D. Berggren, S. Bertling, D. Heijerick, G. Herting,
P. Koundakjian, C. Leygraf, I. Odnevall Wallinder

RELEASE OF CHROMIUM, NICKEL AND IRON FROM STAINLESS STEEL EXPOSED UNDER ATMOSPHERIC CONDITIONS AND THE ENVIRONMENTAL INTERACTION OF THESE METALS

A combined field and laboratory investigation

Cr
Ni
Fe

KTH
VETENSKAP
OCH KONST

UNIVERSITEIT
GENT

SLU
SWEDISH UNIVERSITY OF AGRICULTURAL SCIENCES

EUROFER
European Confederation of Iron and Steel Industries

October 2004

Release of Chromium, Nickel and Iron from Stainless Steel Exposed under Atmospheric Conditions and the Environmental Interaction of These Metals

A Combined Field and Laboratory Investigation

I. Odnevall Wallinder, S. Bertling, G. Herting and C. Leygraf
Div. Corrosion Science
KTH, Dr. Kristinas v. 51
SE-100 44 Stockholm, Sweden

D. Heijerick
Laboratory of Environmental Toxicology and Aquatic Ecology
Gent University
J. Plateustraat 22, BE-9000 Gent, Belgium

D. Berggren
Dep. Soil Sciences
Swedish University of Agricultural Sciences (SLU)
Ulvsv. 17, SE-750 07 Uppsala, Sweden

P. Koundakjian
Stainless Steel Producers Group
EUROFER – European Confederation of Iron and Steel Industries
Rue du Noyer, 211, B-1000 Brussels, Belgium

Corresponding author:
I. Odnevall Wallinder
Phone: +46 (0)8 790 66 21
Fax: +46 (0)8 20 82 84
E-mail: ingero@kth.s

Abstract

This multi-disciplinary research project has been implemented because of increased awareness of the potential environmental effects caused by dispersion of metals from outdoor constructions into the environment. Reliable quantitative data on release rates of chromium (Cr), nickel (Ni) and iron (Fe) from stainless steel exposed outdoors have been practically non-existent until recently, as has information on their chemical speciation and bioavailability after release and their interaction with soil systems. The project comprised three main parts: (1) a 4-year (1998-2002) field exposure of grades 304 and 316 stainless steels; (2) laboratory exposures of the same stainless steels and of pure Cr, Ni and Fe; and (3) percolation studies of Cr- and Ni-containing runoff solutions through soil. The following main conclusions were drawn:

- Yearly release rates from "as-received" (pickled and skin passed) grade 304 stainless steel exposed in Stockholm over the 4-year period ranged from 0.2 to 0.6 mg Cr m^{-2}, 0.1 to 0.5 mg Ni m^{-2} and 10 to 140 mg Fe m^{-2}. Corresponding release rate ranges from grade 316 stainless steel were 0.2 to 0.7 mg Cr m^{-2}, 0.3 to 0.8 mg Ni m^{-2}, and 10 to 200 mg Fe m^{-2}.

- The proportional release rates of Cr, Ni and Fe from stainless steel differ from their proportions in the bulk alloy: on a relative scale, Fe is released at a much higher rate than its bulk content, with Ni and Cr in second and third places, respectively.

- The release rates of Fe and Ni from stainless steel are significantly lower than from the pure metals, but similar for Cr. This is attributed to a protective Cr-rich oxyhydroxide passive film on both stainless steel and pure Cr. It is this passive film that hinders the release of Fe and Ni from stainless steel.

- Metal release rates were strongly influenced by surface conditions (abraded > as-received), and decreased with increasing pH of precipitation and with time during single rain events (first-flush effects). However, no influence of precipitation intensity was discerned.

- Immediately after release, Cr in runoff water is predominantly present as Cr(III) (>98.5%) and Ni as Ni(II) (>99%). These chemical forms change when the runoff water passes through different media (e.g. soils) in accordance with the chemical conditions of the media.

- The actual concentrations of Cr, Ni and Fe in runoff water from stainless steel are far below reported ecotoxic concentrations of the metals for plants and other organisms, and also far below the recommended limits for these metals in drinking water.

- The investigated soils exhibited high retention capacity: >98% Cr and >99% Ni for the OECD soil and >94% Cr and >95% Ni for the Rosenlund soil, simulating 2 to 20 years of outdoor exposure. Most Ni is retained in the top surface layer, suggesting a very fast reaction between Ni in runoff water and soil. A somewhat slower reaction between Cr and soil was indicated.

Key words: atmospheric corrosion, stainless steel, metal release, Fe, Cr, Ni, chemical speciation, ecotoxicity, soil retention, environmental risk assessment

Table of Contents

1 Introduction

1.1 Metal release induced by atmospheric exposure

1.1.1 The metal runoff process – general aspects based on work on Cu and Zn

A large number of different metals and metal alloys, e.g. copper (Cu), zinc (Zn), aluminum (Al), zinc- and aluminum-containing materials (e.g. Galfan, Galvalume), galvanized steel and stainless steel, are used in building construction and can be exposed to the atmosphere. Any metal or alloy exposed to the environment will corrode to some extent, often with the formation of a surface layer of corrosion products: a patina (usually called, for stainless steel, a passive film). The composition and protective characteristics of the patina depend primarily on the type of material and also on prevailing pollutant concentrations. Corrosive pollutants are deposited either through direct transfer of gases and particles to the surface from the atmosphere (dry deposition) or through indirect transfer by precipitation (wet deposition). 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). The rate of corrosion usually decreases with increasing thickness of the patina [(Odnevall and Leygraf 1997), (Graedel 1987), (Odnevall Wallinder and Leygraf 2001)]. Some corrosion products will dissolve and be released from the surface during precipitation events. The metal release rate, or runoff rate, is the amount of metal that is released from the corrosion product per unit of surface area in a given time. Corrosion and runoff are generally ruled by different physical, chemical and electrochemical processes, and also governed by different atmospheric exposure parameters. Hence, it follows that corrosion and runoff proceed independently of each other and with rates that are not necessarily equal or even proportional [(He, Odnevall Wallinder et al. 2001a), (Verbiest, Waeterschoot et al. 1997), (Cramer, Carter et al. 1988)]. The corrosion process takes place at the interface between the metal substrate and the corrosion product (patina or passive film), whereas the runoff process takes place at the interface between the atmosphere and the corrosion product, see Fig. 1.
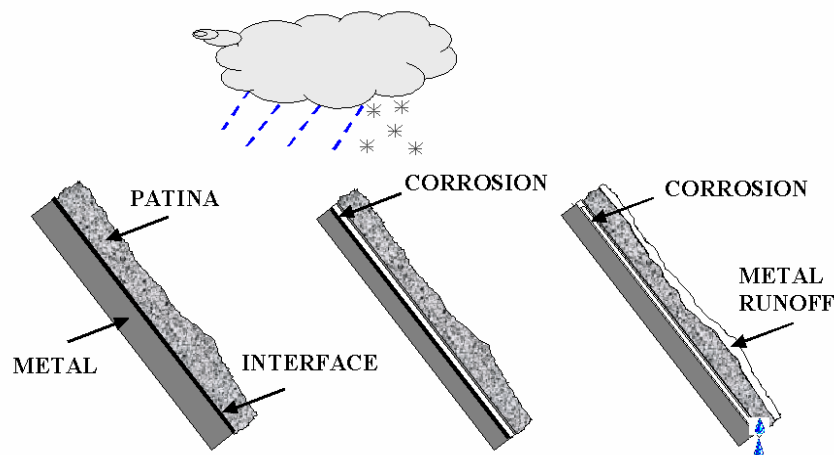
Fig. 1   Difference between corrosion rate and runoff rate.

Runoff rates of Cu and Zn from a large variety of roofing materials have been shown to depend on a combination of environmental and material parameters, including e.g. precipitation characteristics, patina characteristics, pollutant levels, wind direction and building geometry [(Odnevall Wallinder, Verbiest et al. 2000), (Odnevall, Verbiest et al. 1998), (He 2002)]. While the corrosion rates for Cu and Zn both exhibit clear time-dependence, characterized by initially high corrosion rates that then level off, the runoff rates exhibit lower and much more time-independent values as a function of time, at least on a time-scale of the order of years. On a short time scale, corresponding to a single precipitation event, the runoff rates exhibit clear time dependence characterized by initially high rates, the so-called "first flush", which gradually level off to more constant runoff rates at a later stage of the precipitation event [(He, Odnevall Wallinder et al. 2002a), (He, Odnevall Wallinder et al. 2000)].

