copper, were investigated during an eight-year urban field exposure in Stockholm, Sweden.

Naturally and artificially brown-patinated show similar runoff rates of copper (natural: $1.2 \pm 0.3 \text{ gm}^{-2} \text{ yr}^{-1}$, artificial: $1.2 \pm 0.3 \text{ gm}^{-2} \text{ yr}^{-1}$) as a result of similarities in patina constituents (mainly Cu_2O), thickness and morphology, whereas green-patinated copper surfaces (inner layer: mainly Cu_2O and outer green layer of mainly $\text{Cu}_4\text{SO}_4(\text{OH})_6$) show slightly higher runoff rates (natural: $1.5 \pm 0.3 \text{ gm}^{-2} \text{ yr}^{-1}$, artificial: $1.7 \pm 0.4 \text{ gm}^{-2} \text{ yr}^{-1}$) compared to brown-patinated copper, Fig. 25 (left). The reason for somewhat higher runoff rates from green patinas is connected to the morphology of the corrosion product layer, previously discussed in section 3.2.2. Due to low concentrations of SO_2 in Stockholm, a relatively long time-period is expected for artificial patina to obtain similar phases in the corrosion product layer as seen for natural green patina, which may reflect its somewhat higher runoff rate. A fair correlation was observed between the annual runoff rate and the annual rainfall quantity for both artificially and naturally brown-patinated copper, whereas the correlation for artificially and naturally green patinas was not as evident, and hence the layers may also be influenced by other parameters (see section 3.2.2), Fig. 25 (right).

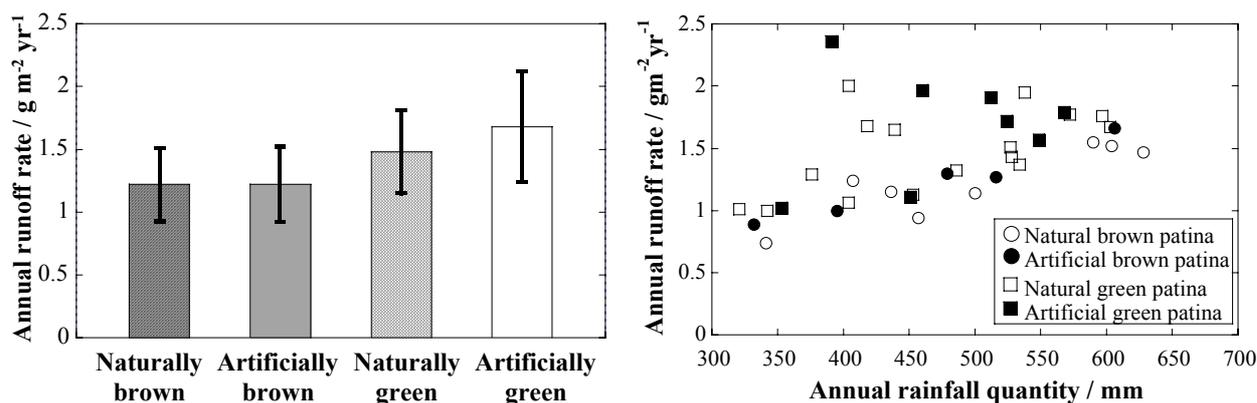


Figure 25. Mean annual release rates of copper from naturally and artificially patinated copper sheet exposed unsheltered during eight years exposure (Artificially brown copper sheet: 6 years) in the urban environment of Stockholm, Sweden (left), and correlation between the annual rainfall quantity and the annual runoff rate for naturally and artificially brown and green patinated copper sheet (right) (Paper VIII).

In conclusion, no large differences in runoff rates of copper were observed from artificially produced copper patina and naturally formed patina. Artificially patinated surfaces, which mimic green patina, show somewhat higher runoff rates until its equilibrium composition and thickness in prevailing environmental conditions are reached. More details are given in Paper VIII.

3.4.4 Surface treated zinc and zinc-aluminium coated steel (Paper IV)

Different surface treatments (chromate, thin organic coating (TOC) or paint) decrease the runoff rate of zinc from the underlying substrate as long as they are not totally degraded. This barrier effect is illustrated for galvanized steel in Fig. 26. The runoff rate of zinc from each surface treatment is normalised to the annual rain quantity impinging each surface and compared with the corresponding rate for bare zinc sheet. A ratio of one implies that the surface treatment has lost its barrier properties. This was the case for galvanized steel with a chromate layer, where the barrier effect was gradually lost during the 5-year exposure. The annual runoff rate increased from 1.4 to 2.1 gm⁻² yr⁻¹ during the time of exposure. The barrier effect of the TOC treatment was also declining with time, but was still present after five years of exposure, reducing the runoff rate with approximately 50% (0.8 gm⁻² yr⁻¹).

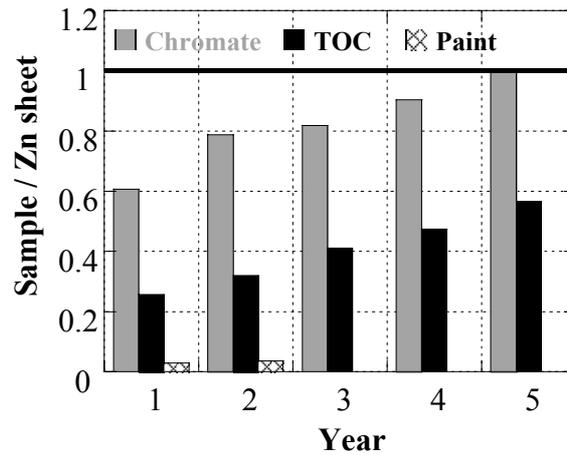


Figure 26. Barrier effect of different surface treatments (chromate, TOC, paint) on galvanized steel during 5 years of exposure in Stockholm, Sweden. Runoff data for each surface treatment is normalized to the annual rain quantity impinging the surface and the corresponding data for zinc sheet. A ratio of one implies that the barrier effect is lost (Paper IV).

The presence of a surface layer with barrier properties, in terms of zinc release, reduces the runoff rate of zinc as long as it is not totally degraded. Polarisation resistance measurements, a measure of the corrosion resistance, were made to investigate changes of the barrier effect of a coating or a surface film (Paper IV). Changes in corrosion resistance during the 5-year exposure are presented in Fig. 27 for materials with and without surface treatments of TOC or chromate. A value below 1 implies a reduced barrier effect and corrosion resistance and vice versa. The formation of corrosion products on materials without any surface treatment (Zinc sheet, Galvalume, Galfan, ZnAl15) improved the corrosion resistance whereas all materials surface treated with TOC or chromate showed a reduced barrier effect, also resulting in increased runoff rates with time.

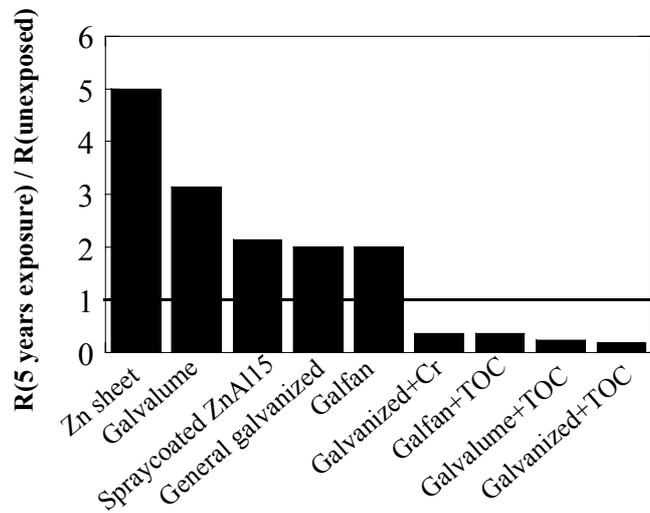


Figure 27. Corrosion resistance quotient for zinc-based materials (with and without a surface treatment of chromate or TOC) after and before five years of urban exposure in Stockholm, (Paper IV).

In conclusion, the presence of a barrier, such as a paint system, a layer of chromate, or a TOC-coating, reduces the runoff rate as long as its barrier properties are kept intact. The barrier effect of prepainted galvanized steel remained unchanged during the 2-year exposure, whereas the effect was completely lost after five years for galvanized steel with a chromate layer (0.1 μm), and significantly reduced for the same material with a TOC layer (1 μm). More details are given in Paper IV.

3.5 Predictive metal runoff rate modeling for real buildings at urban exposure sites (Paper VII)

Site-determined runoff rates, or models/relations that take into account prevailing environmental parameters and building characteristics (thoroughly discussed in section 3.2) can be used to predict metal runoff rates for a building at a specific exposure site. Real data, measured at the site of interest, would of course be preferable, but are time-consuming and complex to monitor. Models or empirical relations are hence useful tools for runoff rate predictions.

The following section presents runoff rate predictions, based on either site-determined standardized runoff rates, or models including the average annual SO₂ concentration in the atmosphere (Zn, Cu) or rain pH (Cu), in addition to annual rainfall quantities and building geometry aspects.

3.5.1 *Predictions based on site-determined runoff rate data*

Site-determined runoff rates can be used to calculate metal flows from any building at the exposure site, and to predict runoff rates at sites of comparable environmental characteristics. However, these calculations must consider the fact that real roofs and buildings show large variations in e.g. orientation, inclination and degree of rain sheltering, exemplified in Fig. 28, which result in runoff rates at least 30% lower compared to the standardized 45° orientation facing south in the northern hemisphere, (Paper VII).



Figure 28. AB Halmstads Varmförzinknings office building, Halmstad, Sweden, illustrating large variations in building geometry and exposure conditions that need to be considered when calculating and predicting metal runoff rates. Reprinted with permission from AB Halmstads Varmförzinkning.

The importance of surface inclination on the runoff rate has been evaluated, in parallel field and laboratory investigations, for zinc and copper [Odnevall Wallinder et. al, 2000]. The work resulted in a factor, able to transform runoff rates from the standardized exposure situation of 45° from the horizontal, to any degree of inclination of interest for a specific building. The relation is described by equation 3.

$$\text{Runoff rate (gm}^{-2}\text{yr}^{-1}\text{)} = R_{45^\circ} \cdot \frac{\cos \theta}{\cos 45^\circ} \quad [\text{eq. 3}]$$

References to available literature data on runoff rates of zinc, copper, chromium, nickel and iron are compiled in Paper II (Cr, Ni, Fe), Paper IV (Zn) and Paper VII (Cu) and in [He, 2002].

In conclusion, accurate calculations and predictions of runoff rates based on measured site-specific runoff rates must consider geometry aspects of the specific building.

As already discussed in section 3.2, several environmental-, material-, and exposure parameters are known to influence the runoff rate. The best outcome of a model in terms of predictability would be detailed site-specific information on all of these parameters. However this is not realistic and feasible. In order for a model to be users-friendly, a balance between the number of parameters and the model predictability needs to be found. In the forthcoming section, a previously deduced empirical relation for zinc runoff, based on the average annual SO₂ concentration, and two newly developed models for copper runoff predictions, one based on rain pH and the other on average annual SO₂ concentration, are presented (Paper VII).

3.5.2 *Predictive runoff rate models based on average annual SO₂ concentration (Cu, Zn), (Paper VII)*

Empirical runoff rate relations have previously been deduced for zinc sheet and zinc-phosphated materials (Zinc Anthra, Zinc Quartz) [Odnevall Wallinder et. al, 1998; Verbiest et. al, 1999]. These relations include the annual average SO₂ concentration (µg m⁻³), and are validated for sites with SO₂ concentrations less than 50 µg m⁻³ and annual precipitation quantities below 1000 mm. The relations are generally described in equation 4, when taking into account the importance of surface inclination of a real building [Odnevall Wallinder et. al, 2000]. Here θ is the degree of inclination from the horizontal, and m, k, constants for Zinc sheet (1.36, 0.16), Zinc Quartz (0.07, 0.17) and Zinc Anthra (0.86, 0.14).

$$Zn \text{ runoff rate } (gm^{-2} yr^{-1}) = (m + k[SO_2]) \cdot \frac{\cos \theta}{\cos 45^\circ} \quad [\text{eq. 4}]$$

Average annual SO₂ concentrations can either be monitored or obtained from existing databases and reports [www.nilu.no/050315, www.slb.nu/050315, Henriksen et. al, 2001]. It should be stressed that since the above-mentioned relations were based on only few available data without considering e.g. precipitation quantities, these relations will be refined with up-to-date knowledge on the runoff process of zinc.

The aim for developing a copper runoff model based on SO₂ concentrations, was to investigate the possibility to build a predictive runoff rate model based on available and easily monitored environmental data such as SO₂ (commonly available at environmental agencies). The most important parameters for runoff rate modeling (defined in section 3.2, schematically depicted in Fig. 29) were screened in combination with published runoff rate data.

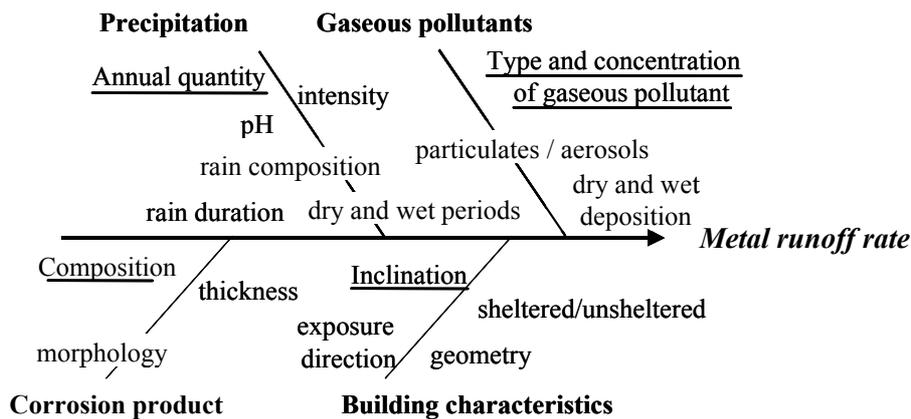


Figure 29. Selection of major environmental-, material- and exposure parameters that influence the runoff rate of metals (Paper VII).

Due to scarce literature data on annual runoff rates of copper from external buildings (Paper VII), and lack of information in these papers on important environmental and surface parameters, the number of parameters considered in the model was reduced to include the annual rain quantity (mm yr⁻¹) and the concentration of gaseous sulfur dioxide, SO₂, (µg m⁻³). The span in data varied between 396 and 3203 mm yr⁻¹, between 0.3 and 59 µg m⁻³, and between 5 and 70° for the annual runoff rate, the SO₂-concentration and the degree of inclination from the horizontal, respectively, (Paper VII). An attempt was made to combine the effect of SO₂ and O₃ in a predictive model since these parameters are known to have a

substantial influence of the corrosion product composition. The combination of SO₂ and O₃ favors the formation of Cu(II)-phases, which in general have higher solubility compared to cuprite (Cu₂O), initially formed on most copper surfaces exposed to atmospheric conditions [Hechler et. al, 1993; Strandberg, 1997]. However, combining SO₂ and O₃ in a model was not feasible since the field data did not show enough variations, enabling comparison of the individual as well as the interacting effect of these parameters. A full interaction model was therefore fitted to observed annual runoff rates, (R in g m⁻² yr⁻¹) for the annual rain quantity (mm in mm yr⁻¹) and the average annual SO₂ concentration (SO₂ in µg m⁻³), by means of PLS (Partial Least Square regression) with the software program Modde6[®], (Paper VII). A relation introducing surface inclination (θ) from the horizontal was supported by data from field and laboratory experiments [Odnevall Wallinder et. al, 2000]. The following relationship was obtained for the SO₂ model:

$$Cu\ runoff\ rate\ (gm^{-2}\ yr^{-1}) = (0.43 + 0.0015 \cdot [mm] + 0.039[SO_2]) \cdot \frac{\cos\theta}{\cos 45^\circ} \quad [eq. 5]$$

The relation predicts approximately 50% of the field data from urban environments within 30% from observed rates. The predictability is reasonably good when considering the wide spread of exposure sites of different exposure conditions, the assumption that annual rain quantity and SO₂ are sufficient to describe the dissolution and runoff of copper at a specific site, and on assumptions and estimates of non-available parameters for some test sites (Paper VII). Within data showing a variability exceeding 30%, three sites are under-predicted and eleven over-predicted by the SO₂-model, Fig. 30. All under-predicted sites have a low Cu₂O/Cu(II)-phase ratio (green patina). However this cannot solely explain the under-prediction since many other test sites also have a low ratio and are still either well or over-predicted. No unambiguous relationship to a certain parameter was seen for the over-estimated sites. This either suggests the presence of an uncontrolled parameter to have an effect on the runoff rate, or that some interacting effect is not being considered or evaluated. Other pollutants may interact with SO₂, hence increasing the true effect of a low SO₂ concentration in the model. Environments with chlorides are not well predicted within this model, (Paper VII).

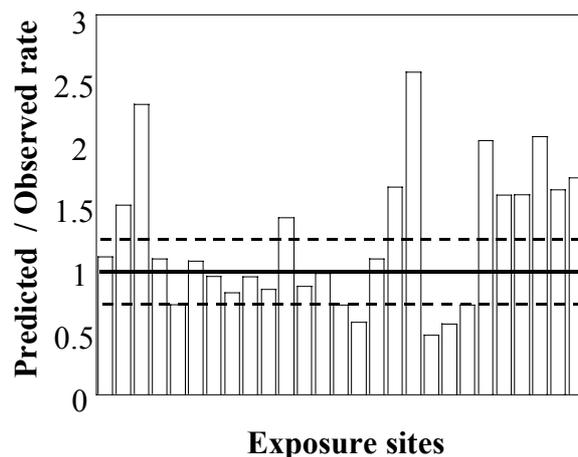


Figure 30. Comparison between observed and predicted annual runoff rates of copper from brown- and green-patinated copper sheet using equation 5 (SO₂ based). The solid line represents a 1:1 relationship, whereas the dashed lines represent 30% deviation (Paper VII).

In conclusion, accurate predictions of metal release rates at specific sites must consider environmental data as well as building geometries including e.g. degree of inclination. Models and empirical relations, based on annual average SO₂ concentrations, are available for runoff rate predictions of copper and zinc. More details are given in Paper VII.

3.5.3 Predictive runoff rate model based on annual rain pH (Cu), (Paper VII)

The pH model comprises data from detailed laboratory investigations exploring the individual effect of environmental parameters on the runoff rate of copper, such as e.g. rain pH, intensity and amount as well as parameters such as corrosion product, surface inclination and orientation, combined with field exposures. The model includes the integration of laboratory and field data on naturally patinated copper into a general model that primarily is based on annual rain pH, annual rain quantity and surface inclination. Laboratory investigations [He, 2002], have shown the rain volume (10 to 600 mm), rain pH (3.8 to 4.8) and surface inclination (20 to 70°) to have significant effects on the copper runoff rate, whereas the influence of other parameters, such as phases and thickness of the corrosion products and atmospheric pollutants, is less obvious. When the pH model was deduced, laboratory results of these parameters were assumed to govern the annual runoff rate. However, the application

of this relation on field runoff rate data, (Paper VII), showed a relatively poor predictive ability with less than 40% of field data predicted within 30 % from observed rates. A plot of predicted rates versus observed rates exhibited a relatively linear relation with a regression coefficient of 0.84 and a slope close to 1. An optimal correlation between predicted and observed data would be a 1:1 relation intercepting origo. The parallel shift with a term of 1.04 indicates that also other parameters are influencing the runoff rate. The term represents the average runoff rate during the initial rain volume impinging a surface (first-flush), which previously has been shown to be influenced by numerous environmental factors preceding a rain episode, e.g. dry deposition of SO₂ and other corrosive stimulators, the length of the dry period, and material characteristics such as corrosion product solubility and thickness [He, 2002]. Taking the effect of first flush into account, the model is described by eq. 6:

$$Cu \text{ runoff rate } (gm^{-2} yr^{-1}) = (1.04 + 0.96 \bullet mm \bullet 10^{-0.62 \bullet pH}) \frac{\cos \theta}{\cos 45^\circ} \quad [\text{eq. 6}]$$

Equation 6 predicts approximately 70 % of the field data within 30 % from observed rates (Paper VII). The model both under- and over-estimates annual runoff rates, as seen in Fig. 31. The most under-predicted site has an average rain pH of 6, which is outside the model validity interval. However the high pH cannot solely explain the divergence from the model, since two other sites with high pH are well described by the model. No unambiguous explanation can be made for the deviation of the other sites.

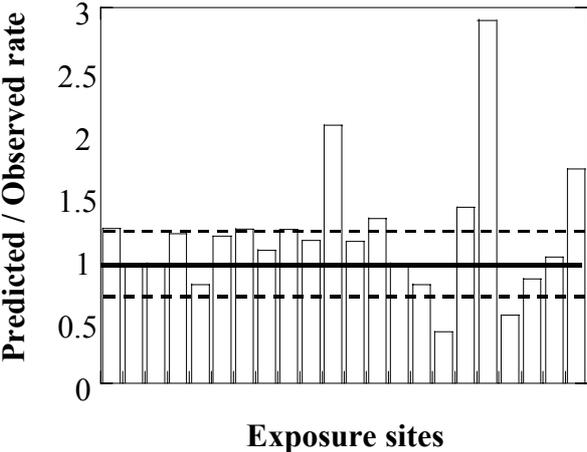


Figure 31. Comparison between observed and predicted values for annual runoff rates of copper from brown- and green-patinated copper sheet using equation 6 (based on average annual rain pH). The solid line represents a 1:1 relationship, whereas the dashed lines represent 30% deviation (Paper VII).

In conclusion, a predictive runoff rate model of total copper from real buildings has been deduced based on real runoff rate data from parallel laboratory and field investigations, which combines environmental data, including annual precipitation quantities and rain pH with building geometry.

3.6 Total concentration, chemical speciation, bioavailability and ecotoxicity of Cu, Zn, Cr, Ni and Fe in runoff water at the immediate release situation (Papers II, IV, V, VIII)

Predicted or measured total metal runoff rates ($\text{g m}^{-2} \text{yr}^{-1}$), cannot directly be used for environmental risk assessments. Instead metal concentrations, considering the chemical speciation (chemical form of the metal), should be used since they relate to bioavailability (extent and rate of uptake by organisms and plants) and ecotoxicity (damaging action upon a ecosystem). The released metal concentration decreases with time during any rain event. Since the concentration also is intimately related to prevailing environmental conditions in terms of e.g. rain pH, pollutant levels, dry and wet periods, the concentration varies significantly between different sampling periods. The released metal concentration will also vary depending on type of material, since corrosion products with different barrier and solubility properties are formed. The chemical speciation of a metal is controlled by a number of physical and chemical factors, such as pH, water hardness, alkalinity, organic and inorganic ligands, temperature and particulate matter [Di Toro et. al, 2001].

In the following sections; total metal concentrations, chemical speciation, bioavailability and ecotoxicity are discussed for copper, zinc, chromium, nickel and iron in runoff water at the immediate release situation. Dilution with storm water from other solid surfaces and retention on natural and man-made absorbing surfaces should also be considered when evaluating the potential environmental interaction (discussed in chapter 4).

3.6.1 Copper-based materials (Paper VIII)

Copper concentrations, measured in collected runoff water samples at the immediate runoff situation, are compiled in Fig. 32 for both naturally brown and green patinated copper from all samplings periods during the eight-year field exposure (Paper VIII). The median copper concentration for naturally patinated copper is 2.6 (between 1.0 and 8.2) and 3.1 (between 1.0 and 15.1 mg Cu L^{-1}) mg Cu L^{-1} , for brown and green patinated copper, respectively. If artificially patinated copper is included, the median copper concentration is about the same, 3.2 mg L^{-1} (between 0.85 and 18 mg L^{-1}).

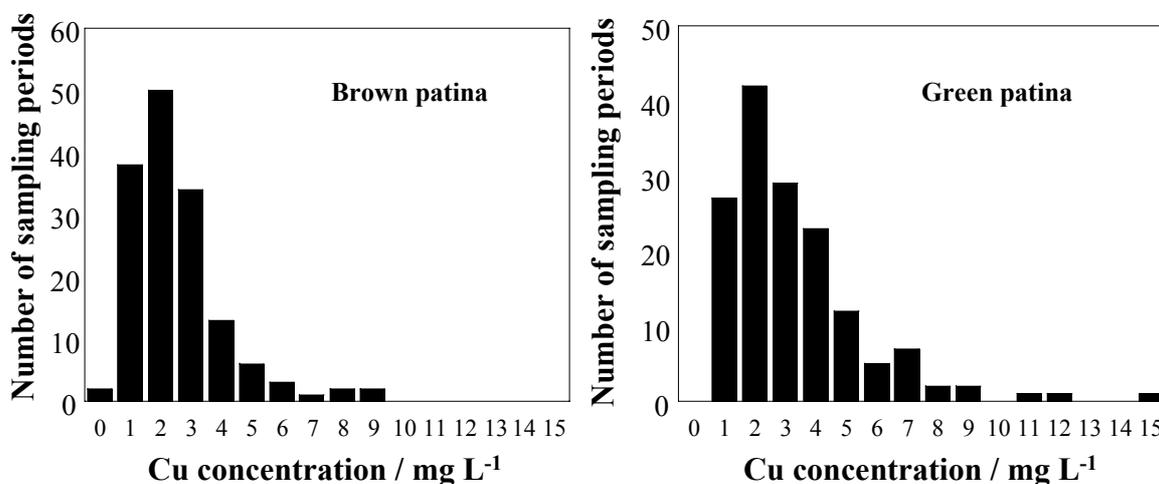


Figure 32. Copper concentration in collected runoff water samples at the immediate runoff situation from naturally brown-patinated (left) and green-patinated (right) copper, (Paper VIII).

The free hydrated ion, $\text{Cu}(\text{H}_2\text{O})_6^{2+}$, is considered to be the most bioavailable form of copper in aqueous media [Kim et. al, 1999; De Schamphelaere et. al, 2004]. Its concentration in natural surface waters is low as a result of its strong affinity to organic complexants [De Schamphelaere et. al, 2002; 2004]. Measurements of the fraction of the free hydrated copper ion ($\text{Cu}(\text{H}_2\text{O})_6^{2+}$) at the immediate runoff situation is presented in Fig. 33 for naturally and artificially patinated copper. The median fraction varies between 64 and 73% for all patinas with 50% of all data between approximately 60 and 80%. Periods of low fractions are most probably a result of higher organic content of the runoff water, e.g. pollen (no measurements of the organic content of the runoff water were performed).

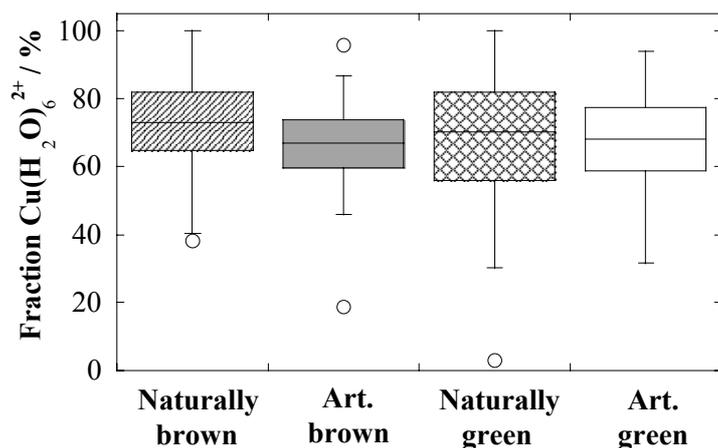


Figure 33. Fraction (%) of the free cupric ion concentration, measured with an ion selective electrode, compared to the total copper concentration released from naturally and artificially brown and green patinated copper. Each box comprises the inner 50% of the data closest to the median (shown as a line). The lines extending from the top and the bottom of each box mark the minimum and maximum values that fall within the median value ± 1.5 times the concentration span of the box. Outliers are displayed as individual points (Paper VIII).

Measurements of the pH of the runoff water from both naturally and artificially patinated copper showed median values of 6.2 as a result of the buffering capacity of the patina. Computer modeling, using MinteqA2, of the chemical speciation of copper in runoff water have been performed for different sampling periods during the first 3 years of exposure. The results show copper to be predominantly present as the free hydrated copper ion with minor constituents of $\text{Cu}(\text{OH})^+$, $\text{Cu}(\text{OH})_2^{2+}$, $\text{CuCO}_3(\text{aq})$ and $\text{CuSO}_4(\text{aq})$ and, hence in a chemical form that is bioavailable towards bacteria and ecotoxic towards the algae *R. subcapitata* (72h-EbC₅₀ – acute effect concentrations from 6 to 24 $\mu\text{g CuL}^{-1}$). Recent studies in surface waters show an optimum copper concentration for *R. subcapitata* between 1 and 35 $\mu\text{g CuL}^{-1}$ [Bossuyt et. al, 2004]. The observed growth inhibition in runoff water and not in the surface water is probably a result of lower complexation towards dissolved organic carbon in the runoff water.

To conclude, information on the total copper concentration in runoff water is not sufficient for adequate risk assessments. Key information includes knowledge on the chemical speciation and the bioavailability of released copper. Chemical speciation analysis and modeling of runoff water at the immediate release situation show the median fraction to vary between 64

and 73% for all patinas, i.e. to be in a bioavailable form as a consequence of small concentrations of organic carbon at the test site. Bioavailability results concur with the ecotoxic response with algae, showing copper to account for the observed toxicity. Results on chemical speciation and bioavailability at the immediate release situation should not be simply extrapolated to real environmental effects since both total concentrations and the chemical speciation of released copper in the runoff water will undergo major changes during environmental entry (further discussed in chapter 4). More details are given in Paper VIII and in reference [Karlén et. al, 2002].

3.6.2 Zinc based materials (Paper IV)

The total zinc concentration varies, at the immediate release situation, between 0.1 and 13 mg L⁻¹ for bare zinc sheet, zinc-aluminium coated steel and surface treated materials during the 5-year exposure. Median zinc concentrations for each material range from 0.2 to 5.5 mg L⁻¹. Figure 34 shows the distribution of zinc concentrations sampled during the first two years of exposure. Prepainted galvanized steel show zinc concentrations close to background concentrations in rainwater (blank) whereas surface treatments (TOC) decrease the total zinc concentration to between 0.5 and 1.6 mg L⁻¹, depending on the substrate. Alloying zinc with aluminium decrease the average zinc concentration from 5 to 1.5 mg L⁻¹.

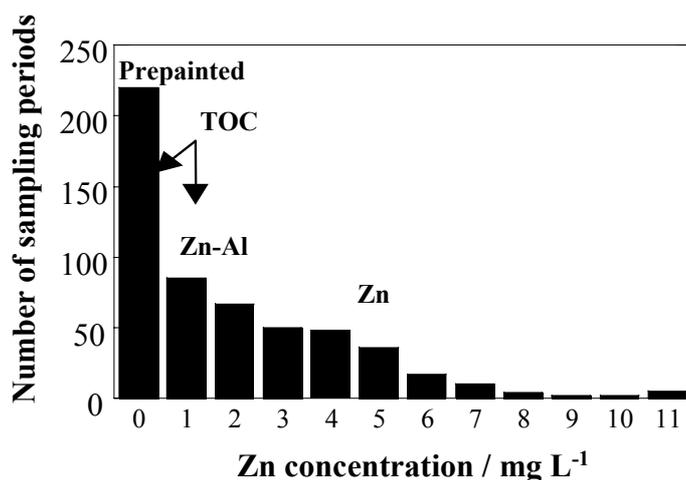


Figure 34. Distribution of zinc concentrations in collected runoff water samples at the immediate runoff situation from 14 zinc based materials during two years of exposure, (Paper IV).