1.1.2 Metal release from roofs – environmental interaction

The cycle of atmospheric corrosion and metal release can be schematically illustrated by the cycle of a particular metal. In Fig. 2, Zn is illustrated going from its most stable state, the mineral, via extraction processes to the metal, which is

thermodynamically a relatively unstable state, through various deterioration processes essentially corrosion and wear back to a mineral form. During transformation from the metallic state back to a mineralized form, the metal can exist in various chemical forms ("species"), among which the free (hydrated) metal ion is usually the most bioavailable form (i.e. available for uptake by organisms, see section 1.2). When forming an integral part of a chemical compound, the metal is usually much less bioavailable, i.e. less able than an ionic species to interact with organisms in the biosphere.
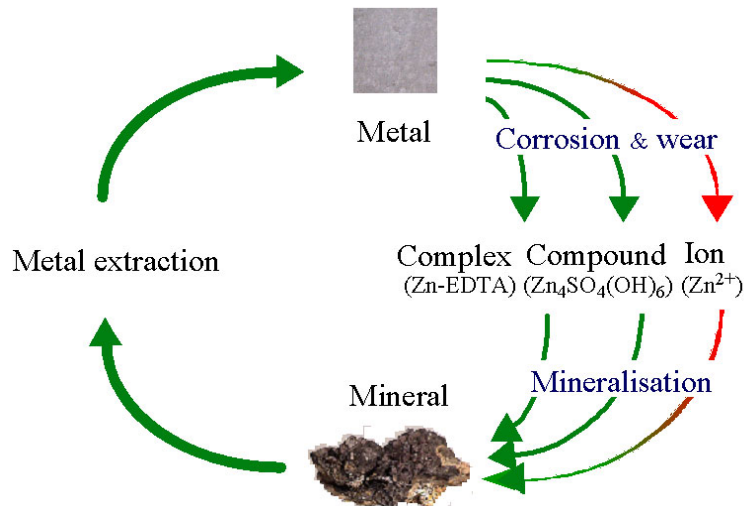

Fig. 2   The Zn cycle

Measurements of metal release at the immediate situation when the runoff water leaves the roof have shown that the majority of released Cu and Zn is in the ionic and, hence, bioavailable form [(Karlén, Odnevall Wallinder et al. 2001; Karlén, Odnevall Wallinder et al. 2002). However, when metal ions are released they rapidly form complexes with other elements present in the surrounding media. Thus, the concentration of metal in its ionic form will decrease during transport to the various potential recipients. Previous investigations have shown the bioavailable and the total concentrations of Cu and Zn present in runoff water to be drastically reduced almost immediately on contact with soil, and the soil system to retain the majority of the supplied metal (80-99% for Cu and Zn) [(Bertling, Odnevall Wallinder et al. 2002a), (Bertling, Odnevall Wallinder et al. 2002b)]. Non-retained metal is mostly complexed to organic material and shows often very low bioavailability. In addition, other surfaces in the vicinity of a building, such as concrete and limestone, have also shown to retain Cu and substantially reduce the concentration of potentially bioavailable ions [(Bertling, Odnevall Wallinder et al. 2002b)].

1.1.3   Atmospheric exposure and metal release from stainless steel

Stainless steels are corrosion resistant alloys (metallic materials consisting of two or more elements) of iron that contain a minimum of 11wt% of chromium. Chromium reacts with oxygen and moisture in the environment to form a protective, adherent, coherent and self-healing oxide film that envelops the entire surface and confers the corrosion resistance. This oxide film, usually known as the passive film is very thin (2-3 nanometres (1 nm=10^{-9} m)). Other alloying elements (e.g. nickel, molybdenum, copper, sulphur, carbon, silicon) may be added, singly or in various combinations and at various concentrations, in order to vary the properties of the stainless steel (e.g. mechanical properties, corrosion resistance), but chromium is the essential alloying element for the formation and stabilization of the passive film. Any effects of other elements in relation to corrosion resistance are only to influence the effectiveness of chromium in forming or maintaining the film (e.g. nickel promotes re-passivation, especially in reducing environments; and molybdenum stabilizes the passive film in the presence of chlorides). Increasing the chromium content to 17 to 20 wt%, greatly increases the stability of the passive film.

Stainless steel grades are differentiated into groups (ferritic, austenitic, martensitic and duplex grades) based on their metallurgy and microscopic structure, which in turn determines their areas of application. Within these groups there are different grades of stainless steel based on compositional ranges. Around 200 grades are in commercial production.

Most stainless steel grades are specifically identified by European (and other e.g. US) standards and, within the specified range, the stainless steel grade will exhibit certain properties, e.g. corrosion resistance, heat resistance etc. The EN standard gives the percentage ranges of the alloying elements. Thus, for example, the austenitic stainless steel AISI 304 is shown to contain no more than 0.05wt% of carbon, 17 to 19wt% of chromium and 8 to 11wt% of nickel.

Traditionally, stainless steels from the grade 304 "sub-family" have been the main ones used for roofs and exterior facades in urban environments; and grade 316 stainless steels in marine environments. However, today, the most common stainless steels used for roofing applications in both environments are the 316 stainless steels [(Avesta 1999)].

Despite the fact that the corrosion resistance of stainless steels is well-known, quantitative data on corrosion rates (expressed as mass loss) of stainless steels in atmospheric conditions are rare. Corrosion rates within the range of 0.2-0.5 $mgm^{-2}year^{-1}$ and approximately 0.1 $mgm^{-2}year^{-1}$, have been reported for 304 and 316 stainless steels, respectively [(Leygraf and Graedel 2000)]. These rates are orders of magnitude lower than those of traditional structural materials such as Zn, Cu and carbon steel.

Long-term exposure data for stainless steel in marine and polluted locations [(Baker and Lee 1990)] have been compiled by NiDI (Nickel Development Institute) and used as guidelines for grade selection in various environments [(NiDI 2002)]. Five years of exposure of grade 304 in various locations in Japan resulted in corrosion rates (based on weight loss) between 0.08 and 0.93 $\mu myear^{-1}$ [(NIDI 1989)]. The average annual corrosion rates of grades 304 and 316 exposed for 20 years in various locations in South Africa were reported to vary between 0.025 and 0.41 $\mu myear^{-1}$ and between 0.025 and 0.28 $\mu myear^{-1}$, respectively [(NiDI 2002)]. Corrosion rates measured after a 12-year sheltered exposure to the polluted, coastal location in Bayonne, New Jersey, US, were 22.6 $mgdm^{-2}year^{-1}$ for 304 and too low to be quantified for 316 [(Johnson and Pavlik 1982)]. Corrosion rates determined after 15 years at the marine site of Kure Beach, North Carolina, US, were <0.025 $\mu myear^{-1}$ for both grades 304 and 316 [(Heidersbach 1987)]. Qualitative evaluation of atmospheric corrosion behaviour, using a photometric technique to measure subtle changes in the surface appearance, has been reported for 38 different grades of stainless steel (including 304 and 316) exposed during 15 years to a marine and 32 years in a semi-rural environment [(Kearns, Johnson et al. 1988)]. Some recent reports focus on the importance of surface finish in the atmospheric corrosion resistance of stainless steel [(Asami and Hashimoto 1996), (Wallinder, Odnevall Wallinder et al. 2003)].

Total dissolution rates of all alloy constituents from stainless steels have been measured in a wide range of corrosive test solutions, e.g. artificial saliva, heat exchange water systems, acetic acid, sodium chloride solutions, sulfuric acid etc. [(Avesta 1999), (Walterson 1999), (Castle and Qiu 1990), (Chiba, Sakakura et al. 1997)]. Depending on the corrosivity of the medium, the total rates vary considerably, from less than 0.3 to 3.4×10^4 $mgm^{-2}year^{-1}$ [(Walterson 1999)]. However, release rate data for individual alloy constituents, including Cr, Ni and Fe, from stainless steel during atmospheric exposure conditions do not seem to be available.

1.2 *Ecotoxicity, chemical speciation, and bioavailability of Cr and Ni in aquatic systems*

Ecotoxicity refers to the harmful effects caused by natural or man-made substances to individual organisms, populations of organisms, communities or ecosystems in the natural environment. A variety of different toxic endpoints can be assessed, e.g. growth inhibition, mobility effects, reproductive effects, mortality. The toxicity is often described as the dose of a substance that results in a particular percentage response. The lethal concentration killing 50% or 10% of the population is expressed as a LC_{50}- or a LC_{10}-value; and the NOEC-value (no observed effect concentration) and LOEC-value (lowest observed effect concentration) are used to determine the borderline between toxic and non-toxic concentrations. The ecotoxic effect on algae is usually expressed as the reduction of growth rate as a function of various concentrations of the test substance. The concentration causing a 50% reduction of the algal growth is denoted the EC_{50} value. When comparing the toxicity of different substances, it is important to remember that the LC_{50} or EC_{50} value increases with decreasing toxicity, i.e. a higher concentration is needed to produce the same toxic effect.