The pH of the collected runoff water (103 sampling periods for each material) for different materials varies significantly. Compared to pH sampled from the blank (median value 5.0), the uncoated materials show a higher pH (median value 6.6) in the runoff water as a result of a high buffering capacity of species released from the corrosion product layer (e.g. basic zinc carbonates). The increase in runoff pH is less for coated materials (median value 5.3) as a result of the barrier effect, and even lower for pre-painted materials, showing similar values as the impinging rainwater. Since the sampling periods differ in length and also include dry periods, deposition of e.g. dust and particles from roads and constructions may contribute to an increased or decreased pH for specific sampling periods.

The chemical speciation of zinc in runoff water was predicted at the immediate release situation with the water ligand computer model Minteqa2A, using input data of the chemical composition from two different sampling periods during the first year of exposure [Karlén et. al, 2001b; Heijerick et. al, 2002a]. The location of the test site, on the roof of an eight-store high building, permits the presence of only small amounts and easily moveable organic matter, e.g. pollen, to be present. As a consequence, zinc in runoff water was predicted to be predominantly present (95 to 99.9%) as the hydrated zinc ion, $Zn(H_2O)_6^{2+}$, for all materials at the immediate release situation.

The bioavailability of zinc in the runoff water was investigated with a zinc-specific biosensor test (Biomet[®]) for three sampling periods during the first two years of the five-year exposure (Paper IV). The results, show a high correlation between zinc bioavailability and the total zinc concentration, in agreement with the findings from the speciation modelling, Fig. 35. Similar conclusions could be drawn from acute toxicity results from 72-h standard algae tests with *Raphidocelis subcapitata*, performed for all zinc-based materials and 5 different sampling periods over the five-year exposure. The results show a fairly good correlation between the acute ecotoxic response and the total zinc concentration (Paper IV). The toxic response increased with increasing concentration of zinc in the runoff water, which suggests zinc to account for the observed toxicity. No toxicity was observed from the blank sample (Toxic Units - T.U. <1), which indicates no external contribution to any observed toxicity for the investigated materials. A lower toxicity was measured for alloyed samples and samples with barrier layers, as a result of lower zinc concentrations. Proportionality constants, representing the amount of total zinc (in μgL^{-1}) causing 50 % growth inhibition, were derived based on observed toxic data (in T.U.) and the total zinc concentration in the runoff water samples for

each material [Heijerick et. al, 2002a]. Calculated constants range from 19 to 138 $\mu\text{g L}^{-1}$, with a mean constant of 69 $\mu\text{g L}^{-1}$. This value is consistent with literature data (30 to 170 $\mu\text{g L}^{-1}$, with a median constant of 60 $\mu\text{g L}^{-1}$ [Toussaint et. al, 1995]) for acute zinc toxicity to *R. subcapitata*, and shows the toxicity in the runoff water samples to be predominantly caused by zinc.

It must be stressed that the observed toxicity at the immediate release situation should not be simply extrapolated to effects in the environment since various physico-chemical processes alter the bioavailability and toxicity of zinc. Dilution with e.g. storm water as well as organic and inorganic complexation will change the chemical speciation and in most cases the bioavailability with several orders of magnitude.

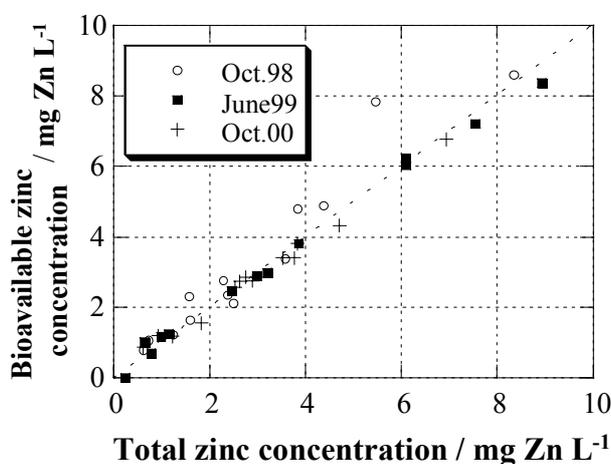


Figure 35. Correlation between the bioavailable zinc concentration (zinc-specific biosensor, Biomet[®]), and the total zinc concentration (Paper IV).

In conclusion, information on the total zinc concentration in runoff water is not sufficient for adequate effect assessments. Chemical speciation modelling and zinc-specific bioavailability investigations of runoff water at the immediate release situation, show the majority of the total zinc concentration to be in a bioavailable form due to low concentrations of organic carbon at the urban test site. Bioavailability results concur with the ecotoxic response with algae, showing zinc to account for the observed toxicity. The acute toxicity decreased with decreasing zinc concentration and increasing barrier effect of the investigated materials. Dilution with urban storm water results in significantly lower total zinc concentrations during environmental entry.

3.6.3 Stainless steel (Paper II)

Due to the presence of the passive film, the exposure of stainless steels results in low metal concentrations ($\mu\text{g L}^{-1}$) in the runoff water. Annual total release rates of chromium, nickel and iron from planar surfaces of massive stainless steels (grades 304 and 316), exposed at 45° from the horizontal, facing south, were determined during a four-year exposure in the city of Stockholm (Paper II). Metal concentrations of chromium, nickel and iron are compiled in Fig. 36 for each element and year of exposure for both grades of stainless steel (Paper II). The detection limit ($0.5 \mu\text{g Cr L}^{-1}$, $0.1 \mu\text{g Ni L}^{-1}$) was used as input value for individual sampling periods when the metal concentration was below this limit during that particular sampling period. Each box comprises the inner 50% of the data close to the median (shown as a line). The lines extending from the top and the bottom of each box mark the minimum and maximum values that fall within the median value ± 1.5 times the concentration span of the box. Outliers are displayed as individual points. Note that iron data are divided with a factor of 100 in the graph.

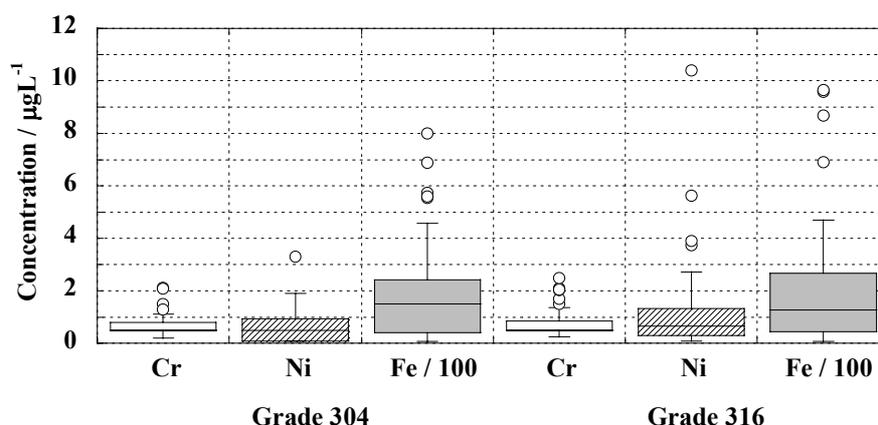


Figure 36. Concentrations of chromium, nickel and iron in runoff water from stainless steel grades 304 and 316 during individual sampling periods of the urban four-year exposure (data on Fe reflect the last three years of exposure), (Paper II).

In addition, $\text{Cr}(\text{OH})^{2+}$ and a small fraction of $\text{NiSO}_{4(\text{aq})}^{2+}$ were identified. By assuming small amounts of dissolved organic carbon in the runoff water ($0.1 \text{ mg humic acid L}^{-1} + 0.1 \text{ mg fulvic acid L}^{-1}$), a total reduction of the free $\text{Cr}(\text{III})$ ion concentration and a reduction of the free $\text{Ni}(\text{II})$ ion concentration by a few percent, were predicted as a result of complexation.

Algal tests (*R. subcapitata*) were performed for a selection of runoff water samples at the immediate release situation (Paper II). The results showed some runoff water samples (from both grades), sampled directly after release from the stainless steel surfaces, to be slightly toxic towards the alga *R. subcapitata*. The actual effect concentrations causing 50 % inhibition ranged between 0.3 and 2 $\mu\text{g total (Cr+Ni)L}^{-1}$ in runoff water at the immediate release situation for all three sampling periods. These values are far below reported Ni concentrations showing toxic effects towards *R. subcapitata*, i.e 50-750 $\mu\text{g NiL}^{-1}$ [NiDI, 2000]. Similarly, when running control tests using $\text{K}_2\text{Cr}_2\text{O}_7$ (pH 7.8) and $\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$ (pH 6.5-7.5), 72h-EbC₅₀ effect concentrations of approximately 400 $\mu\text{g Cr(VI)L}^{-1}$ and between 90 and 192 $\mu\text{g Ni(II)L}^{-1}$, respectively, were obtained. It should be noted that Cr in runoff water is present as Cr(III) and not as Cr(VI). No control tests were performed with Cr(III)-compounds. Since the concentrations of chromium, nickel and iron at the immediate release situation are far below reported concentrations causing ecotoxic effects (species-dependent), it was assumed that the observed toxic effects towards *R. subcapitata* in the runoff water were not related to the release of chromium, nickel and iron from the stainless steel grades. The reason for the slight toxicity cannot be explained, but may be caused by some other physico-chemical component in the runoff water that was not measured. It should also be noted that slightly toxic responses were observed with some of the samples from the blank surface. These anomalies cannot be explained and need to be evaluated further.

In conclusion, sub-ppb ($\mu\text{g L}^{-1}$) concentrations of chromium and nickel are released from stainless steel, whereas Fe concentrations are significantly higher (mg L^{-1}). The majority of released metals are present in an ionic form, since very little organic matter exists at the immediate release situation. Released metal concentrations are below published effect concentrations for the metal sensitive green algae *R. subcapitata* and are not assumed to cause any detrimental effects on the environment.

3.7 Runoff rates, metal concentrations, chemical speciation and ecotoxicity of metals released from external constructions – a summary

Depending on type of material and environmental characteristics, a variety of corrosion products can form on a metal surface. The rate of corrosion product formation, the corrosion rate, decreases generally with time, since the process is diffusion controlled. Dose-response functions are available that relate environmental parameters to corrosion rates, for predictions at specific sites. Such functions are also useful tools for material selection at specific exposure situations.

Metals in soluble phases within the corrosion product layer can, as a result of a corrosive environment, dissolve and be released during a precipitation event (metal runoff). The rate of metal runoff does not equal corresponding corrosion rates since each process is governed by different mechanisms and influenced by different environmental and surface parameters. Similar rates are expected when the layer of corrosion products has reached its steady state thickness in the ambient atmosphere. Since metal runoff results in a somewhat reduced layer thickness, the metal strives to regain its steady state thickness, during which the corrosion rate equals the runoff rate (on a long-term perspective).

The metal runoff rate is governed by a large number of interacting parameters and varies significantly both within, and between precipitation events, primarily as a result of ambient environmental, material and building geometry characteristics. The rain intensity has no direct influence on the runoff rate of chromium and nickel. For copper and zinc, a low intensity results in a high runoff, due to long contact time-periods between rain water and the corrosion product layer, and vice versa. Rain pH is the most important environmental parameter to influence runoff rates of copper, zinc, chromium and nickel since acidity increases the solubility of phases within the corrosion product layer. For copper and zinc, the runoff rate increases with decreasing rain intensity, rain pH and degree of inclination, and increasing exposed surface area and rain volume.

Runoff rates are fairly constant on an annual perspective, as long as prevailing environmental conditions, such as annual precipitation and concentrations of corrosive pollutant, remain about the same. Released metals from arbitrary external constructions can interact with the environment and should be considered within the framework of risk assessment to determine metal flows in the society. Long-term runoff rates of metals have been determined from

copper-based materials, zinc-based materials, and stainless steel exposed at 45° facing south at an urban site in Stockholm, Sweden. Bare copper and zinc sheet show runoff rates between 1.2 and 1.5 g m⁻² yr⁻¹ for copper, and between 1.9 and 2.5 g m⁻² yr⁻¹ for zinc. Metal release from stainless steel grades 304 and 316 range between 0.23 and 0.30 mg m⁻² yr⁻¹ for chromium, between 0.28 and 0.52 mg m⁻² yr⁻¹ for nickel, and between 65 and 85 mg m⁻² yr⁻¹ for iron, (Fig. 37).

Adequate risk assessments require information on metal concentrations in runoff water. Data on total metal concentrations need to be complemented with knowledge on its chemical form (speciation), which relates to the bioavailability of the released metal. Chemical speciation analysis and modeling of runoff water, at the immediate release situation at the exposure site in Stockholm, Sweden, show the majority of released total metal concentrations to be in a bioavailable form. The reason is connected to the location of the test site with scarce organic matter present at the immediate release situation. A detailed compilation of total metal concentrations and corresponding chemical speciation is presented in Fig. 37. Measured total concentrations of Cr and Ni are far below reported ecotoxic concentrations for these metals. Average effect concentrations, causing 50% growth reduction after 72 h to the green algae *R. subcapitata*, were 69 and 15 µg L⁻¹ for zinc and copper, respectively. Results on chemical speciation and bioavailability at the immediate release situation, should not be simply extrapolated to real environmental effects since both total concentrations and the chemical speciation of released metals in the runoff water will undergo major changes during environmental entry (further discussed in chapter 4).

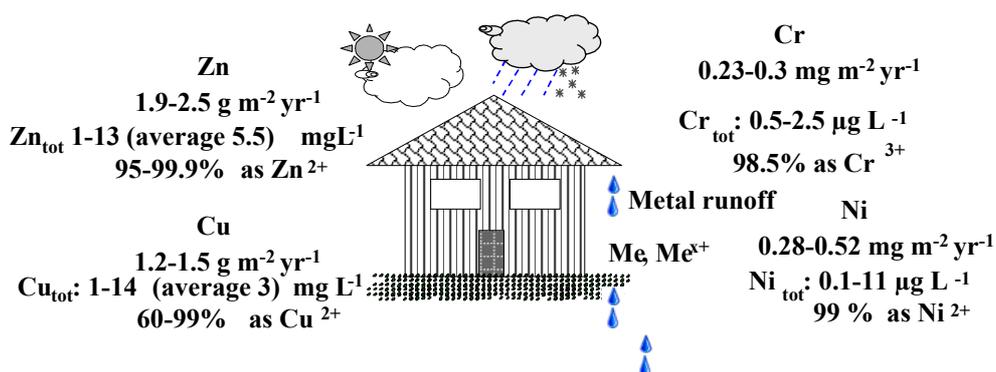


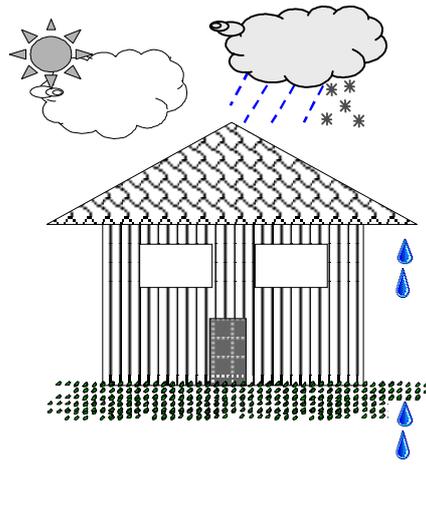
Figure 37. Compilation of results on the runoff rate, metal concentrations and chemical speciation at the immediate release situation for pure metals.

Compared to pure metals, alloying results in lower runoff rates due to smaller effective surface areas of the base metal and to the ability of alloying elements to reduce the solubility of corrosion products formed. Runoff rates from individual alloy constituents cannot be predicted based on runoff rates from the pure metals and the nominal bulk alloy composition.

Artificially produced and/or pre-oxidized corrosion products might result in somewhat higher runoff rates compared to a naturally formed corrosion products, as long as their equilibrium composition and thickness in the ambient environmental conditions not is reached.

The presence of a barrier, such as a paint system, a chromate layer, or a thin organic coating (TOC), reduces the metal runoff rate as long as its barrier properties are kept intact. The barrier effect of a prepainted galvanized steel remained undisturbed during the two-year exposure, whereas the effect was completely lost after five years for galvanized steel with a chromate layer (0.1 μm) and significantly reduced for galvanized steel with a TOC layer (1 μm).

Predictive runoff rate relations of total zinc and copper from real buildings are available, based on real runoff rate measurements and knowledge on the runoff process. Parameters considered in the relations are annual precipitation quantities (Cu), average annual SO₂ concentrations (Cu, Zn), and rain pH (Cu) combined with degree of surface inclination.



Issues addressed within this chapter:

- *What capacities have soils of various characteristics, and limestone systems, to retain metals in runoff water?*
- *In what way is the retention capacity of metals influenced by soil characteristics, including cation exchange capacity (CEC), soil pH, fraction of organic matter and clay?*
- *Are the total metal concentration and the chemical speciation, bioavailability and ecotoxicity of metals in runoff water changed during soil and limestone interaction?*
- *Can retained metals become mobilised in the future?*
- *Are retained metals in soil available for plant uptake?*
- *Can laboratory derived data be used to understand real scenarios at field conditions?*
- *What is the retention capacity of released copper by limestone?*

4.1 Occurrence and retention possibilities in soil

Soil is composed of a solid phase of weathered minerals (oxides and layer silicates) and decaying organic matter (humus) in close contact with a solution phase. Due to its complex composition, the soil can interact with metals through a variety of physico-chemical processes, as briefly discussed below [McBride, 1994]. 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, oxides and humus) carries, in most cases, an excess of negative charge. This results in a surface potential, which affects the distribution of cations, including metal ions, and anions in the solution phase. The negative surface charge is counterbalanced by cations, which thereby are affected by two counteractive forces, electrostatic attraction towards solid surfaces, and diffusion back into the bulk solution. Electrical attraction in soil is controlled either by fixed charge constituents (*e.g.*, clay minerals such as hydrous silicates that develop a negative charge as a result of lattice substitutions), or by variable charge constituents (*e.g.*, the surface charge of humus and oxides of iron, manganese, aluminium or titanium that varies with pH of soil solution). On a weight basis, clay minerals adsorb smaller quantities of cations than other main sorbents in the soil, *e.g.* humus [Merian, 1991]. Ions might bond to the solid phase by chemisorption or cation exchange. These processes involve strong surface complex formation with covalent bonding (chemisorption) and exchange between cations in the solid phase, and metal ions in the soil solution by ion binding (cation exchange). The cation exchange capacity (CEC) is a measure of the number of cations that can be attached to a surface by electrostatic interaction. 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, minerals are the main contributors together with humus. Chemisorption results in stronger bonds compared to electrical attraction. Secondary minerals can precipitate at high pH (>7-8) and high metal concentrations. Figure 38 shows the main processes for metal retention in soil and complexation in solution (Me_xR), and how these processes affect the chemical speciation and thereby the bioavailability, potential for groundwater leaching (mobility) and plant uptake.

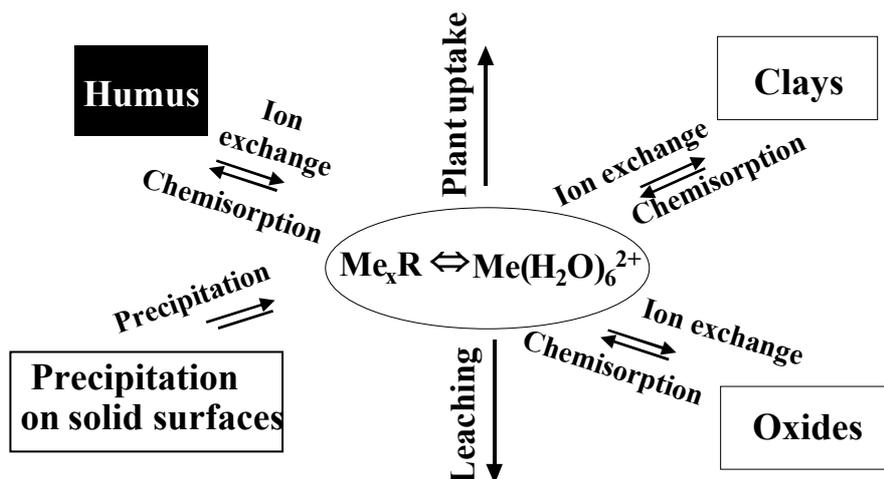


Figure 38. Interactive processes determining retention and bioavailability of metals in soil.

The distribution of a metal in soil between solution and solid phases can quantitatively be described by the distribution coefficient (K_d). Since the coefficient is both metal- and soil specific, it must be experimentally determined for each unique situation in order to predict metal concentrations in the soil solution and its potential mobility. The reason is that the coefficient depends on a large number of parameters such as soil pH, total dissolved metal concentrations and dissolved organic carbon (DOC). Any change in these parameters would affect its value. The distribution coefficient is calculated as the ratio between the “available” zinc concentration in the solid phase, and the concentration of zinc in the soil solution. An example is given in Fig. 39 (left) showing results from batch experiments with zinc in $\text{Ca}(\text{NO}_3)_2$ [Bertling, unpublished data]. Data show the zinc concentration in the solid phase to increase with increasing soil pH at a specific solution concentration of zinc. The combined effect of pH and organic matter in the soil on the distribution coefficient, can be described by a regression equation (eq. 7), schematically illustrated in Fig. 39 (right) [Degryse, 2003a]. The equation includes the effect of soil pH, soil organic matter (OC in %) and the Ca concentration in soil solution ($\text{Ca}_{\text{pw}}=1$ mM used for the calculations). The K_d^{lab} value was calculated based on the available zinc concentration (determined by isotopic dilution [Degryse, 2003a]) and the soil solution concentration of zinc.

$$\log K_d^{\text{lab}} = -2.54 + 0.73 \text{ pH} + 0.82 \log \text{OC} - 0.46 \log \text{Ca}_{\text{pw}} \quad [\text{eq.7}]$$

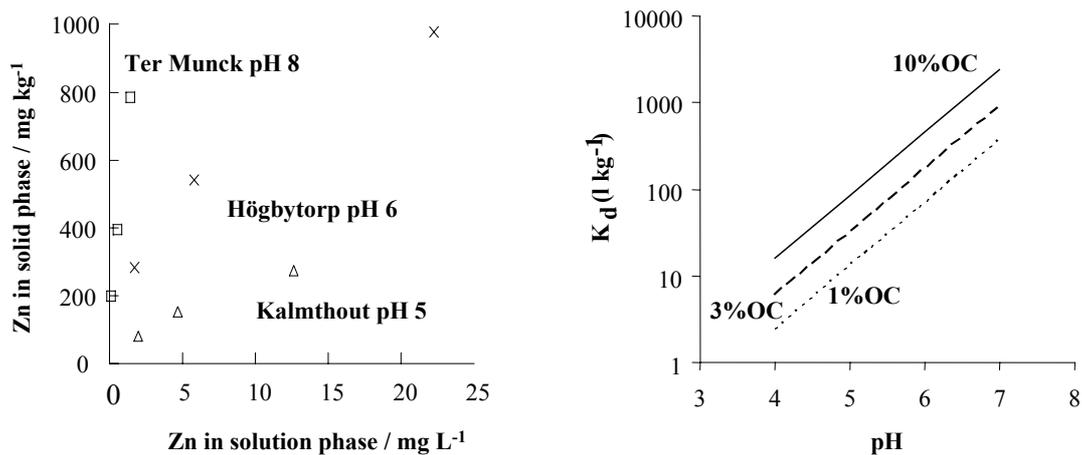


Figure 39. Sorption isotherms of zinc from batch experiments (0.2 mmol Ca(NO₃)₂, solid/liquid ratio 1:10 kg L⁻¹) for three soils; Ter Munck (□, pH 8), Högbytorp (x, pH 6) and Kalmthout (Δ, pH 5) (left) [Bertling, unpublished data]. The effect of soil organic matter (%OC) on the distribution coefficient at different soil pH, predicted with eq. 7 (assuming a solution concentration of Ca of 1mM) [Degryse et. al, 2004].

Metals introduced to soil are quickly retained by adsorption processes (chemisorption and cation exchange). The subsequent immobilisation, caused by diffusion and occlusion in, e.g. oxides, which leaves metals unavailable for plants and organisms, are much slower processes, [Almås et. al, 2000; Gerth and Tiller, 1988]. These processes are described as irreversible and cause immobilisation of metals. Previously discussed soil interactions with metal ions will from here on be described as retention processes. Microbial activity and CO₂ –dissolution may influence soil pH to some extent, and thereby indirectly influence the metal retention capacity of soils. Figure 40 illustrates the dominating mechanism for metal retention and immobilisation at different reaction times and metal concentrations. The figure shows surface precipitation (e.g. of sparingly-soluble (hardly soluble) carbonates, phosphates or oxides) to occur only at very high metal ion concentrations.

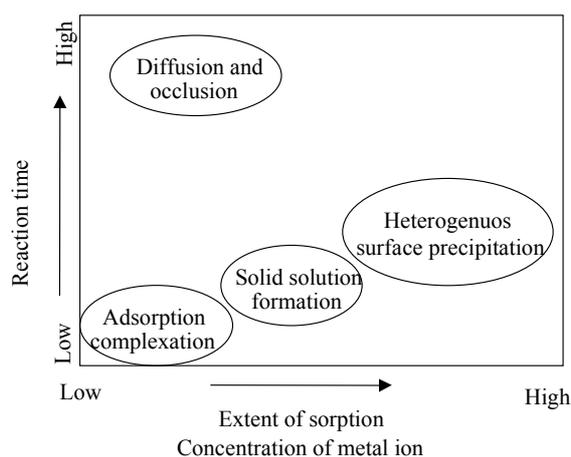


Figure 40. Possible fates of metals introduced to soil for different reaction times and metal concentrations.

Copper (Cu) occurs in the solid and solution phases of the soil predominantly as the divalent cation, Cu(II) [McBride, 1994]. In the solid phase, Cu associates with sulphides to highly insoluble minerals, Cu_2S and CuS , during reducing conditions. Cu^{2+} is strongly adsorbed to most solid phases of the soil (oxides of manganese, aluminium and iron, silicate clays, and humus). For soils with high concentrations of Cu, precipitation of cupric hydroxide, oxide, or hydroxyl-carbonates (malachite and azurite) is possible above pH 6. Trace concentrations of Cu, found naturally in most soils, are probably primarily dispersed on sorption sites, and at structural (octahedral) sites of oxides and silicates. Organically complexed Cu(II) is more strongly bonded, compared to any other divalent transition metal. The availability of these complexes is rather low, thereby limiting the bioavailability. Due to the high affinity of Cu^{2+} to solid soil phases, Cu is rated as a low-mobility element in near neutral soils where it mainly is mobilised as soluble organic complexes. In more alkaline soils, where the free Cu^{2+} solubility is exceedingly low, soluble complexes of Cu(II) (hydroxyl, carbonate, organic carbon etc) form and increase the total Cu solubility. As a consequence, mobility may be significant at high pH conditions. Over a fairly wide range of pH, most of the total dissolved Cu in surface soils is present in the form of Cu(II)-organic complexes.

Divalent Zn(II) is the only oxidation state possible for zinc (Zn) in soil [McBride 1994]. In acid, aerobic soils, Zn has medium mobility, and is bonded in exchangeable forms on clays and organic matter. At higher pH, chemisorption on oxides and aluminosilicates, and complexation with humus, decreases the solubility of Zn(II) markedly. The mobility of Zn in

neutral soils is, as a consequence, very low. If soils are slightly alkaline, even though the activity of the free Zn^{2+} ion is extremely low, Zn(II)-organic complexes can become soluble and increase the mobility. In soils with high concentrations of Zn, precipitation of oxide, hydroxide, or hydroxycarbonate may limit the free Zn^{2+} concentration, at and above pH 6. Under acidic oxidising conditions, Zn^{2+} is one of the most soluble and mobile trace metal cations. Complexation towards organic carbon is weak at a low soil pH.

Chromium (Cr) occurs in soils either as Cr(III) or Cr(VI). Soil conditions generally favor Cr(III), which is a very immobile cation that complexes strongly with organic matter and chemisorbs onto oxides and silicate clays, even at a quite low soil pH. Furthermore, Cr(III) readily substitutes Fe(III) in mineral structures, and precipitates as insoluble $Cr(OH)_3$ at higher pH. Cr(III) is therefore relatively immobile in most soils and generally unavailable to plants, unless the soil is exceedingly acidic [McBride, 1994]. At higher pH values, a small fraction of Cr(III) in soils can be oxidized to Cr(VI), the most toxic form of Cr. Naturally occurring Mn-oxides, if present in soil or sediment, may promote this oxidation. Free Cr^{6+} adsorbs less strongly than free Cr^{3+} , and its mobility and bioavailability are consequently higher. However, Cr(VI)-containing pollutants are spontaneously reduced to Cr(III) in contact with soil. This occurs typically under acid conditions and in the presence of organic matter, which supplies reducing agents and complexing groups that stabilize Cr(III) and hence detoxifies Cr(VI). Cr is considered to be an immobile element and relatively difficult to extract from soils even with aggressive chemical agents.

Divalent nickel, Ni(II), is the most stable form of nickel (Ni) in soil environments. The electronic structure of the cation favors the formation of relatively stable complexes with organic matter [McBride, 1994]. Bioaccumulation of Ni in humus is pronounced and bonding to organic ligands containing nitrogen and sulfur is preferred for free Ni^{2+} . Being the smallest of the divalent transition metal cations, Ni^{2+} fits easily into octahedral sites, and coprecipitates into naturally occurring oxides of manganese and iron in soils. Chemisorption on oxides, noncrystalline aluminosilicates, and layer silicate clays is the prevailing bonding mechanism above pH 6. Exchangeable and soluble Ni(II) is predominantly occurring at lower pH. Since solubility decreases markedly at higher pH, the mobility of Ni, rated as medium in acid soils, becomes very low in neutral to alkaline soils. Under reducing conditions, Ni^{2+} -ions are incorporated into sulfides that restrict mobility to very low levels [McBride, 1994].

In summary, soil exhibits different retention possibilities for metals by chemisorption, cation exchange and/or precipitation processes. Metal ions in the soil solution are often found as organic complexes of lower bioavailability compared to free hydrated metal ions. Cu, Zn, Cr and Ni are preferentially strongly bonded to organic soil matter, but also enclosed in clay and oxides with a low bioavailability and mobility at moderate soil pH, as a result.

In the following sections, the potential environmental effect of metal transport to aquatic recipients and retention reactions in soil will be discussed.

4.2 Environmental fate of corrosion-induced runoff water in contact with soil

The following sections discuss the interaction between Cu, Zn, Cr and Ni in runoff water (at concentrations representative of a bare metal roof inclined 45° from the horizontal, facing south) and soil systems, representative of urban European conditions. The discussion will primarily be illustrated with results from the investigations with zinc-containing runoff water.

4.2.1 Soil retention capacity as a function of soil pH, organic matter content and cation exchange capacity (Cu, Zn, Cr, Ni), (Paper III)

The ability for a soil system to retain metals depends on the number of available retention sites defined by the clay-, oxide- and humus content of the soil, as well as on competing ions such as H⁺ (defined by the soil pH) and dissolved organic matter (DOC), previously discussed in section 4.1. The effect of soil characteristics (pH, DOC and CEC) on the retention of metals is illustrated for zinc in Fig. 41 (left) for five European soils exposed to runoff water (5 mg L⁻¹). The soils represent large variations in composition with a clay content between 1 and 30 %, a content of organic matter between 1.5 and 8.6 %, a CEC capacity between 0.7 and 13.4 cmol kg⁻¹ and a pH between 4.09 and 7.95. These characteristics are in agreement with typical European soils which typically have a clay content between 10 and 20%, a fraction of organic matter between 2 and 10%, a pH ranging from 6 to 7, and a CEC of 10 cmol kg⁻¹. The soil retention is defined as the percentage of introduced zinc that has been sorbed by each soil. The data include natural leaching of zinc, which is a substantial part of the initial leaching (see Fig. 41 right). Soil characteristics, such as CEC, pH and dissolved organic matter influence both the level of retention during exposure (mainly DOC and pH) and the time before the soil breakthrough capacity is reached

(mainly CEC and pH). Even though the investigated soils show a large variation in soil characteristic, the variation in zinc retention was rather limited for all soils. One exception is the Rosenlund soil, with a low pH (4.09) and a very low CEC (0.7 cmol kg^{-1}). Compared to the other soils investigated, the Rosenlund soil showed a lower retention, and a shorter time period before reaching a decreased retention.