Different test durations and evaluation methods are used to analyze the acute toxicity (short-term effects due to high concentrations) and chronic toxicity (long-term effects due to low concentrations). Acute responses have a sudden onset, after or during relatively high exposures, that are often of short duration (typically 4-7 days) with a lethal or non-lethal endpoint. Chronic responses are caused by relatively low exposures that occur over a long time (several weeks or years). A chronic toxic response is usually characterized by relatively slow expression of the toxic effect(s) and their long duration. Since the toxicity of a substance is usually not the same for all organisms, a battery of tests with different organisms is recommended when evaluating the ecotoxicity of the substance. Aquatic toxicity is usually evaluated using fresh water organisms (fish, Daphnia, algae) using standardized ecotoxicity tests (e.g. those in the OECD Test Guidelines). Algal tests are commonly used since they are internationally recognized and algae represent one of the most sensitive organisms towards metals.

In order to have a biological effect, the metal has to be in a bioavailable state, which means that it is in a chemical form (species) that can be taken up by an organism. The bioavailability of a metal in natural systems is influenced and controlled by a large number of physical and chemical factors including e.g. pH, redox potential, hardness of water, alkalinity, organic and inorganic ligands, particulate matter and temperature [(Di Toro, Kavvadas et al. 2001)]. Aquatic organisms of higher trophic level can control the uptake route in a depletion situation.

The hydrated free Ni ion, $Ni(H_2O)_6^{2+}$, has been reported to be toxic to a variety of algae, invertebrates and fish [(Duke 1980)]. However, the ion shows a strong affinity for organic complexing agents and is therefore only present in low concentration in natural systems [(NiDI 2000)]. Cr(VI) is considered the most toxic form of Cr whereas Cr(III) is less toxic and is mostly bound to organic matter in aquatic systems. In the presence of organic matter, Cr(VI) is reduced to Cr(III); however, the extent of reduction is dose-dependant [(Cervantes, Campos-Garcia et al. 2001), (Pacyna and Nriagu 1988)].

Relatively few researchers have investigated the bioavailability of Cr and Ni from an ecotoxicological point of view. A summary of the results from some key publications found is given below.

Algae are sensitive to metals and are, hence, key species used in water quality criteria setting and risk assessment of metals. Acute toxic effects on the green algae *Pseudokirchneriella subcapitata Korshikov* [(Hindak 1990)] (a species formerly and better known as *Raphidocelis subcapitata* or *Selenastrum capricornutum*) have been found at Ni concentrations of 0.05-0.1 mgL^{-1} [(NiDI 2000)]. The same algae exposed to $NiSO_4$ and $NiCl_2.6H_2O$ at pH 7.9 and a hardness of 200-210 mgCaCO$_3$L^{-1}, showed 72-h EC$_{50}$-values of 0.7-0.75 mgNiL^{-1} [(NiDI 2000)]. There are few reports on the acute effects of Cr on algae. Several algae (*Oscillatoria*, *Phormidium*, *Scenedesmus* and *Pandorina*) showed tolerance to total Cr concentrations of 20-80 mgL^{-1}, discharged into a river in waste from a paper mill [(Cervantes, Campos-Garcia et al. 2001)]. Algae have also been shown to develop tolerance to Cr(VI), which may explain large differences in published toxicity data [(Cervantes, Campos-Garcia et al. 2001)]. Data have been reported that show normal algal growth of *Scenedesmus* and *Selenastrum* in the presence of 100 mgL^{-1} Cr(III) but with 100 mgL^{-1} Cr(VI) growth was significantly inhibited [(Brady, Letebele et al. 1994)].

Other reported toxicity data for highly soluble Ni compounds show 48-h LC$_{50}$ values between 0.51 and 7.3 mgNiL^{-1} and NOEC-values of 0.01-0.22 mgNiL^{-1} (hardness 50-200 mgCaCO$_3$L^{-1}) for *Daphnia magna*; and 96-h LC$_{50}$-values of 7.8-35.5 mgNiL^{-1} and NOEC-values of 0.06-0.24 mgNiL^{-1} (hardness 50 mgCaCO$_3$L^{-1}) towards rainbow trout [(NiDI 2000)]. Another study reports 24-h EC$_{50}$ values of 10-10.9 mgNiL^{-1} for *Daphnia magna* [(Khangaroth and Ray 1987)].

Acute toxicity studies on Ni(II)-compounds and Cr(VI)-compounds in marine organisms, including crustaceans, molluscs, fish, annelids and echinoderms, showed 96h-LC$_{50}$ values of 2-350 mgNiL^{-1} and 2-105 mgCr(VI)L^{-1} [(Florence, Staober et al. 1994)]. 24-h LC$_{50}$-values of 0.4-7.7 mgNiL^{-1} and 24-h LC$_{50}$-values of 2.6-9.5 mgCr(VI)L^{-1} have been reported for freshwater ciliate species [(Madoni 2000)-Ni, (Madoni 1994)-Cr(VI)]. Exposure of the unicellular marine diatom, *Nitszchia obsetium*, to Cr and Ni compounds showed EC$_{50}$-values of >5 mgCr(III)L^{-1}, 3.5 mgCr(VI)L^{-1} and 0.25 mgNiL^{-1} [(Florence, Staober et al. 1994)].

In other studies, reported LC$_{50}$ values have been observed at concentrations ranging from 32 µgCrL^{-1} for algae to 118 mgCrL^{-1} for fish. For Ni, toxic effects have been reported at total concentrations ranging from 50 µgNiL^{-1} for rainbow trout to 11 mgNiL^{-1} for Fowler´s toad [(Gauglhofer and Bianchi 1991; Sunderman and Oskarsson 1991)].

In all, the sensitivity of (aquatic) organisms to Cr and Ni is clearly related both to the organism species and to the chemical speciation of the metal.

1.3   Interaction between Cr and Ni released from stainless steel and soil

As used in this context, "soil" consists of a thin layer of loose earth materials composed of weathered minerals (oxides and layer silicates[1]) and decaying organic matter (humus), with all solid phases and water in close contact. Due to its complex composition, soil can interact with metals through a variety of physico-chemical processes, as briefly discussed below [(Mcbride 1994)]. Irrespective of the process, the bioavailability of retained metal is often reduced in comparison to the free, hydrated, metal ion.

In soils, the solid phase (clay or humus) usually carries an excess negative surface charge. This leads to a surface potential that determines the distribution of cations (including metal ions) and anions in the liquid phase. Two opposing forces, electrical attraction and diffusion back into the bulk solution, act on cations, which have to counterbalance the negative surface charge. In addition to the electrostatic attraction, ions might bond to the solid phase by chemisorption processes. The latter type of bonding is much stronger. Figure 3 shows the main processes for metal retention in soil and complexation in solution (Me$_x$R), and how these processes determine the bioavailability of metals. Metal retention processes in soil can be divided into the following main groups:

- chemi- or physisorption
- cation exchange, and
- precipitation of secondary minerals.

---

[1] A term that is used by soil scientists and refers to how clay minerals are built up like composites with oxygen-bridges (binding sites for metals) and silicon.
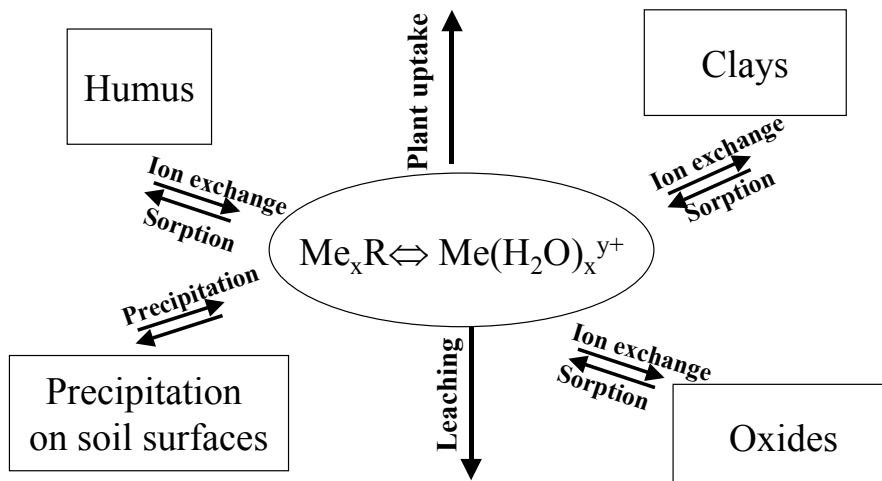
Physisorption in soil is controlled either by fixed charge constituents (e.g. in clay minerals such as hydrous silicates that develop negative charge as a result of lattice substitutions), or by variable charge constituents (e.g. the surface charge of humus and oxides of iron, manganese, aluminum or titanium that varies with the pH of soil water). At a soil pH below 7, clay minerals adsorb far smaller quantities than other main sorbents in the soil, e.g. humus.

Cation exchange is governed by the number of ions exchangable (cation exchange capacity, CEC) with metal ions. Silicates, oxides and humus all contribute to the CEC. In the top-soil layer, humus is the main contributor to CEC, whereas in deeper soil layers, minerals are the main contributors to CEC together with humus. The overall exchange process is diffusion controlled, and equilibrium is often obtained within an hour. Cations bound to the surface of minerals can diffuse into the interior of the solid phase. The relative diffusion rate depends, among others, on the ionic diameter of the cations. In the interior, these cations can neutralize negative charges and remain fixed. The processes are described as irreversible and cause metals to become immobilized [(McBride 1994)].

Other processes, such as microbial activity and CO_2–dissolution, may influence soil pH to some extent, and thereby indirectly influence the metal retention capacity of soils. Figure 4 shows different metal retention mechanisms as a function of reaction time and solubility of the adsorbate. The figure shows that surface precipitation (e.g. of sparingly-soluble sulfides, carbonates, phosphates or oxides) occurs only at very high metal ion concentrations, in fact, far higher than those usually found in runoff water. For this reason, surface precipitation is not regarded as an important retention process within this context.
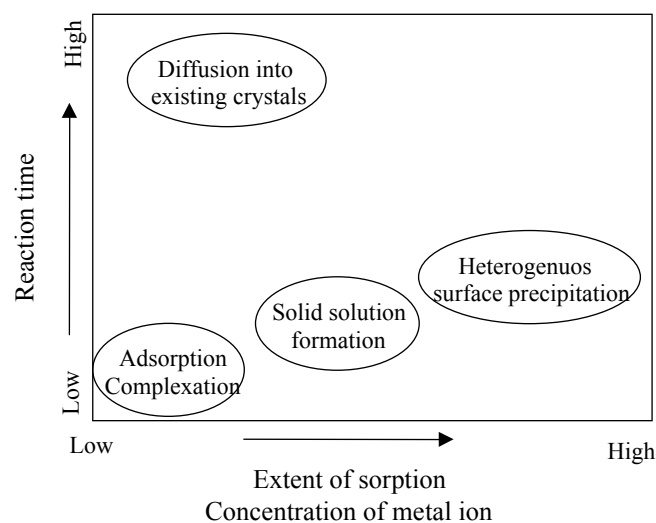
Cr in soils generally occurs as Cr(III) ions (chromic) or Cr(VI) ions (chromate, CrO_4^{2-}). Soil conditions generally favor the chromic form, which is a very immobile cation that complexes strongly with organic matter and chemisorbs onto oxides and silicate clays, even at quite low pH. Furthermore, Cr(III) readily substitutes Fe(III) in mineral structures, and precipitates as insoluble $Cr(OH)_3$ at higher pH. The chromic form is therefore, very 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. Chromate adsorbs less strongly than the chromic form, and its mobility and bioavailability are consequently higher. Generally, however, if pollutants containing chromate are applied to soils, most or all chromate is spontaneously reduced to Cr(III). This occurs typically under acid conditions and with organic matter present. Organic matter supplies reducing agents and complexing groups, which stabilize the chromic form. Soil therefore has the ability to detoxify Cr(VI). Cr is considered to be an immobile element and relatively difficult to extract from soils even with aggressive chemical agents.

Toxicity of Cr to plants is occasionally seen in unusually Cr-rich soils formed from the parent rock, serpentinite, or under high pH conditions that are favorable for Cr(III) oxidation [(McBride 1994)]. The chronic toxicity of Cr(III) to *Eisenia fetida, Enchytraeus albidus* and *Folsomia candida*, all invertebrates, has been evaluated for OECD soil (Guideline 207, 1984: 70% sand, 20% kaolin clay and 10% finely ground *Sphagnum* peat, adjusted to pH 6 with $CaCO_3$) spiked with $Cr(NO_3)_3.9\ H_2O$ [(Koen et al. 2002)]. The 21-day EC_{50} value for cocoon production in *Eisenia fetida* was 892 (679-1110)[a] mgCrkg^{-1} dry weight. For reproduction, a 42-day test in *Enchytraeus albidus*, resulted in an EC_{50} value of 637 (355-791)[a] mgCrkg^{-1} dry weight, while for *Folsomia candida* a 28-day EC_{50} value of 604 (254-3380)[a] mgCrkg^{-1} dry weight was observed.

Ni(II) is the most stable form of Ni in soil environments. The electronic structure of the cation favors the formation of relatively stable complexes with organic matter. Bioaccumulation of Ni in humus is pronounced and bonding to "softer" organic ligands containing nitrogen and sulfur is preferred for Ni(II). As the smallest of the divalent transition metal cations, Ni(II) fits easily into octahedral sites, co-precipitating into naturally occurring oxides of Mn and Fe in soils. Chemisorption on oxides, noncrystalline aluminosilicates, and layer silicate clays is favored above pH 6, but lower pH favors exchangeable and soluble Ni(II). Because 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(II)-ions are incorporated into sulfides that restrict mobility to very low levels [(McBride 1994)].

Toxicity of Ni to plants is observed in acid soils formed from serpentinite or other ultrabasic rocks. High levels of organic matter in Ni-rich soils can mobilize Ni(II) as organic complexes, at least at higher pH values [(McBride 1994)]. The chronic toxicity of Ni for the invertebrates *Eisenia fetida, Enchytraeus albidus* and *Folsomia candida* has recently been evaluated for OECD soil (Guideline 207, 1984: 70% sand, 20% kaolin clay and 10% finely ground *Sphagnum* peat, adjusted to pH 6 with $CaCO_3$) spiked with $NiCl_2$ to nominal concentrations of 100, 180, 320, 560 and 1000 mgNikg^{-1} dry weight [(Lock and Janssen 2002)]. The 21-day EC_{50} value for cocoon production in *Eisenia fetida* was 362 (241-508)[a] mgNikg^{-1} dry weight. For the reproduction of *Enchytraeus albidus*, a 42-day EC_{50} of 275 (217-346)[a] mgNikg^{-1} dry weight was observed and for *Folsomia candida* a 28-day EC_{50} value of 476 (347-671)[a] mg Nikg^{-1} dry weight.

In summary, soil exhibits different retention potential for Cr and Ni by sorption, cation exchange or precipitation processes. Metal ions in the soil solution are often found as organic complexes possessing a lower bioavailability compared to free hydrated metal ions. Cr(III), the species of Cr most common in soil, is very immobile in most soils and generally unavailable to plants, unless the soil is exceedingly acid. Ni(II) favors the formation of relatively stable complexes with organic matter, although not as stable as in the case of Cr(III). Toxicity of Cr(III) and Ni(II) to plants seem to occur only at locations with acid soils formed from serpentinite or other ultrabasic rocks. Chronic EC_{50} values for toxicity to invertebrates range from 604 to 892 mg total Crkg^{-1} dry weight and from 275 to 476 mg total Nikg^{-1} dry weight.

1.4 Project aim and outline

This research project was initiated partly in response to the increased awareness in society of the potential effect that the dispersion of metals from outdoor constructions may have on the environment, and partly because stainless steel is being increasingly used in outdoor applications (e.g. roofs) and there was a lack of data on release rates of alloy constituents from stainless steel induced by atmospheric exposure.
The project was divided into three different sub-projects: field exposures, laboratory exposures, and soil percolation studies, all aiming to define the metal release process and the environmental interaction of metal-containing runoff water. Key information obtained within each sub-project is shown schematically in Fig. 5.

---

[a] values representing 95% confidence interval

The aim of the *field exposure* was to provide quantitative data on release rates of Cr, Ni and Fe from two different stainless steel grades (304, 316) freely exposed for four years in the urban environment of Stockholm. Computer modeling was used to predict the chemical speciation of the released metal (Cr, Ni). In separate, laboratory-based experiments, the potential toxicity to algae was examined for the released metals as they actually occur when the runoff water leaves a roof surface.

The aim of the *laboratory exposures* was to investigate the effect of rain intensity, pH, and quantity on the release rates of Cr and Ni and, further, to show the effect of surface condition (abraded, as-received) on the release rates of Cr and Ni. Laboratory exposures were also performed to demonstrate the differences in metal release rates into rainwater from the stainless steel alloys compared to the pure metals (Fe, Cr, Ni) under identical exposure conditions.