The somewhat lower initial retention, seen in Fig. 41 (left), is related to the presence of dissolved organic matter mobilized within the soil, which forms soluble complexes with zinc, small enough to be transported through the soil. This was mostly pronounced for soils with relatively high content of soil organic matter (Kalmthout and Högbytorp), since the amount of dissolved organic matter is closely related to the content of soil organic matter. The contribution of natural leaching of zinc from the soil itself compared to the total leaching is exemplified for the Rosenlund soil, Fig. 41 (right). The results show a correlation between the zinc concentration in the percolate water and the zinc concentration as a result of natural leaching during the time of exposure. In addition, the concentration of zinc percolating through the soil is closely related to the concentration of dissolved organic matter. As a result of a decreasing concentration of dissolved organic carbon, the zinc concentration in the percolate water decreased. When the numbers of available retention sites became fewer the zinc concentration started to increase, (Fig. 41 right).

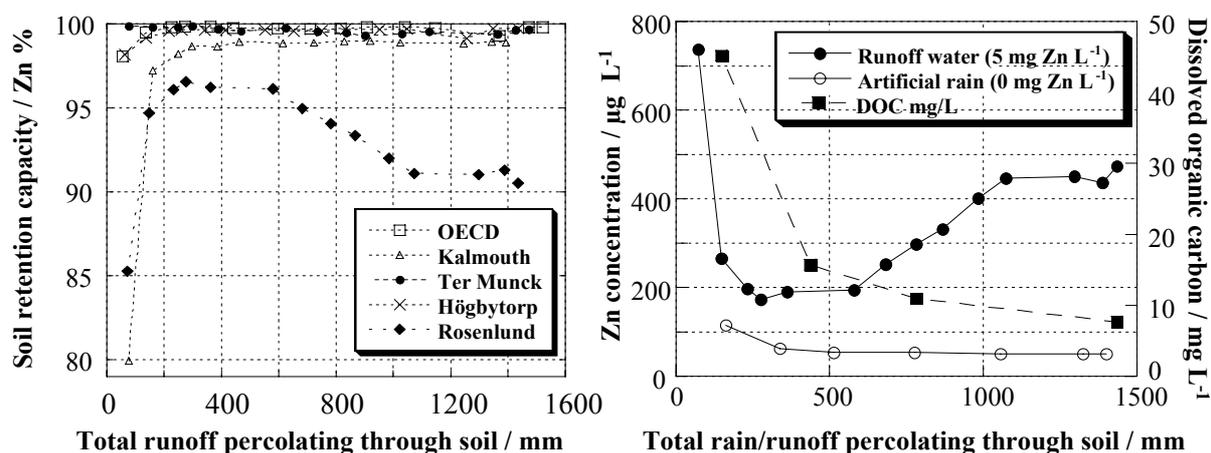


Figure 41. Zinc retention for five soils representative of Europe (left) [(Paper III), Bertling unpublished data]. Total zinc concentrations in percolate water from the Rosenlund soil after interaction with rainwater (o, 0 mg Zn L^{-1}) and runoff water (•, 4.2 mg Zn L^{-1}) and corresponding concentrations of dissolved organic matter (DOC) leaching from the soil during exposure (▪), (right).

The effect of soil CEC (cation exchange capacity of clays, oxides and humus), pH and organic matter content on the retention of zinc is illustrated in Fig. 42 after 120 and 1200 mm percolation of runoff water. All soils, except Rosenlund (CEC 0.7, pH 4.09), maintain a high retention during the exposure period. The results show the retention of zinc to increase with increasing soil CEC and pH, Fig. 42 (left). The influence of soil organic matter is less obvious, as a consequence of the soil clay content contributing to the retention of zinc in soils, Fig. 42 (right).

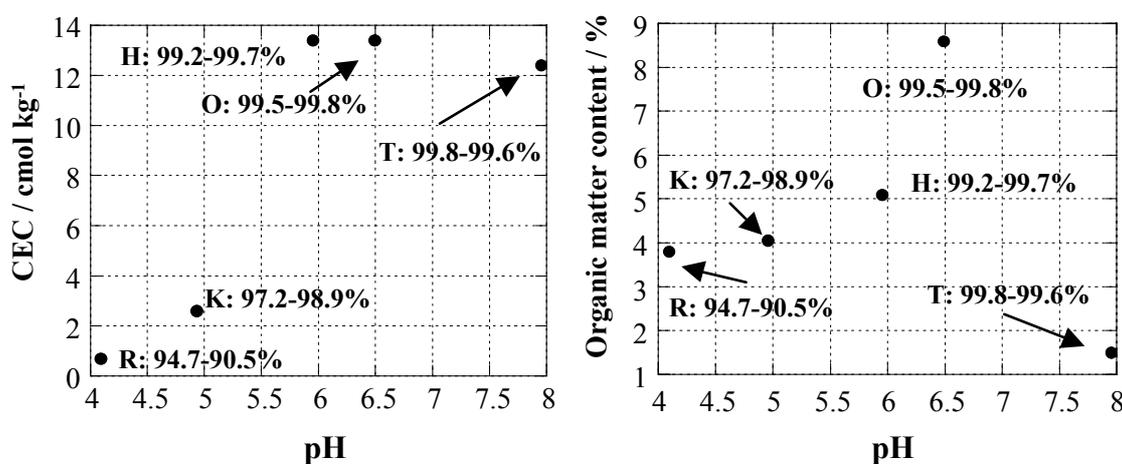


Figure 42. Effect of CEC (cation exchange capacity) and pH (left) and organic matter and pH (right) on soil retention of zinc during continuous exposure to runoff water (120-1200 mm) containing zinc (5 mg L^{-1}). H=Högbytorp soil, O=OECD soil, T=Ter Munck soil, K=Kalmthout soil, R=Rosenlund soil.

More details on the interaction between zinc-containing runoff water and soil are given in Papers III and IV.

The interactions of corrosion induced metal-containing runoff water with soil were also investigated for copper (Paper V) and for stainless steel (chromium/nickel), (Paper II). The results are similar to the findings for zinc with relatively high retention for all metals (Cu, Cr, Ni) and soils, (OECD, Rosenlund, Högbytorp) investigated. The OECD soil, with a high clay content (20 %), a pH of 6.49, a high fraction of organic matter (8 %) and a high cation exchange capacity ($13.4 \text{ cmol kg}^{-1}$), showed retentions of 99.9 % for copper, between 93 and 99 % for nickel and between 88 and 98 % for chromium, during the simulated time period (1500 mm). A somewhat lower, but still high retention capacity was seen for Cu (99 %), Ni

(65-95 %) and Cr (85-94 %) in the Rosenlund soil, despite a significantly lower pH, content of organic matter and clay, and cation exchange capacity. The reason for the somewhat lower retention capacity of the Rosenlund soil, compared to the OECD soil, is primarily a result of a lower pH. This is related to a higher competition between protons and metals for retention sites, and less sites of negative surface charge that attract metal cations. Since a large fraction of metals in the percolate water was the result of natural leaching, it can be concluded that the majority of introduced zinc, copper, chromium and nickel actually was retained in the soil. More details are given in Papers (II, V).

In conclusion, soil characteristics representative of European conditions result in a significant retention of copper and zinc (98-99 %) and chromium and nickel (88-99 %), for most soils investigated during the simulated time period (3.5 years). Metal retention was predominantly influenced by the prevailing soil pH.

4.2.2 *Breakthrough capacities (Cu, Zn), (Paper IV, VIII)*

Long-term data, including the break-through capacity of a soil, are essential for risk assessment. A second column investigation was therefore initiated (Papers IV, VIII) with the aim to reach the breakthrough capacity for copper (Högbytorp, Kalmthout and Kövlinge) and zinc (Högbytorp, Kalmthout and Ter Munck), without focusing on initial reactions previously thoroughly monitored (Papers II, III, V, simulating up to 3.5 years of exposure). The results are here illustrated for zinc, Fig. 43. All soils show similar retention of zinc (~99%) during the first 6000 mm of percolation, whereafter the soil with the lowest pH (Kalmthout) shows a decreased retention. Similar observations are made after 7000 mm, for the soil with low organic material content (Ter Munck), and after 11000 mm for the soil with the most representative soil characteristics for urban sites of Europe (Högbytorp).

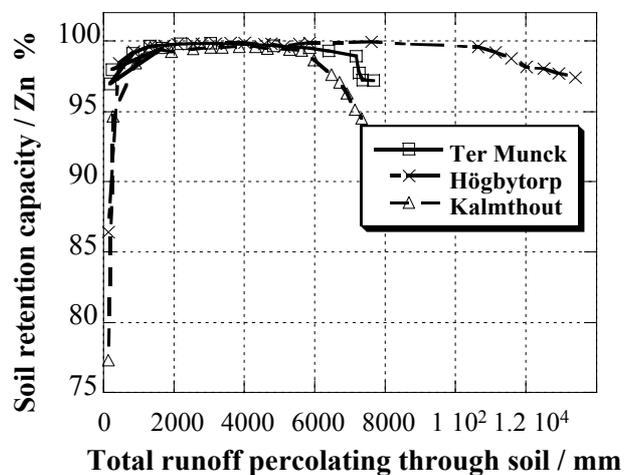


Figure 43. Zinc retention capacities of soils representative of European conditions; Ter Munck (\square), Högbytorp (x), and Kalmthout (Δ) topsoils (Paper IV).

A similar behaviour was seen for copper. More details are given in Paper VIII.

The breakthrough capacity of the soils was defined as the limit where copper and zinc concentrations started to increase, compared to the low steady state concentrations during exposure. This is of course far from the total breakthrough capacity of each soil, which would result in similar copper and zinc concentrations in the percolate water as in the introduced runoff water, see section 4.3.3. However, for risk assessment, this increase in metal concentration is of larger importance, since it would result in elevated metal concentrations transported towards a recipient. The retention capacity of each soil is calculated and expressed per kilogram of soil for both zinc and copper in Fig. 44.

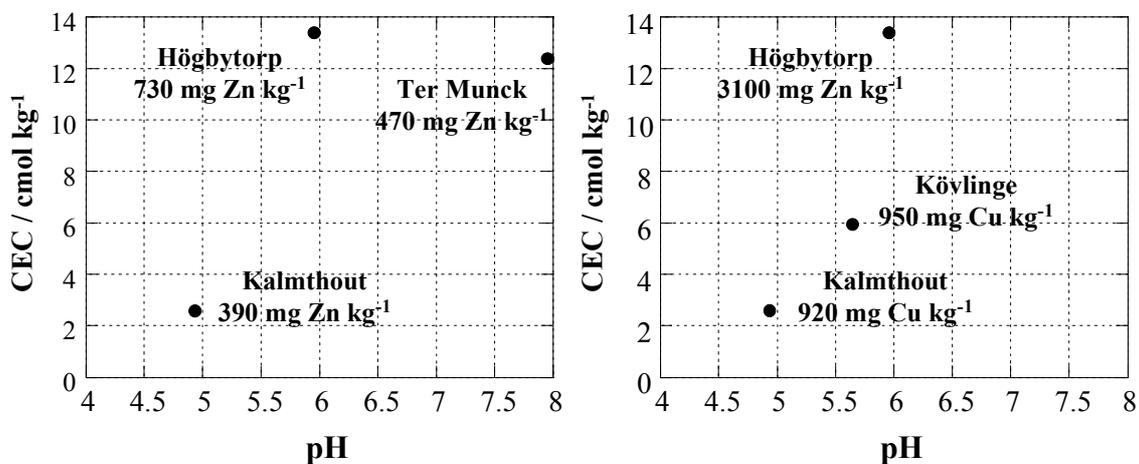


Figure 44. Effect of CEC (cation exchange capacity), pH and organic matter content on the soil retention capacity of zinc (left), and copper (right) during continuous exposures to runoff water.

Retention capacities (e.g. break-through capacities) might, during slow field introductions of metals, be higher due to more time for inward diffusion and occlusion reactions to occur, thereby re-generating adsorption sites on solid phases within the soil. This is exemplified when comparing distribution coefficients (distribution of a metal between the solid and solution phases in soil) of zinc derived from batch experiments (further explained in chapter 2) with column-exposed soil, aged for 11 months before extraction with rainwater of pH 4.3. Ageing results in higher zinc retention compared to the batch exposures for both the Högbytorp and the Kalmthout soil, illustrated for Högbytorp in Fig. 45 (left). The effect is more pronounced for higher concentrations of introduced zinc.

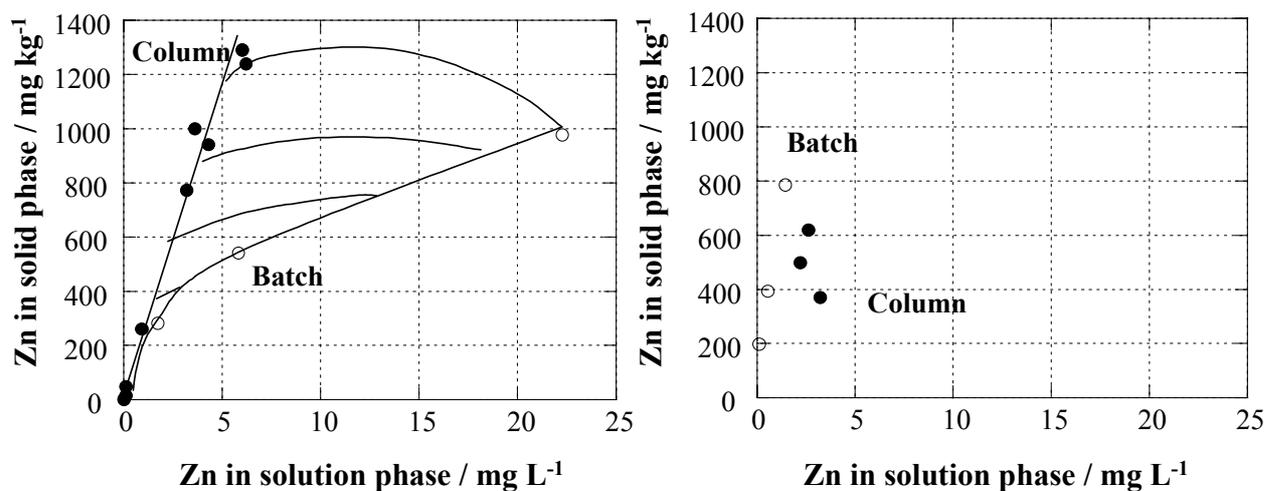


Figure 45. Sorption isotherms of zinc from batch experiments (o) performed at each soil pH (0.2 mmol $\text{Ca}(\text{NO}_3)_2$, solid:liquid ratio 1:10 kg L^{-1}), compared to extractions after column exposure and ageing, pH 4.3 (\bullet), for the Högbytorp soil (left) and the Ter Munck soil (right) [Bertling, unpublished data].

The opposite was seen for Ter Munck, Fig. 45 (right), with a somewhat lower retention observed after column exposure, compared to batch exposures. In general the soil has a very high ability to buffer the solution pH. This imposes that it is not the difference in pH, between the two extractions, that causes the lower ability for column exposed Ter Munck, to retain zinc. However, pH measurements of percolate water during the column exposure indicate that the long term introduction of runoff water with pH 6.2 gradually have decreased the soil solution pH (reflecting the soil pH, if equilibrium conditions can be assumed), from 7.2 to 6.4. Ter Munck is a clay soil with low organic matter content, and the retention ability is thereby significantly influenced by a pH change, altering the variable surface charge (see section 4.1). The combined effect of a decreased soil pH, due to the long exposure time, and the lower solution pH used for the extractions, has probably caused the decreased retention ability. The results point at the fact that clay soils are more easily influenced by exposure conditions, than soils with a higher content of organic matter. The importance of organic matter distribution, ratio of extract soil:solution, pH and metal concentration, when using extractions for understanding metal distribution between the solid and solution soil phases, have been extensively evaluated by Yin et. al, [2002] and Sauvé et. al, [2000].