The aim of the *soil percolation study* was to examine how Cr and Ni released from stainless steel during atmospheric exposure will interact with a soil system. This was accomplished by determining the soil retention capacity of Cr and Ni and concomitant mobilisation of retained metals.
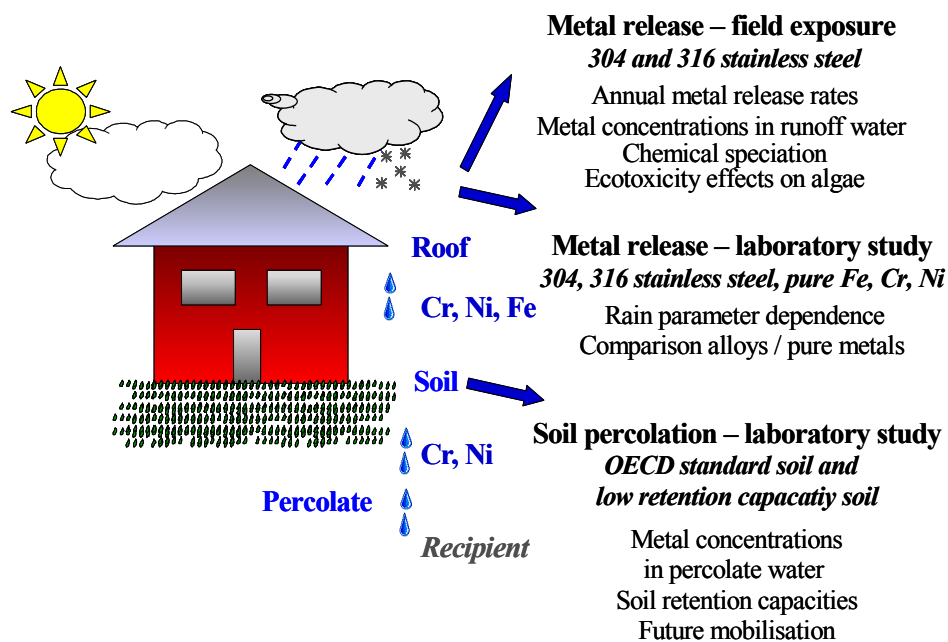

Fig. 5   Key information obtained within each sub-project of the research program

2 Experimental work

2.1 Material and surface preparation

2.1.1 Alloys and metals

The stainless steels investigated were grades 304 and 316 flat products, supplied by Avesta Sheffield[b], with 2B surface conditions; cold rolled, heat treated, pickled and skin passed (from here on denoted as "as-received"). These types of material are recommended for, and used in outdoor applications for facades, wall claddings and roofs [(Tochihara, Ujiro et al. 1986; Avesta 1999)]. Their chemical compositions are given in Table I. Pure Fe and Ni and electrolytic Cr were used for the laboratory investigation on differences in metal release rates from pure metals and alloys.

Table I   Nominal chemical composition (wt-%) of 304 and 316 stainless steel

Grade	C	N	Cr	Ni	Mo	Fe
304	0.04	0.06	18.3	8.7	--	balance
316	0.04	0.04	16.8	10.7	2.2	balance

Single-sided panels, sizes 300 cm^2, 60 cm^2 and 100 cm^2 were used for each grade in the outdoor field exposure, the laboratory exposure investigating the effect of various rain parameters and the laboratory exposure on pure metals and alloys, respectively. As a result of difficulties in producing 100 cm^2 of electrolytic Cr, the sample size used for this material was approximately 25 cm^2. Prior to exposure, the panels were ultrasonically degreased in consecutive steps in acetone and isopropyl alcohol and dried with cool nitrogen gas in order to decrease surface contamination. In addition, both laboratory investigations included abraded panels (1200P SiC-paper) providing a more uniform surface state for the different panels. Beeswax was used to protect the edges during the laboratory investigations. Single panels were used for the outdoor exposure whereas all laboratory exposures used duplicate panels. Previous outdoor exposures have shown single panels to be sufficient and, furthermore, the panel area used to be representative for roofs with much larger surface areas [(Odnevall Wallinder, Verbiest et al. 2000)].

2.1.2 Soil

A soil percolation system using columns filled with soil, through which runoff water with known metal concentrations was introduced, was used to study changes in Ni and Cr total concentration and speciation during transport of runoff water from roofing material to the environment.

Two different soil types were used in this study: "OECD soil" (a reference soil previously used in a number of studies and therefore giving the opportunity to compare this study to other work [(Lock and Janssen 2002a; Lock and Janssen 2002b)]); and a soil sampled in Rosenlund, Sweden. The OECD soil was mixed in accordance with OECD Test Guideline 207 [(OECD 1984)] (70% sand, 20% kaolin clay and 10% finely ground *Sphagnum* peat, adjusted to $pH_{25°C}$ 6 with $CaCO_3$). The Rosenlund soil was not dried after sampling but kept at 8°C before exposure in the percolation study. The soils were sieved (<2 mm) under ambient moisture conditions, homogenized and stored at room temperature (OECD) and 8°C (Rosenlund) prior to use. Soil characteristics are given in Table II. Details on analytical procedures are given in section 2.5.

Table II   Characteristics of OECD and Rosenlund soils used in the soil percolation study

Soil data	Clay %	C_{org} % dry weight	pH H_2O, 8°C	CEC $Cmolkg^{-1}$	Cr_{EDTA} $mgkg^{-1}$	Cr_{7MHNO3} $mgkg^{-1}$	Ni_{EDTA} $mgkg^{-1}$	Ni_{7MHNO3} $mgkg^{-1}$
OECD	20	8.6	6.49	13.4	0.4	1.0	0.5	1.8
Rosenlund	7	3.8	4.09	0.7	1.8	4.0	2.5	1.7

Me_{EDTA} is an estimation of the exchangeable fraction and $Me_{7M\ HNO3}$ is an estimation of the total Cr or Ni content in the soil. CEC equals the cation exchange capacity.

---

[b] Now Outokumpu Stainless

The Rosenlund soil is regarded as a low retention soil for metals, characterized by a clay content of 7% (typically for a "normal" soil between 10-20%); a comparably low fraction of organic material, 3.8% (typically 2-10%); low pH 4.09 (typically 6-7); and a very low cation exchange capacity (CEC) 0.7 cmolkg^{-1} (typically 10). As the pH of this soil is below 6-7, the soil oxides (mainly Mn and Fe) will have a positive charge and will therefore not contribute to the CEC. Average concentrations of total Cr and Ni for some unpolluted soils from Western Europe are shown in Table III. Such values can, however, vary widely from site to site. It should also be stressed that the concentration of metals in the bed-rock (50 m) varies significantly due to e.g. natural differences in mineral composition. For instance, in Sweden the concentrations vary between 22 and 600 mgCrkg^{-1} dry weight and between 7 and 260 mgNikg^{-1} dry weight [(Walterson 1999)].

Table III   Mean concentrations of total Cr and Ni content in unpolluted soils from Western Europe [(Frink 1996)-a) (Walterson 1999)-b]

Country	Belgium a)	Germany a)	Sweden a)	Sweden b)
mg Cr/kg DW	90	55	2.3	2.5 - 17
mg Ni/kg DW	33	15	4.4	5 - 10

DW – dry weight

2.1.3   Artificial rain and artificial runoff water

The composition of the *artificial rain* used in the laboratory exposures is given in Table IV and resembles the atmospheric rain in the central and southern parts of Sweden [(Granat 1990)].
All chemicals used to make the artificial rain (NH_4NO_3, Na_2SO_4, K_2SO_4, $MgSO_4 \cdot 7H_2O$, $CaCl_2 \cdot 2H_2O$ and H_2SO_4) were of analytical grades and mixed with ultrapure water (18 MΩcm^{-1}). The concentrations of the metals of interest (Cr, Ni) in the artificial rain water were below the limit of detection (<0.5 µgL^{-1}).

Table IV   Chemical composition of artificial rain (mgL^{-1})

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

The use of artificial rain for simulating rain water has been verified elsewhere [(He, Odnevall Wallinder et al. 2001b; He, Odnevall Wallinder et al. 2002b)]. To investigate the effect of pH, the original pH value of 4.3 was adjusted to 2.5 and 3.5 using HClO$_4$ and to 5.7 using NaOH. The range of pH was based on yearly average measurements of rain pH from a large number of test sites in Europe, within the UN/ECE exposure program, Fig. 6 [(UN/ECE 1997)]. pH 2.5 was added in order to determine the pH-dependence of metal release from stainless steel, although it is not representative of rain pH in Europe.
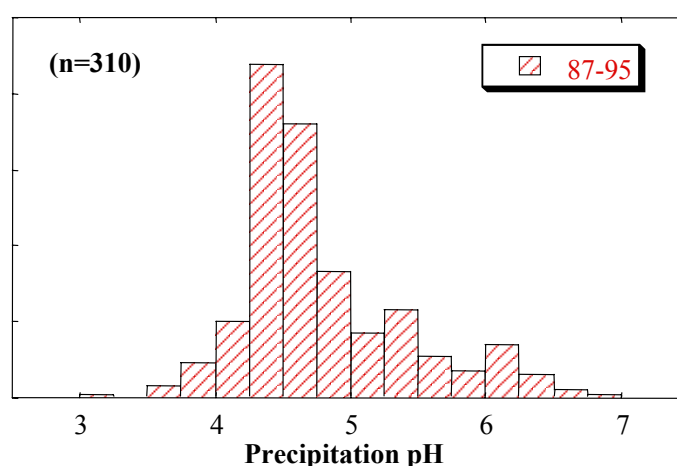