A total runoff quantity of 6600-13600 mm was introduced at a flow rate of 2 mm h^{-1} , to the different soils in the column investigation with zinc (Paper IV). Based on average rainfall quantities of Europe ($\approx 600 \text{ mm yr}^{-1}$), these quantities correspond to a simulated time-period between 10 and 20 years. However, the flow rate from a down pipe dewatering a building is significantly higher compared to average rainfall quantities, and ranges typically between 5 and 10 cm h^{-1} . However, the infiltrating water flux into soils with vegetation is lower, since field conditions involve surface runoff and water uptake from the solution phase of the soil. Soil porosity and preferential routes, including micro cracks and roots, have also a large effect of the actual rate of water infiltration in soil. Assuming a rate of 400 mm yr^{-1} ($\approx 60\%$ infiltration) to be representative of field conditions, the column study on zinc (Paper IV) simulates a time-period between 16 (Kalmthout) and 34 (Högbytorp) years of runoff water interaction. A high retention (98-99%) was seen for both soils at a comparative exposure time-period (e.g. 15 years, or 6000 mm). For copper, the simulated time-period was 19 years, also showing high retention, similar to the observation seen for zinc (Paper VIII). For chromium and nickel, the simulated exposure time was almost 35 years, as a result of a 10-fold increase in metal concentrations in the artificial runoff water compared to real runoff water (Paper II).

The focus has so far been directed towards the amount of metals that can be introduced to a specific soil system, before the soil retention capacity is reached. If the retention capacity is defined as the point where the metal concentrations in percolate water reach No effect concentrations (NOEC) for aquatic organisms, the only effect prior to reaching the breakthrough capacity would be a result of retained metal. For of Cr and Ni, NOEC concentrations for soil invertebrates ($604\text{-}892 \text{ mg Cr kg}^{-1}$, $275\text{-}476 \text{ mg Ni kg}^{-1}$) are significantly higher than the dose introduced to the soils during the exposure period simulating 35 years of field conditions ($0.15 \text{ mg Cr kg}^{-1}$ and $0.3 \text{ mg Ni kg}^{-1}$). The time for reaching the lowest NOEC value would be at least 30 000 years, which suggests the released Cr and Ni quantities not to have any influence on the environment. Breakthrough studies of Cu and Zn, simulating between 18 and 34 years (Zn, 55 g soil) and 19 years (Cu, 27 g soil) of exposure, resulted in metal concentrations exceeding fresh water NOEC values for the metals. The time-periods needed to reach NOEC values for 1 kg of the investigated soil would be 50 (Zn) and 30 (Cu) years, assuming a NOEC value of 50 mg kg^{-1} and runoff water concentrations of 5 and 3 mg L^{-1} for Zn and Cu, respectively. In field, dilution with urban

storm water results in lower concentrations and thereby increased time to reach the retention capacity (see further section 4.3.4). As previously discussed, the total amount of metal is a poor predictor of environmental effects, since it is the bioavailable fraction that might affect organisms and plants. Therefore, plant availability of retained Cu and Zn, was evaluated by the DGT technique (section 4.3.6).

In conclusion, when soil interacts with metal containing runoff water most metals are retained in the soil. This results in low metal concentrations transported towards a recipient such as a river or ground water. With time, retained metals form more stable compounds within the solid material of the soil and, hence, less bioavailable metal fractions. The time to reach NOEC values for Cr and Ni is predicted to 30 000 years per kilogram of soil and 30 and 50 years per kilogram of soil for Zn and Cu, respectively (valid for undiluted runoff water). More details are given in papers IV and VIII.

4.2.3 Change in total metal concentration, chemical speciation and ecotoxicity during soil interaction (Cu, Zn, Cr, Ni), (Papers II, III, IV, VIII)

Large variations in metal concentrations in runoff water occur as a result of prevailing environmental and material parameters (see section 3.2). Metals were introduced to the soil columns at concentrations representative of field conditions (Papers IV, VIII) for zinc (4.8 mg Zn L^{-1}) and copper (4.2 mg Cu L^{-1}). The concentration of chromium ($0.007 \text{ mg Cr L}^{-1}$) and nickel ($0.014 \text{ mg Ni L}^{-1}$) was enhanced 10 times to increase the possibility of detection in the percolate water (Paper II). The metal concentration in the percolate water, *i.e.* after soil interaction, comprises both introduced metal concentrations, and natural leaching of metals from each soil. All metals investigated, copper (Papers V, VIII), zinc (Papers III, IV) and chromium/nickel (Paper II), show similar behavior with initially high metal concentrations and high concentrations of dissolved organic matter in the percolate waters. This is mainly a result of the use of dried soil for the laboratory investigations. With time, the concentrations of dissolved organic matter decreased and measured metal concentrations were comparable to background values (Cu, Cr and Ni) or somewhat higher (Zn). This is exemplified for zinc in Fig. 46. An increase in concentration was seen at the breakthrough capacity of each soil.

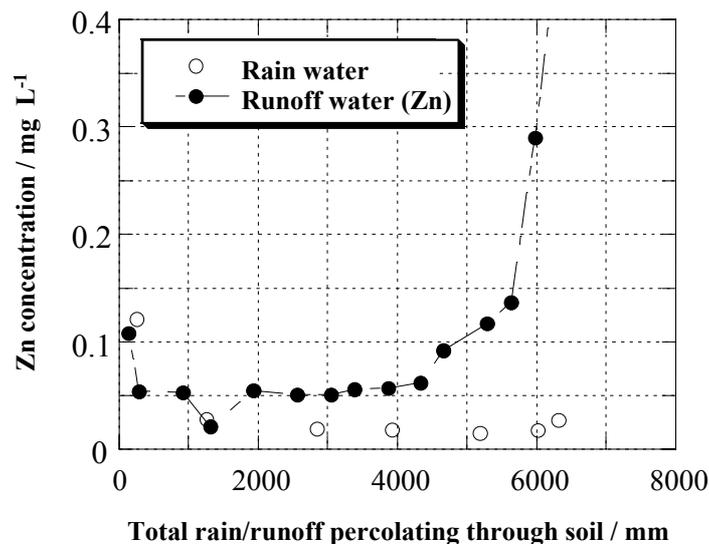


Figure 46. Total zinc concentration in percolate water from the Kalmthout soil after interaction with rainwater (0 mg Zn L^{-1}) and runoff water (4.2 mg Zn L^{-1}), (Paper IV).

Computer modeling, using WHAM(V) was performed to predict the chemical speciation of the metals of interest (Cu, Zn, Cr, Ni) in the percolate waters. Input data for the modeling calculations were based on chemical analysis of percolate water for the investigated soils, see papers II (Cr, Ni), IV (Zn) and VIII (Cu). The results are illustrated for zinc and copper in Fig. 47, showing the concentration of the free metal ion and organically complexed metal in runoff water and percolate water, before the breakthrough capacities were reached. The concentrations are expressed as the mean value for each metal and soil investigated. The figure clearly shows the total metal concentration and the ionic fraction to be significantly reduced upon soil interaction. Similar trends were observed for chromium and nickel (Paper II). Due to the very low total concentrations of Cr and Ni in field runoff water ($\text{Cr} < 0.5\text{-}2.5 \mu\text{g L}^{-1}$, $\text{Ni} < 0.1\text{-}11 \mu\text{g L}^{-1}$, (Paper II), no effect is expected in solution or retained conditions.

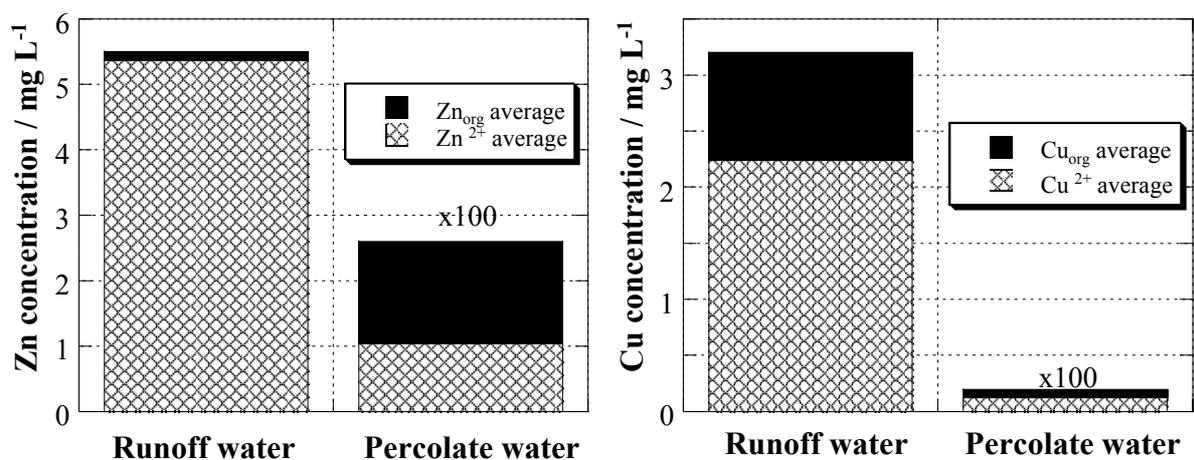


Figure 47. Predicted fraction of the free metal ion and organically complexed metal for zinc (left) and copper (right) in runoff and percolate waters (prior to reaching the soil retention capacities). All predictions have been made using WHAM(V).

In conclusion, the major fraction of introduced metals (Cu, Zn, Cr, Ni) in runoff water is retained within the soil with low total concentrations of metals in the percolate water as a result. The chemical speciation changes from mainly free metal ions to organically complexed metals in the percolate water. More details are given in papers II, IV and VIII.

4.2.4 Using laboratory data to predict field conditions, (Paper IX)

With the aim to simulate more realistic field scenarios, laboratory obtained long-term breakthrough curves for copper and zinc were modelled with HYDRUS-1D[®] [Cerník et. al, 1994] using soil properties (pH, organic carbon content) as input parameters, and a Langmuir-Freundlich model for describing metal retention (Paper IX, Bertling unpublished data). Laboratory results were successfully modelled and therefore further extrapolated to different realistic field scenarios. The aim was to evaluate differences in breakthrough capacities depending on soil and runoff water characteristics. Data valid for the laboratory column study (left) and input data used for the HYDRUS-1D[®] modelling are schematically illustrated in Fig. 48.

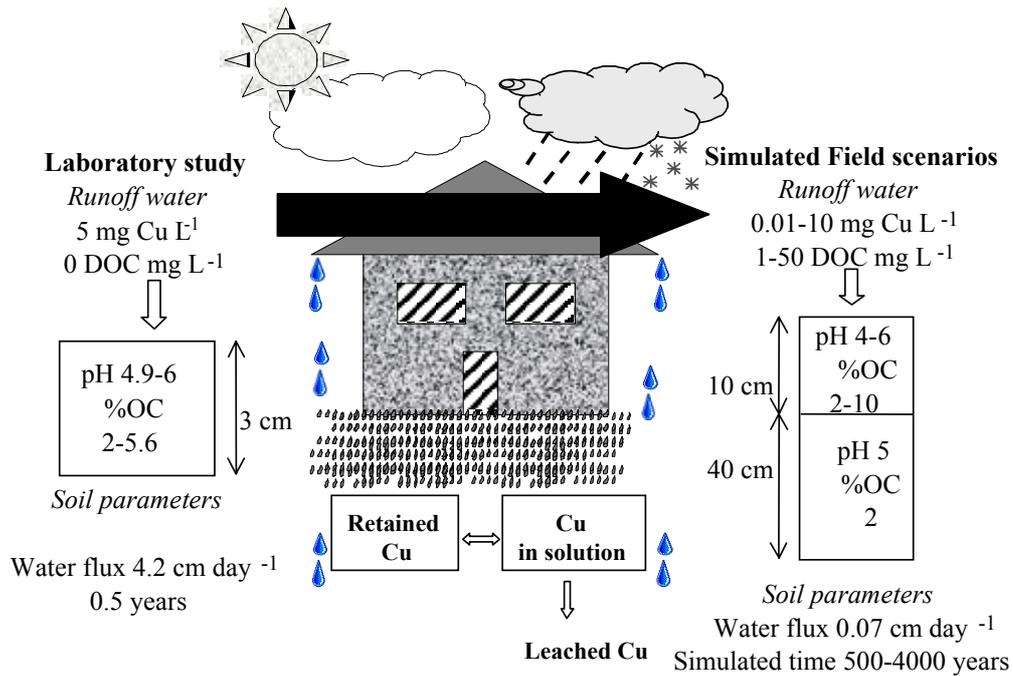


Figure 48. Variations in soil and runoff water parameters in the column experiments and in the transport modelling of the different field scenarios (Paper IX).

The time-period for the Högbytorp topsoil to show a decreasing retention of copper, not reached during the laboratory exposure, was predicted to approximately 44 years (17 500 mm runoff water). The model predicts longer breakthrough times with increasing pH and organic matter content of the soil, and with decreasing concentrations of copper and DOC in the runoff water. The time span for copper-containing runoff water (0.01 - 10 mg Cu L⁻¹) to reach a soil depth of 50 cm, varied between 170 and more than 8000 years for the predicted field scenarios. The laboratory simulations of copper included a soil system with one top layer and one subsoil layer from the same site (Kövlinge). Modelling of this system resulted in a predicted breakthrough time-period of approximately 500 years, Fig. 49.

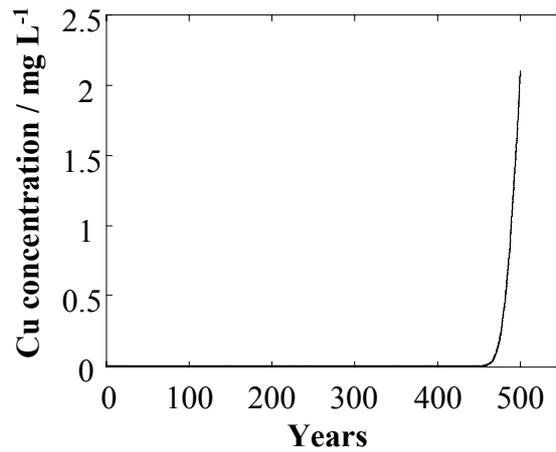


Figure 49. Predicted breakthrough curve of copper at a depth of 50 cm for the Kövlinge soil (using measured soil properties of the top- and subsoil), assuming a concentration of 5 mg Cu L⁻¹ and a DOC concentration of 20 mg L⁻¹ in the runoff water. The thickness of the topsoil was assumed to be 10 cm.

Ageing reactions, using a two-site model with kinetic parameters [Degryse et. al, 2004] were taken into account for transport modelling of zinc. In agreement with the findings of copper, the time to breakthrough was longer for higher pH and higher contents of organic matter in the soil, and lower soil solution concentrations of calcium (Ca). In total, eight scenarios were modelled, varying the pH (3.5, 4, 5 or 6), the organic carbon content of the topsoil (2 or 5 %), the thickness of the topsoil (5 or 10 cm), and the soil solution concentration of Ca (0.1, 1 or 5 mM). The time span for zinc in runoff water (5 mg Zn L⁻¹) to reach a soil depth of 50 cm, varied between 4 and 454 years for the predicted field scenarios. No modelling was performed for chromium and nickel.

In conclusion, when soil interacts with metal containing runoff water, most metals are retained in the soil. This results in low metal concentrations transported towards a recipient, such as a river or ground water. Predictions of zinc and copper transport through 50 cm soil profiles resulted in breakthrough times between 4 and more than 8000 years. These results stress the importance of using accurate information on runoff water and soil characteristics for risk assessment.

4.2.5 *Potential for future mobilisation of retained metals (Cu, Zn, Cr, Ni), (Papers II, III, IV, V, VIII)*

The previous section has shown a high ability of soil to retain Cu, Zn, Cr and Ni, as long as the numbers of retention sites are not fully occupied, i.e., the break-through capacity is not reached. It is therefore important to evaluate whether metals are retained irreversibly or in a reversible way, resulting in elevated equilibrium soil solution concentrations. The potential for future mobilisation was evaluated by sequential extraction of three vertical segments of each exposed soil. The extraction was performed in sequence with artificial rainwater (Paper II, IV, VIII) and EDTA. The results are illustrated for Cu (Paper VIII) and Zn (Paper IV) in Fig. 50 as mean values of the reversible bonded (mobilized) fraction of the metals for the investigated soils. Minimum and maximum values are illustrated with the arrow for each segment. The segments represent the top layer, the middle layer and the bottom layer, of 3 and 5 cm thick soil cores for Cu and Zn, respectively.

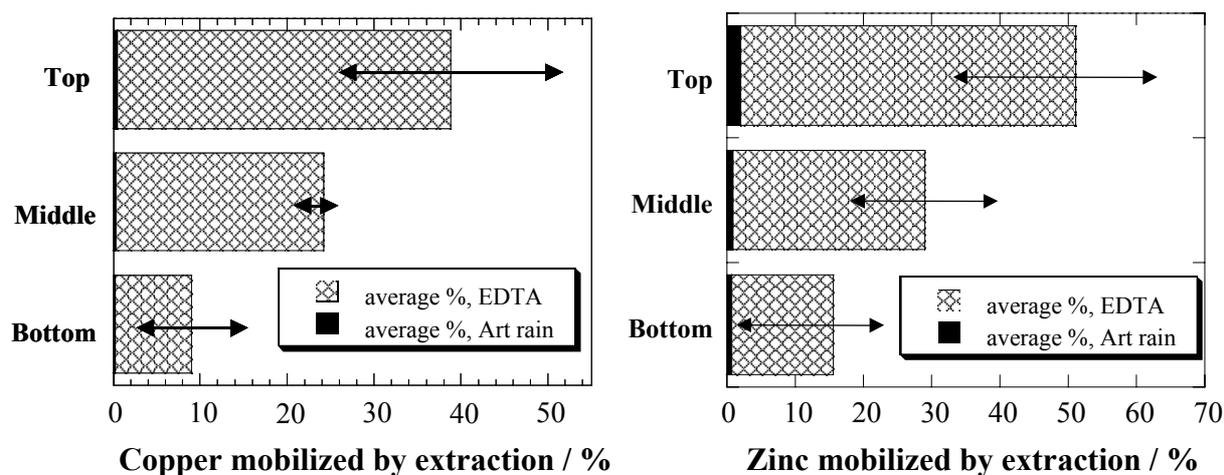


Figure 50. Average percentage (compared to introduced) of reversible bonded Cu (Paper VIII) and Zn (Paper IV) from three vertical segments of the soils investigated by sequential extraction with artificial rain (black) at pH 4.3 and EDTA (striped). The arrows illustrate minimum and maximum data for each segment.

Only a small fraction of introduced copper (0.05-0.5%) and zinc (2.6-5.6%) was mobilized during extraction with artificial rain, simulating an outdoor rain event. Cu and Zn concentrations in the rainwater extracts gradually decreased with the depth of the soil core, ranging from values close to the introduced runoff water concentrations (4.8 mg Cu L^{-1} ,

4.2 mg ZnL⁻¹) to concentrations found in percolate waters after exposure termination (0.7-0.001 mg CuL⁻¹, 1.5-0.015 mg ZnL⁻¹). A large fraction of retained Cu (Kalmthout 63%, Högbytorp 81%) and Zn (Kalmthout and Högbytorp, 85 %, Ter Munck, 99.9 %), became mobilized when using the strong complexing agent EDTA. The Högbytorp soil (high clay and organic matter content) shows a similar behavior of mobilization for both Cu and Zn retained in soil. For the Kalmthout soil (high organic matter content, but low pH and clay content), a larger fraction of the retained Zn compared to Cu was mobilized. Numerous studies [McBride, 1994] have shown Cu to have a stronger affinity towards organic matter compared to Zn, which might explain the obtained results. According to a comprehensive data compilation [Lofts and Tipping, 1998], organic matter retains zinc much stronger compared to ferric oxides and clay minerals. This may explain the lower mobilization of retained zinc in the Kalmthout and the Högbytorp soil compared to the Ter Munck soil. More Cu and Zn were mobilized from the top segment compared to the lower segments, which suggest that *i*) more metals retained in the top segment compared to the lower segments, implying a very fast reaction with soil, and *ii*) the breakthrough capacity was not completely reached during the simulated exposure.

For Cr and Ni, no increased extractability after exposure compared to unexposed soil, was seen for rain water extractions (Paper II). EDTA extractions showed no mobilization of retained Cr, but a two-fold increase of the extractability of Ni for the OECD soil and 53 times in case of the Rosenlund soil, compared to unexposed soil.

In conclusion, a small fraction of introduced copper (0.05-0.5 %) and zinc (2.6-5.6 %) was mobilised by extractions with artificial rain. Cu and Zn concentrations in the rainwater extracts gradually decreased with soil depth, ranging from values close to the introduced runoff water concentration to concentrations found in percolate waters. The major fraction of retained Cu and zinc (63-99 %) was extractable with EDTA. Possible artefacts caused by the accelerated introduction of Cu and Zn in this study, compared to real field exposures, needs to be further explored. For Cr and Ni, no increased extractability towards rain water (Cr and Ni) and EDTA (Cr) was seen after exposure to runoff water simulating 20-25 years of field exposure. The extractability of Ni increased twice in the case of the OECD soil and 53 times in the case of the Rosenlund soil.

4.2.6 *Plant availability of retained metals (Cu, Zn), (Papers IV, VIII)*

The availability of retained copper [Bertling, unpublished data] and zinc (Paper IV) in soil for plant uptake was evaluated by the DGT (Diffuse Gradients in Thin films) technique (section 2.5) [Zhang et. al, 2001a; 2004]. The results are presented as the total concentration of introduced copper and zinc to each soil, and the available metal fraction after exposure, measured with DGT (C_{DGT} and C_e) in Table 3 (Cu) and Table 5 (Zn). The C_{DGT} concentration reflects the mean metal concentration at the interface between the DGT membrane and the soil, whereas C_e describes the sum of metal in solution and labile metal (both in solution and in solid phases of the soil) required to maintain the C_{DGT} concentration. C_{DGT} is maintained approximately constant, as long as the kinetically labile (free and irreversible bonded copper fraction) reservoir is not substantially depleted close to the DGT membrane. The DGT membrane mimics plant uptake since both plants (by rhizosphere processes), and DGT (diffusion into the membrane), locally lowers metal solution concentrations in soil, initiating the supply from reversible bonded copper. This situation of transport-limited plant uptake is the worst case, since metal is supplied both from the soil solution and the solid phase. As a result C_e only provides an assessment of the potential risk for the particular soil. Table 3 shows the measured copper concentration (C_{DGT}) and the effective copper concentration (C_e) to increase with increasing amount of introduced copper, and decrease with soil depth. DGT-measurements of 29 different field contaminated soils of varying total copper concentrations (19-8645 mg kg⁻¹), suggest that a plant does not longer solely determine the copper uptake at C_e values above 2 mg Cu L⁻¹ [Zhang et. al, 2001b]. Severe copper phytotoxicity was observed for pepperwort (*Lepidium heterphyllumin*) above this value [Zhang et. al, 2001b], however the authors state that further work is required to establish toxicity threshold values (e.g. EC₅₀). Comparison with this value should hence be done with caution. For the laboratory exposed soils within this study, the comparison with a C_e value of 2 mg Cu L⁻¹ implies that exposures simulating 18 years of field exposure to undiluted copper containing runoff water (4.8 mg CuL⁻¹), cause affects plants down to 2 and 3 cm for the Högbytorp and the Kalmthout soil respectively, c.f. Table 3. A 3 year simulation shows only the outermost top soil layer (1 cm; Högbytorp, 2 cm; Kalmthout) to have reached C_e values of 2 mg Cu L⁻¹ or more.

Table 3. DGT results expressed as the time-averaged copper concentration at the diffusive gel/soil interface (C_{DGT}) and the effective copper concentration (C_e) for the Högbytorp and the Kalmthout topsoil for different soil depths. Top (0-1 cm), Middle (1-2 cm), Bottom (2-3 cm).

| Soil | Depth | C_{DGT} mg L ⁻¹ | C_e mg L ⁻¹ |
|---|--------|---------------------------------|-----------------------------|
| Högbytorp 1030 mg Cu kg soil ⁻¹ * | Top | 2.5 | 32 |
| | Middle | 0.8 | 10 |
| | Bottom | 0.0 | 0 |
| Högbytorp 186 mg Cu kg soil ⁻¹ * | Top | 0.2 | 2 |
| | Middle | 0.002 | 0 |
| | Bottom | 0.001 | 0 |
| Kalmthout 1030 mg Cu kg soil ⁻¹ * | Top | 1.3 | 16 |
| | Middle | 1.2 | 14 |
| | Bottom | 1.1 | 13 |
| Kalmthout 180 mg Cu kg soil ⁻¹ * | Top | N.A. | N.A. |
| | Middle | 0.2 | 2 |
| | Bottom | 0.001 | 0 |

* Introduced copper N.A. not analysed
 $R_{diff}=0.08$, transformation factor of C_{DGT} to C_e [Zhang et. al, 2004].

In Table 4, C_{DGT} and C_e concentrations can be compared to the extractable copper fraction from the different samples, thereby providing the opportunity to relate the copper fraction available to plants, to the total pool of exchangeable copper. Results in Table 4 suggest that exchangeable fractions larger than 470 and 278 mg Cu kg soil⁻¹ for Högbytorp and Kalmthout soil respectively, might have an influence on pepperwort plants. At the same fraction of exchangeable copper, the Kalmthout soil has a higher C_e concentration than the Högbytorp soil. The results emphasise the importance of relating soil toxicity to availability, either through soil characteristics, or direct measurements.

Table 4. DGT results expressed as the time averaged Cu concentration at the diffusive gel/soil interface (C_{DGT}) and the effective zinc concentration (C_e) for the Högbytorp and the Ter Munck topsoil compared to the extractable fraction of Cu with EDTA.

| Soil | C_{DGT} mg L ⁻¹ | C_e mg L ⁻¹ | EDTA extractable mg Cu kg soil ⁻¹ |
|-----------|---------------------------------|-----------------------------|---|
| Högbytorp | 2.5 | 32 | 1594 |
| | 0.8 | 10 | 827 |
| | 0.2 | 2 | 470 |
| | 0.01 | 0 | 67 |
| | 0.002 | 0 | 8 |
| | 0.001 | 0 | 3 |
| Kalmthout | 1.3 | 16 | 777 |
| | 1.2 | 14 | 650 |
| | 1.1 | 13 | 480 |
| | 0.2 | 2 | 278 |
| | 0.001 | 0 | 2 |

0.5M NH₄Ac+0.02M EDTA (1:16)

R_{diff}=0.08, transformation factor of C_{DGT} to C_e [Zhang et. al, 2004].

DGT-measurements were also performed for zinc (Paper IV), Table 5. DGT-measured zinc concentrations (C_{DGT} and C_e) increase with increasing amount of introduced zinc, and decrease with soil depth in the case of the Högbytorp soil. At similar amounts of introduced zinc the Ter Munck soil shows much higher C_{DGT} and C_e concentrations compared to the Högbytorp soil. This is possibly a consequence of differences in soil characteristics, which imply that inorganically retained zinc (soil oxides and clays) is more accessible for plant uptake, compared to organically complexed zinc (organic matter). Measured concentrations are in agreement with literature data on a laboratory exposed soil of similar characteristics [Degryse et. al, 2003b], but somewhat higher compared to a field contaminated soil [Almås et. al, 2004]. The discrepancy between laboratory and field exposed soil is probably caused by significantly shorter time periods for natural soil processes to occur in laboratory exposed soil.

Table 5. DGT results expressed as the time averaged Zn concentration at the diffusive gel/soil interface (C_{DGT}) and the effective zinc concentration (C_e) for the Högbytorp and the Ter Munck topsoil for different soil depths. Top (0-2.5 cm), Middle (2.5-4.5 cm), Bottom (4.5-7 cm).

| Soil | Layer | C_{DGT} mg L ⁻¹ | C_e mg L ⁻¹ |
|---|--------|---------------------------------|-----------------------------|
| Högbytorp 890 mg Zn kg soil ^{-1*} | Top | 17.4 | 217.1 |
| | Middle | 15.7 | 195.7 |
| | Bottom | 11.9 | 148.8 |
| Högbytorp 489 mg Zn kg soil ^{-1*} | Top | 15.6 | 195.2 |
| | Middle | 4.0 | 49.8 |
| | Bottom | 0.1 | 1.2 |
| Ter Munck 467 mg Zn kg soil ^{-1*} | Top | N.A. | N.A. |
| | Middle | N.A. | N.A. |
| | Bottom | 7.0 | 87.2 |

*Introduced zinc N.A. not analysed
 $R_{diff}=0.08$, transformation factor of C_{DGT} to C_e [Zhang et. al, 2004].

In Table 6, C_{DGT} and C_e concentrations are compared to the extractable zinc fraction from the different segments. The potential risk concentration (2 mg L⁻¹) was well exceeded for the Ter Munck and the Kalmthout soil exposed to undiluted runoff water, simulating 18 years of exposure. This was also the case for the Högbytorp soil at a zinc load of between 16 and 49 mg Zn kg soil⁻¹ (EDTA extractable fraction).

Table 6. DGT results expressed as the time averaged Zn concentration at the diffusive gel/soil interface (C_{DGT}) and the effective zinc concentration (C_e) for the Högbytorp and the Ter Munck topsoil compared to the extractable fraction of Zn with EDTA.

| Soil | C_{DGT} | C_e mg L ⁻¹ | EDTA mg Zn kg soil ⁻¹ |
|-----------|-----------|-----------------------------|-------------------------------------|
| Ter Munck | N.A. | N.A. | 618.7 |
| | N.A. | N.A. | 499.2 |
| | 7.0 | 87.2 | 370.9 |
| Högbytorp | 17.4 | 217.1 | 1240.3 |
| | 15.7 | 195.7 | 1291.5 |
| | 10.8 | 134.9 | 1001.2 |
| | 15.6 | 195.2 | 943.2 |
| | 11.9 | 148.8 | 773.9 |
| | 4.0 | 49.8 | 261.9 |
| | 0.5 | 6.3 | 48.7 |
| | 0.1 | 1.2 | 16.0 |
| | 0.0 | 0.2 | 2.1 |
| Kalmthout | 15.0 | 187.6 | 1107.7 |
| | 9.6 | 120.2 | 475.5 |
| | 2.7 | 34.3 | 167.8 |

0.5M NH₄Ac+0.02M EDTA S:L/1:10)

R_{diff}=0.08, transformation factor of C_{DGT} to C_e

[Zhang et. al, 2004].

In conclusion, most introduced copper and zinc seems to be available for plant uptake, possibly as a consequence of the accelerated introduction compared to real field exposures. DGT measured concentrations were affected by soil characteristics, which implies DGT to be a powerful tool to relate soil toxicity with plant availability.

4.3 Environmental fate of corrosion-induced runoff water in contact with limestone

4.3.1 Retention of limestone (Cu), (Papers V, VI)

Results on the interaction of copper-containing runoff water with limestone are based on a field exposure (1.5 years) with a copper roof, dewatered with two separate down-pipes (Paper V). One of the pipes was partly filled with limestone as absorbing material, and the other pipe kept as a reference. In parallel, laboratory percolation studies were performed to improve the understanding of the retention process, and if possible, optimise the retention of copper by limestone (Paper VI).

Results from the field study are displayed in Fig. 51. For most sampling periods, limestone retains between 10 and 20 % of all released copper. Two sampling periods show a negative retention, *i.e.* a higher copper concentration in the runoff water percolating through limestone compared to the reference. This implies retained copper to become mobilized during certain exposure conditions. The retention capacity depends on a number of parameters, including the specific surface area of the limestone, the rain intensity and flow rate through the pipes, the length of dry periods in-between rain events, and the concentration of copper in the runoff water.