Fig. 6   Annual rain-pH distribution of different test sites in Europe during an eight-year field exposure [(UN/ECE 1997)]

In order to obtain a well-defined runoff water *(artificial runoff water)* for the percolation study, the pH of the artificial rain and runoff water was adjusted to 5.93 with NaOH, in agreement with runoff water collected from roofs (between pH 4.8 and 6.35). Results from chemical modeling with the present field data (see section 3.3) for all sampling periods show the majority of Ni (>99%) to be present as the free Ni(II)-ion in runoff water from both grades 304 and 316. Similar results were seen for Cr, with more than 98.5% present as free Cr(III)-ions. Based on these results, the Cr and Ni in the artificial runoff water were added as $Cr(NO_3)_3.9H_2O$ (quality purum) and $Ni(NO_3)_2.6H_2O$ (quality purum). The final Cr and Ni concentrations of the artificial runoff water were 7 μgL^{-1} and 14 μgL^{-1}, respectively. These concentrations are about ten times higher than the field data collected during the runoff exposure program. The higher concentrations were used to increase the possibility of detecting Cr and Ni in the percolate solutions (ICP-MS detection limits for Cr and Ni are both approximately 0.5 μgL^{-1}) since it was assumed that most of the metals would be retained in soil.

2.2   Field exposures of metal release

Metal release exposures were performed at an urban test site located within the campus area at the Royal Institute of Technology in Stockholm, Sweden, Fig. 7. The site is located on the roof of an eight-story building and is surrounded by built-up areas with relatively high traffic intensity.

South
4 5°

Fig. 7   Field exposure test site for metal release studies.

Yearly environmental data (T (temperature), RH (relative humidity), SO_2, NO_2, O_3, PM_{10} (aerosol particles <10 µm)) were supplied by the Stockholm Environment and Health Protection Administration. Rain pH and annual rain quantities were measured at KTH. Average data for each year within the total four-year exposure period are given in Table V.

Table V   Average environmental parameters for each year of exposure during the total four-year exposure in Stockholm, Sweden

Exposure year	Time period	T [°C]			RH [%]	SO_2 [μgm^{-3}]	NO_2 [μgm^{-3}]	O_3 [μgm^{-3}]	PM_{10} [μgm^{-3}]	*Rain pH*	*Rain mm* [mmy^{-1}]
		mean	min	max							
1	98-07 99-07	7.0	-17.1	26.1	80.6	3.3	55	48	17	*5.0*	*603*
2	99-07 00-07	8.3	-13.0	30.8	80.1	2.8	55	52	18	*5.2*	*584*
3	00-07 01-07	7.8	-18.5	27.1	74.7	2.6	49	45	19	*4.9*	*757*
4	01-07 02-07	8.5	-16.4	30.9	78.1	2.3	51	52	19	*5.3*	*792*

Rain pH and mm from collected rain volumes impinging an inert sample holder inclined 45° from the horizontal. PM_{10} is the concentration of particles smaller than 10 μm.

Metal release measurements were performed between July 1 1998 and July 1 2002. Cr and Ni were measured during the entire exposure period whereas Fe was measured during the last three years of exposure. Following the ISO standard [(ISO8565 1992)], the panels were mounted on Plexiglas™ fixtures at 45° from the horizontal, facing south, from which runoff precipitation was collected and transported to acid-cleaned polyethylene containers, Fig. 8. Acid-cleaning (10% HNO_3) of the containers was essential due to the very low concentrations (μgL^{-1}) of released Cr and Ni. Any contamination from collecting vessels could markedly affect the results. Non-acid-cleaned vessels have previously shown to affect trace-metal analysis of atmospheric precipitation [(Ross 1986).]. The containers were changed approximately every second week. In

parallel, rainwater impinging a Plexiglas fixture was collected to measure the background concentration levels of Fe, Cr and Ni in rain water at the test site.
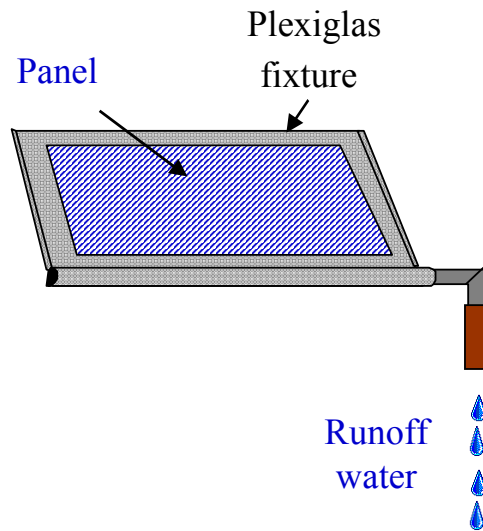

Fig. 8   Schematic view of fixture used for metal release rate measurements

2.3   Laboratory exposures for metal release

An experimental apparatus to simulate rain events was constructed for the laboratory investigation. Various rain intensities were obtained by introducing clean compressed air into the orifice of a thin tube with flowing artificial rain (see section 2.1.3), hence forming small drops leaving the orifice. Intensities between 4 and 50 mmh^{-1} were produced by carefully adjusting the flow rate of the rainwater and the air. A rain intensity of 2-4 mmh^{-1} is representative for Sweden. Two collecting vessels made of Plexiglas, exposing the panels at an inclination of 45° from the horizontal, were located below the tube, Fig. 9. The experiments were performed in ambient laboratory air and temperature (22°C).
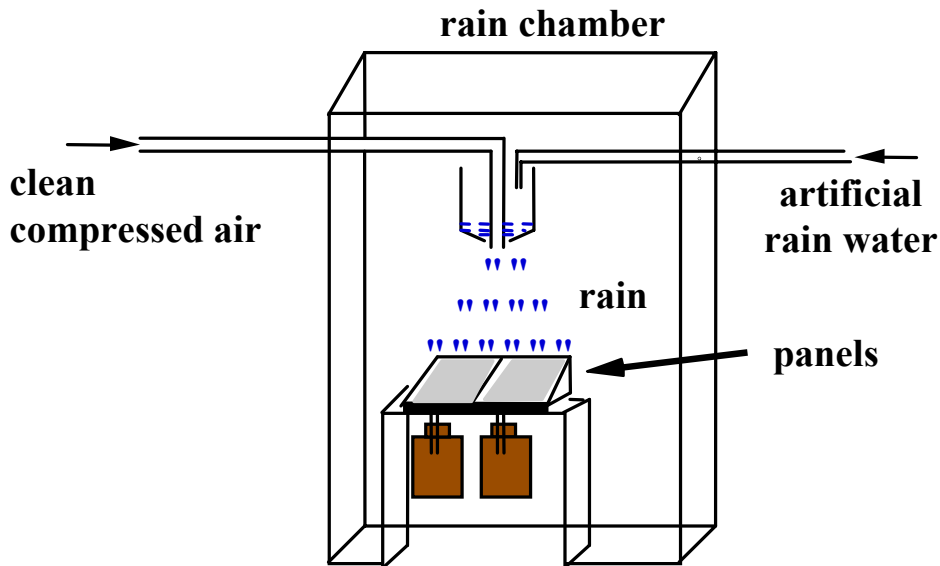

Fig. 9   Experimental set-up for rain simulation

All laboratory tests investigating the effects of different rain parameters on the metal release rate are schematically represented in Fig. 10. The number of panels in each test is given in parenthesis.

5 mm/h (2)
10 mm/h (9)
14-20 mm/h (4)
36-40 mm/h (2)

10 mm/h (2)

10 mm/h (2)

5 mm/h (5)
10 mm/h (4)
14-22 mm/h (3)
42 mm/h (1)

10 mm/h (2)

10 mm/h (2)

pH 3.5 pH 4.3 pH 5.5

pH 3.5 pH 4.3 pH 5.5

as-received

304

abraded

as-received

316

abraded

pH 2.5 pH 3.5 pH 4.3 pH 5.7

pH 4.3

10 mm/h (2)

10 mm/h (2)

6 mm/h (2)
9-11 mm/h (4)
14-24 mm/h (7)
35 mm/h (2)

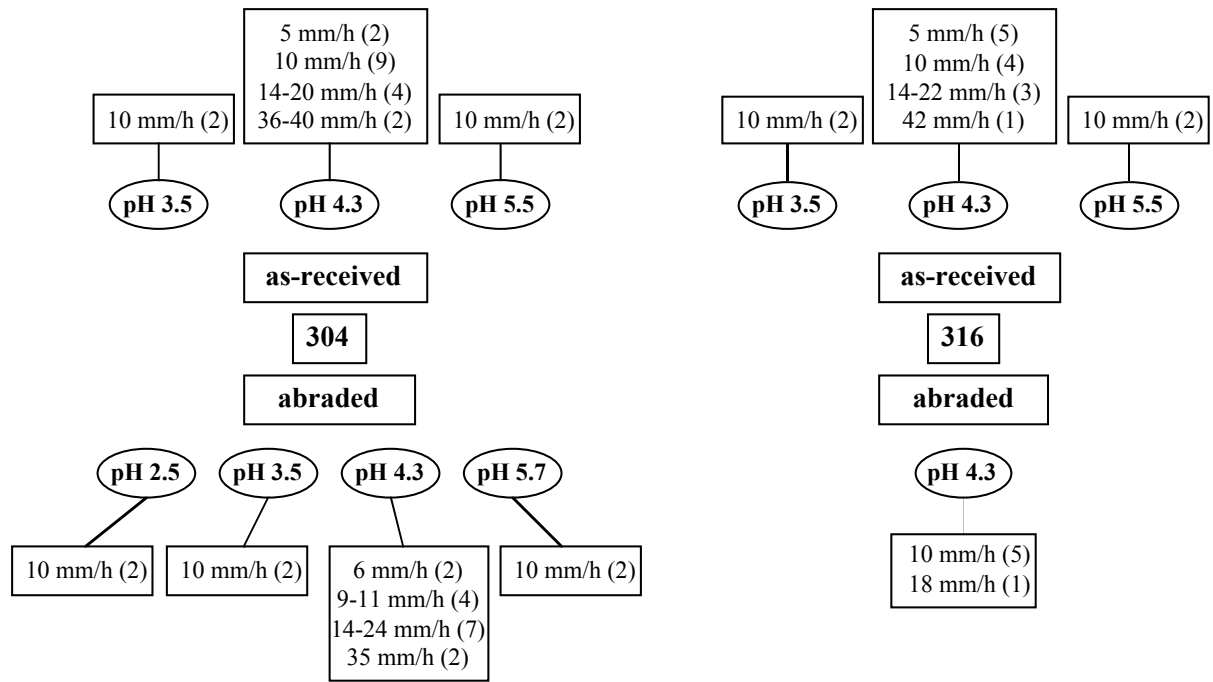10 mm/h (2)

10 mm/h (5)
18 mm/h (1)

Fig. 10   Laboratory tests performed on 304 and 316 stainless steels in as-received and abraded conditions, respectively. The values in parentheses refer to the number of panels investigated

The rain device was also used to investigate differences between metal release rates of Cr, Ni and Fe from pure metals and 304 and 316 stainless steels, respectively.

Runoff water was collected after 30 minutes, 1h, and then every hour during a continuous eight-hour rain episode at a constant rain intensity of about 4 mmh^{-1} and a pH of 4.3 (see section 2.1.3). The tests are illustrated in Fig. 11.

pH 4.3

4 mm/h

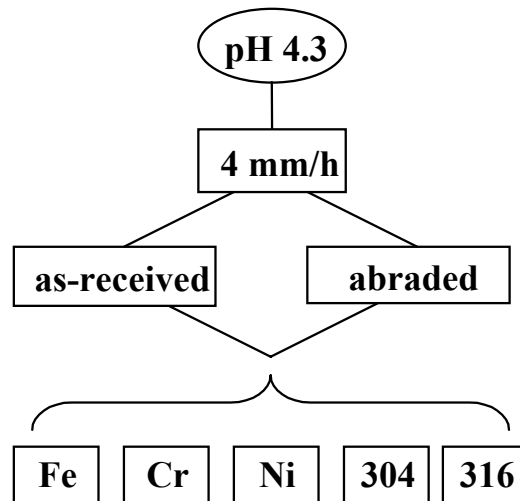as-received   abraded

Fe   Cr   Ni   304   316

Fig. 11   Experiments performed in the pure metals/alloy investigation

2.4   Soil percolation study

Changes in total concentration and chemical speciation of Cr and Ni in runoff water from stainless steel in contact with soil were evaluated with soil column experiments, shown in Fig. 12.
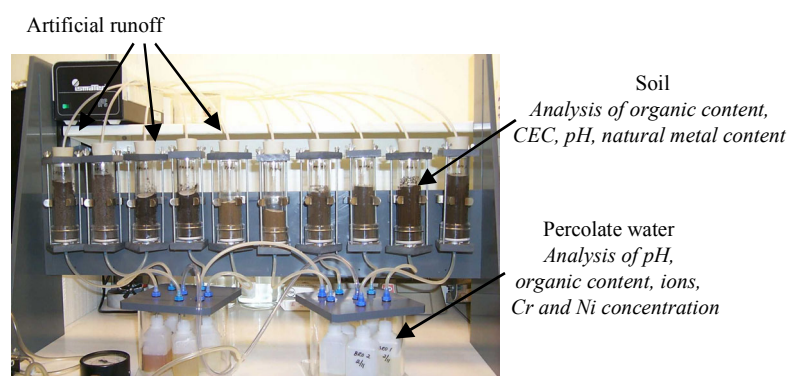
Artificial runoff

Soil
Analysis of organic content, CEC, pH, natural metal content

Percolate water
Analysis of pH, organic content, ions, Cr and Ni concentration

Fig. 12   Experimental setup showing the soil cores, collecting vessels and the pump providing artificial runoff water to the soil cores

A similar set-up has previously been used for investigating organic processes in clay soils [(Jonsson 1999). (Zysset and Berggren 2001)] and Zn retention in soil [(Bertling, Odnevall Wallinder et al. 2002)]. The diameter of each glass column is 32 mm and the height is 140 mm. In order to avoid contamination, all columns, preparation and storage vessels were soaked in 10% HNO_3 for at least one day, rinsed three to four times with ultra-pure water (<18 MΩcm^{-1}) and sealed before use. The soil had an initial water holding capacity of ~15% and was packed in each column by gravity. Each soil core was about 7 cm in height, corresponding to a dry weight of 55g soil. A sintered glass-filter disc (Duran P4; pore size diameter 9-15 μm), a 0.2 μm filter (Gelman Supor), and a glass-fibre filter (Gelman A/E 1.0 μm) were placed between the bottom cover of the column and the soil core.

The artificial runoff water entered each soil core through a glass filter ensuring a uniform wetting of the whole soil core surface. A peristaltic pump was used to keep a constant rain intensity of 2 mmh^{-1} (equivalent to a supply of 1.5 mLh^{-1} for this column size). Various rain intensities were initially evaluated (1-4 mmh^{-1}), but since variation of intensity was found not to affect the retention of metals in the soils, a medium value working well in the soil set up was chosen. The reason for the lack of effect on retention by rain intensity is that adsorption of Cr and Ni by organic material is a very fast reaction. When the adsorption sites on the organic material are fully occupied and adsorption on oxides then plays a greater role for the retention of Cr and Ni, rain intensity may affect the retention of metals by the soil.

The investigations were performed at 8°C with aerobic conditions (achieved by a permanent vacuum of –100 mbar at the outlet of the columns) in a dark room. Percolate water samples were collected once a day, and pH, TOC[c] and total Cr and Ni concentrations for each sample were measured (see section 2.5). The column experiments were conducted continuously for approximately one month. The total volume of added artificial runoff was 1200 mL for the OECD soil and 820 mL for the Rosenlund soil, corresponding to rain quantities of 1400 and 1000 mm, respectively. These quantities are equivalent to 2-2.5 years of rain in Stockholm (500 mmyear^{-1}). The total quantities of Cr and Ni added to the soil cores were 8 and 17 µg for the OECD soil and 6 and 11 µg for the Rosenlund soil, respectively.

2.5   Methods of analysis

2.5.1   Metal concentration

Total concentrations of Cr, Ni and Fe in runoff water were determined using graphite furnace atomic absorption spectroscopy, GF-AAS (Perkin Elmer SIMAA 6000) or Inductively Coupled Plasma – Atomic Emission Spectroscopy, ICP-AES (ARL ICP 3520B). GFAAS analyses were performed at the Swedish Pulp and Paper Research Institute and ICP-AES analyses at the Department of Chemistry, KTH. The limits of detection were 0.5 µgL^{-1}, 0.1 µgL^{-1} and 8 µgL^{-1} for Cr, Ni and Fe, respectively. Control samples with 1 µgCrL^{-1} and 1 µgNiL^{-1} were analyzed before and in between regular measurements showing a deviation maximum of 7% from the ideal value. Before analysis, all runoff water solutions were acidified to a pH below 3 using HNO_3.

Inductively Coupled Plasma – Mass Spectroscopy, ICP-MS (Perkin Elmer ELAN 5000) measurements of soil percolation samples were performed at ITM, Institute of Applied Environmental Research, Stockholm University. The detection limit was 0.1 µgL^{-1} for both Cr and Ni.