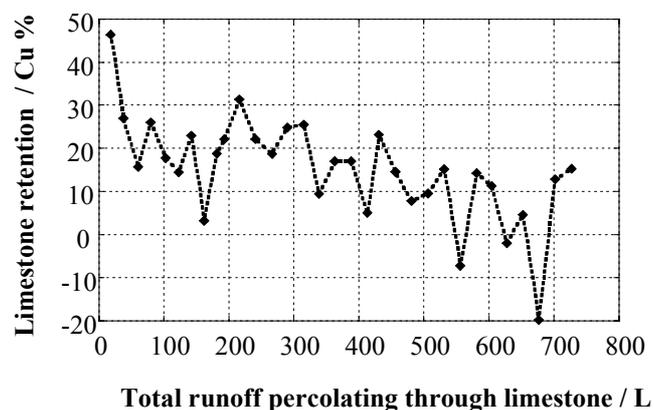


Figure 51. Changes in retention of copper to limestone during a 1.5-year field exposure of copper roof with one down-pipe partly filled with limestone.

The effect of specific parameters on the copper retention of limestone was evaluated in laboratory investigations (139 experiments). The following parameters and intervals were investigated based on current knowledge on the copper runoff process, and results from the field investigation with limestone; $1 < \text{Cu}/\text{mgL}^{-1} < 14$, $1 < \text{dry period at } 22^\circ\text{C}/\text{days} < 7$, $5.5 < \text{runoff water pH} < 6.5$, $15 < \text{rain duration}/\text{min} < 60$, $16 < \text{flow rate}/\text{mLmin}^{-1} < 32$, $3.7 < \text{specific surface area of limestone particles}/\text{cm}^2\text{g}^{-1} < 14.8$ and $47 < \text{amount of limestone}/\text{g} < 94$. The results are illustrated in Fig. 52, showing the specific surface area of limestone (A), the total copper concentration in runoff water (Cu) and the interaction between the two terms (Cu*A) to have the largest effect on the retention of copper by limestone. The interaction term implies that a reduced retention, caused by an increased copper concentration in runoff water (Cu), is compensated if the specific surface area of the limestone (A) is increased. The pH of runoff water alone has a very small affect on the retention, but interacts with the term for specific surface area (pH*A). This may suggest competition between Cu^{2+} ions and H^+ ions for exchange sites in limestone. The flow rate did not show any large effect on the retention of copper by limestone.

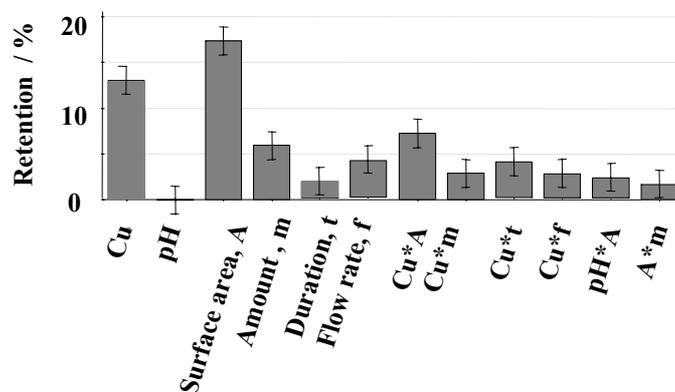


Figure 52. Effect of copper concentration (Cu), runoff water pH (pH), surface area of limestone (A), amount of limestone (m), rain duration (t), flow rate (f) and their interaction terms on the retention of copper by limestone.

The investigated span in flow rates was lower compared to field conditions. This could be compensated by using a larger amount of limestone, thereby increasing the number of possible retention sites for copper ions. Most of the terms in the model include the copper concentration, and show its importance, both alone and interacting with other parameters.

In conclusion, the most significant parameters to influence the retention of copper by limestone are the specific surface area of limestone, the copper concentration in runoff water, and the amount of limestone. Two of these parameters involve limestone properties and can, consequently, be varied in order to optimize the retention of copper by limestone at a given runoff water interaction.

4.3.2 Change in total metal concentration, chemical speciation and bioavailability during limestone interaction (Cu), (Paper V)

The interaction between copper-containing runoff water and limestone shows a reduction of both the total copper concentration in runoff water and the concentration of free copper ions ($\text{Cu}(\text{H}_2\text{O})_6^{2+}$). This is illustrated, in Fig. 53 for two sampling periods during the field investigation.

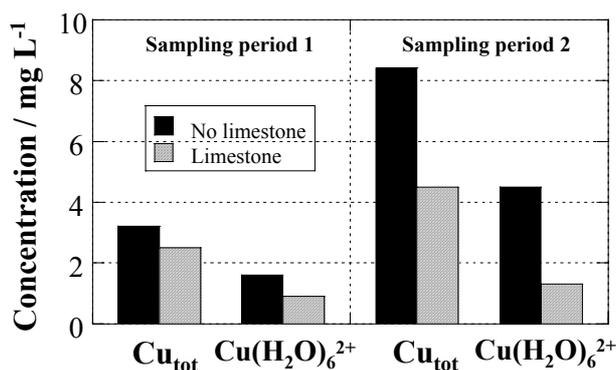


Figure 53. Effect of limestone on the total copper concentration (atomic absorption spectroscopy) and the free copper ion concentration (ion selective electrode) in runoff water for two different sampling periods during the field exposure.

Recent investigations have shown almost all copper (including e.g. $\text{Cu}(\text{H}_2\text{O})_6^{2+}$, $\text{Cu}(\text{OH})^+$ and $\text{Cu}_2(\text{OH})_2^{2+}$) in runoff water, sampled directly after release from the roof, to be bioavailable [Karlén et. al, 2002]. However, bioavailability investigations on runoff water after limestone interaction show the bioavailability to be reduced and directly connected to the concentration of $\text{Cu}(\text{H}_2\text{O})_6^{2+}$, without any contribution from any other copper species. This is in agreement with speciation modelling using Minteqa2, showing $\text{Cu}(\text{H}_2\text{O})_6^{2+}$ and non-bioavailable species, such as $\text{CuCO}_{3(\text{aq})}$, to exist in the runoff water after limestone interaction.

Although these specific results cannot be generalized to any wider range of exposure conditions, they nevertheless illustrate a rapid reduction of the most bioavailable form of copper in contact with limestone.

In conclusion, both the total copper concentration, and the most bioavailable copper species, the free copper ion ($\text{Cu}(\text{H}_2\text{O})_6^{2+}$) in runoff water, are significantly reduced in contact with limestone.

4.4 Environmental fate of corrosion-induced runoff water in contact with soil and limestone - a summary

In conclusion, the aim of the investigations, that focus on the environmental fate of corrosion-induced runoff water in contact with soil and limestone, has been to illustrate the capacity of different natural surfaces to retain and immobilize metals. The work has involved thorough studies on the capacity of soil to retain and immobilize copper, zinc, chromium and nickel in runoff water, and the capacity of limestone to retain copper. The investigations are based on parallel field and laboratory exposures. The overall results are schematically summarized in Fig. 54. Soil shows a very high capacity to retain metals (96-99.8 %), and limestone to have a substantial capacity to retain copper (5-47 %), as long as the retention capacity of each material is not reached. Laboratory studies have shown the possibility to significantly improve the retention capacity of limestone. The interaction between metal-containing runoff water with soil, and limestone, results in a significant decrease of the fraction of free metal ions, and consequently a reduction of the most bioavailable and ecotoxic metal species. The investigation shows organic matter to be an efficient medium for retaining metal ions. Solid surfaces, such as limestone, possess the ability to retain copper in runoff water, thereby forming naturally existing minerals. However, changes in natural systems must be considered, e.g., temperature, pH, microbial activity, weathering of minerals, deposition of new organic material, as well as dilution effects caused by urban storm water. Any surface with significant immobilization ability, in combination with low possibility of subsequent mobilization, is an excellent candidate for neutralizing metal release and its potential ecotoxic effects. A significant fraction of retained Cu, Zn and Ni in soil was extractable towards the strong complexing agent EDTA, which implies the possibility of future mobilisation. DGT

analyses of exposed soil segments indicate retained Cu and Zn to be available for plant uptake.

Computer modelling, with the Windermere Humic Aquatic model (WHAM), and biosensor tests with Biomet™, show the bioavailable fraction of metals to be reduced during passage through soil and limestone. Computer modelling with HYDRUS-1D has improved the current understanding of metal transport through soil profiles at field condition. The predictions imply a time-period for copper and zinc to be transported to a depth of 50 cm to vary between 4 and more than 8000 years, as a result of variations in runoff water and soil characteristics.

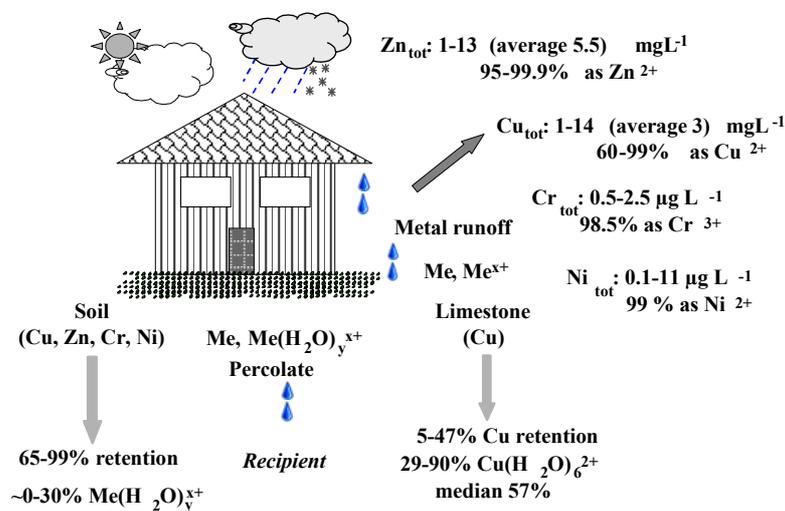


Figure 54. Compilation of results on the environmental fate of corrosion-induced runoff water in contact with soil and limestone.

Chapter 5 General conclusions

The overall aim of this multidisciplinary thesis is to generate scientific insight and relevant data for exposure and effect assessment of corrosion-induced metal release from external constructions. The thesis comprises data on long term metal runoff rates, predictive metal runoff rate models, total metal concentration in runoff, chemical speciation and bioavailable fraction in metal runoff, both at the release moment and after environmental interaction with e.g. soil and limestone. The metals investigated are copper, zinc, chromium and nickel, the two last mentioned from stainless steels.

The importance of using *long term runoff rate* data (several years) in risk assessments should be stressed, due to the long time needed for the metal and its patina to reach equilibrium in the ambient environment. While the runoff rates obtained are based on standardized exposure conditions (45° inclination facing south) in Stockholm, Sweden, two *predictive runoff rate models* were successfully developed in order to transform copper runoff rate data from Stockholm to other exposure sites. One model is based on rain pH, yearly precipitation and building geometry, and the other on average annual SO₂ concentration, yearly precipitation and building geometry.

Total metal concentrations in runoff vary both within and between different precipitation events, and are influenced by material properties (e.g., corrosion product solubility and specific surface area), as well as exposure parameters (e.g., rain volume, intensity, contact time and pollutants). The total metal concentration in runoff water is not sufficient, however, for adequate effect assessments. Additional key information required includes the chemical speciation of the released metal and its bioavailability.

The *metal chemical speciation* in runoff was obtained experimentally through an ion selective electrode (for copper), and through speciation modelling with the Windermere Humic Aquatic model (WHAM (V)). *Bioavailability* assessments were successfully performed through bioassay tests. All methods show that the majority (60-99%) of the metal in runoff exists in its most bioavailable form, the hydrated metal ion, at the metal release moment and will undergo major reductions in bioavailability upon environmental entry. The latter was evaluated through model column studies of the capacity of soil to retain and immobilize the

investigated metals in runoff water and the capacity of limestone through model and field column studies) to retain copper.

The *retention of metals by soil* for all metals investigated is very high (96-99.8%) and limestone also exhibits a substantial capacity (5-47%) to retain copper until each materials retention capacity is reached. Complementary laboratory studies demonstrated the possibility to improve the *retention of copper to limestone* significantly, by increasing the effective surface area for retention through a decreased fraction and increased amount of limestone. Computer modelling with WHAM(V) and biosensor tests (Biomet™) show the bioavailable fraction of metals to be reduced during passage through soil and limestone and consequently reduce the most bioavailable and ecotoxic metal species. Any surface with significant retention ability, in combination with low possibility of subsequent mobilization, is an excellent candidate for neutralizing metal release and its potential ecotoxic effects.

Computer modelling with HYDRUS-1D was used to extrapolate laboratory deduced soil results to real field scenarios. These predictions imply a time-period of between 4 and 8000 years, depending on runoff water and soil characteristics, before *saturation in the soil retention capacity* of copper and zinc is reached. A significant fraction of retained copper, zinc, chromium and nickel were extractable towards the strong complexing agent EDTA, implying the possibility of future mobilisation. DGT- (Diffuse Gradients in Thin films-) analyses of exposed soil indicate that retained copper and zinc are available for plant uptake.

These general conclusions show that performing a risk assessment of the environmental fate and impact of corrosion-induced metal release from outdoor constructions requires a complete set of data on annual runoff rates, concentrations, chemical speciation and bioavailability and its changes during environmental entry, together with knowledge on, e.g., type of material, service life of coating, building geometry, and dewatering system. In addition to the general conclusions, some metal specific conclusions are summarized below.

Long-term runoff rates for bare *copper* sheet are based on 8 years of exposure and range from 1.2 to 1.5 g m⁻² yr⁻¹, depending on year and annual rainfall quantity (460-790 mm yr⁻¹). Total copper concentrations in runoff vary between 1 and 14 mg L⁻¹ (average 3 mg L⁻¹) and the average effect concentration causing 50% growth reduction after 72 h (EC₅₀) to the green

algae *Raphidocelis subcapitata* at the copper release moment is $15 \mu\text{g L}^{-1}$. *Artificially formed copper patinas* might exhibit different runoff rates compared to naturally formed patinas, until their equilibrium composition and thickness in the actual environment is reached.

Long-term runoff rates for bare *zinc* sheet are based on 5 years of exposure and range from 1.9 to $2.5 \text{ g m}^{-2} \text{ yr}^{-1}$ with total zinc concentrations that vary from 1 to 13 mg L^{-1} (average 5.5 mg L^{-1}). A considerable variation in average annual runoff rates (0.07 - $2.5 \text{ mg Zn m}^{-2} \text{ yr}^{-1}$) was observed between different *commercial zinc-based materials*. This was attributed to alloying zinc with aluminium (Galfan, Galvalume, Spraycoated ZnAl15) or to surface treatments of zinc (chromating, TOC on zinc, Galfan and Galvalume, and pre-painted galvanized). The average effect concentration causing 50% growth reduction after 72 h (EC_{50}) to the green algae *Raphidocelis subcapitata* is $69 \mu\text{g L}^{-1}$. The barrier effect of a pre-painted galvanized steel remained undisturbed during the 2-year exposure, whereas the effect was completely lost after five years for galvanized steel with a chromate layer ($0.1 \mu\text{m}$) and significantly reduced for a zinc surface with a TOC layer ($1 \mu\text{m}$).

Long-term runoff rates for *chromium and nickel from stainless steel* of grade 304 and 316 are based on 4 years of exposure and range from 0.23 - 0.30 chromium, 0.28 - 0.52 nickel and 65 - 85 iron $\text{mg m}^{-2} \text{ yr}^{-1}$, respectively. The corresponding chromium concentrations in the runoff range from 0.5 to $2.5 \mu\text{g L}^{-1}$, and nickel concentrations from 0.1 to $11 \mu\text{g L}^{-1}$, respectively. These concentrations are far below reported ecotoxic concentrations for chromium and nickel.

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