---

[c] Total organic carbon

2.5.2 Surface composition of stainless steel

The chemical composition of the outermost surface layer of the stainless steel was investigated using X-ray Photoelectron Spectroscopy, XPS (Kratos AXIS HS). Wide scans and detailed scans (pass energy of 80 eV) of Cr 2p, Ni 2p, Fe 2p, Mo 3d, C 1s, O 1s were obtained with a monochromatic AlKα X-ray source (1486.6 eV) operated at 300 W (15 kV/20 mA). The area of analysis was approximately 0.4 mm^2. Sensitivity factors (Cr 2p - 2.3 and Fe 2p - 3.0) supplied by Kratos were used to investigate the chromium content of the surface film defined as ($Cr_{ox}/(Cr_{ox}+Fe_{ox})$).

2.5.3 Corrosion resistance of stainless steels

Electrochemical potentiodynamic polarization measurements were performed at room temperature using artificial rain as the test solution. A conventional three-electrode electrochemical cell with an Ag/AgCl reference electrode and a platinum counter electrode was used for all measurements. Prior to exposure, the specimens were cleaned in acetone and isopropyl alcohol. The exposed sample surface area was 0.5 cm^2. A delay of 40-60 minutes was set before the measurements to stabilize the open-circuit potential. Polarization scans were then performed using a Solartron Interface 1287 instrument starting at a potential of –0.1 V vs. open-circuit potential to about 0.8 V vs. Ag/AgCl at a scan rate of 10 mVmin^{-1}. Each electrochemical measurement was repeated three times. The polarization resistance was evaluated with linear regression within 20 mV below and above the open circuit potential using the CorrWare software.

2.5.4 Algal toxicity

All tests with *Raphidocelis subcapitata* were conducted in accordance with OECD Test Guideline No. 201 [(OECD 1984); (ISO 1989)]. *R. subcapitata* Printz starter cultures were obtained from the Culture Centre for Algae and Protozoa (CCAP 278/4) and were grown in ISO-medium [(ISO, 1989)] at 20 ± 1°C with continuous light (5000 lux) and continuous aeration (filtered air). Each week, cultures were visually inspected for contamination using a microscope with 10x20 magnification.

Prior to use, the runoff waters were filtered with a 0.45µm filter (Sapor® 450 membrane filter, Gelman Laboratory) in order to remove any particulate material (e.g. pollen).

Algal tests were performed in 100 mL Erlenmeyer's flasks, each containing 50 mL of test medium. Each test consisted of six control replicates and three replicates for each of five runoff dilutions (1:2 dilution series). The range of the tested dilutions was based on the measured total Cr and Ni concentrations. Carbon-filtered deionized water was used as the dilution medium. Nutrients were added to the control medium (deionized water) and all test solutions, as described in the ISO Guideline 8692 [(ISO 1989)]. Each concentration was inoculated with 10,000 cells mL^{-1}.

Tests were carried out under continuous uniform illumination. A light intensity of 4000 Lux was measured at the surface of the light table. The cell density was measured after 24, 48 and 72 hours with the aid of an electronic particle counter (Coulter Counter model DN). At the same time, the pH of the medium was measured and noted. Tests were considered as valid when the pH variation at the end of the test was less than 1 pH-unit and if the final cell concentration in the control exceeded 160 000 cellsmL^{-1}.

The 72h-EbC$_{50}$ values were calculated using the 'area under the curve' method described in OECD Test Guideline 201 [(OECD 1984)] and transformed into Toxic Units (T.U.):

$$T.U. = \frac{1000}{E_b C_{50}(mL_{runoff} / L_{iso-medium})}$$

The actual effect concentration, i.e. the total Cr+Ni+Fe concentration causing 50% inhibition, was calculated in order to relate the toxicity to the total amount of the released metal in the runoff water according to the following formula:

$$actual\ effect\ concentration = total\ concentration\ (mg / L_{runoff}) \times E_b C_{50}\ (mL_{runoff} / L_{iso-medium})$$

All ecotoxicity tests were performed at the University of Gent, Belgium.

2.5.5 Computer modeling of chemical speciation

The chemical speciation of Cr and Ni in runoff water was calculated using the water-ligand model MINTEQA2 [(Allison and Brown 1991)]. The modeling was based on chemical analysis of the total Cr and Ni concentration as well as pH, alkalinity and concentration of sulfate and chloride in runoff water from three different sampling periods, Oct. 1998, June 1999 and Oct. 2000, during the four-year exposure. Alkalinity was determined with the Hach titration method using phenolphthalein and bromocresol green-methyl red as indicator solutions. Sulfate concentrations were measured with the Spectroquant® 14791; Sulfaver 4 method, and chloride concentrations with the Spectroquant® 14755 method. All physico-chemical measurements were performed at the University of Gent, Belgium.

The chemical speciation of Cr and Ni in percolate water was calculated using the Windermere Humic Aqueous Model (WHAM V) [(Tipping and Hurley 1992)]. This model includes organic material and thereby the ability of organic material to form complexes with metals in solution. Data used for the calculations, at atmospheric CO_2 pressure, are the total concentrations of Cr and Ni in the percolate water (ICP-MS - ITM, Institute of Applied Environmental Research, Stockholm University), ionic species (IC, Sarasep AN-1, - Dept. of Land and Waste Resources Engineering, Royal Institute of Technology, Stockholm) and their concentrations in the percolate water, amount of organic material (TOC-5000A Shimadzu analyser – Swedish University of Agricultural Sciences, Uppsala), temperature and pH.

2.5.6 Soil characteristics

Soil pH was measured in a water extract at 8°C with a combined glass electrode (Radiometer GK2401C 291-3-065). Total content of organic carbon in the soil (C_{org}) was determined using a LECO CHN-932 analyzer. The cation exchange capacity (CEC) was calculated from the Ca, Mg, Na and K content of the soil (determined by extraction with 0.1 M $BaCl_2$ and analysed with atomic absorption spectroscopy, Analyst 300 Perkin Elmer). The natural Cr and Ni concentrations in the soils were determined as the exchangeable concentration of the metals, defined as Cr and Ni extractable using the complexing agent EDTA (0.5 M NH_4Ac+0.02 M EDTA), and the total concentration of Cr and Ni, obtained through extraction with 7 M HNO_3. All extractions were performed for 24 hours.

2.5.7 Soil extractions

After exposure to Cr- and Ni-containing runoff water, each of the two soil cores was divided into 7 segments. Extractions were performed for three segments, 1, 2 and 7, of soil from the top, next to top and bottom of the column, respectively. The two extractions were performed in a sequence starting with artificial rainwater (see section 2.1.3) followed by EDTA (0.5 M NH_4Ac+0.02 M EDTA). 5g dry weight of soil from each of the three segments were individually mixed with 40 mL artificial rain. After 24 hours, the soil samples were shaken for 1 hour, centrifuged, and total Cr and Ni concentrations analyzed with ICP-MS (Perkin Elmer ELAN 6100). This extraction was followed by an EDTA extraction mixing the same soil samples with 40 mL EDTA, shaken for 1 hour after 24 hours, centrifuged and analyzed with ICP-MS (Perkin Elmer ELAN 6100). The detection levels were 0.06 μgL^{-1} and 0.04 μgL^{-1} for Cr and Ni, respectively.

3 Results and discussion - metal release studies in parallel field and laboratory exposures

In the following sections, quantitative results from the four-year urban field exposure, i.e. release rates of Cr, Ni and Fe from stainless steels (grades 304 and 316), chemical speciation modeling of released metals, and ecotoxic effects of metal runoff water are presented and discussed. All results relate to the immediate release situation of runoff water that leaves planar surfaces exposed at 45° from the horizontal, facing south. Results from laboratory investigations are presented to illustrate the effects of individual rain parameters on the release rates and the differences in metal release rates from alloys and pure metals.

3.1 Comparison of released quantities of Cr and Ni from as-received stainless steel grades 304 and 316 in individual sampling periods during the first year of urban field exposure

Outdoor rain events show large differences in rain intensity and duration. In addition, the pH and rain composition as well as the length of time between rain events can vary significantly over a given period of time. Field data during the first year of exposure comprise 17 different sampling periods characterized by varying rain conditions and number of rain events. These sampling periods can be used to make comparisons between the 304 and the 316 stainless steels. Annual metal release rates are determined as the sum of the released quantity during each sampling period and normalized in relation to the exposed surface area. In Fig.13, the released Cr and Ni quantities are shown for each sampling period together with the corresponding rain quantity for the 304 (upper curve) and 316 grades (lower curve), respectively. No distinct pattern related to the rain quantity can be discerned for any of the panels. For some sampling periods of equal rain quantity, the Cr release is higher than the Ni release, whereas for other episodes the opposite is seen. The released Cr quantity varied during the different sampling periods from less than 0.5 $ngcm^{-2}$ (the Cr detection limit) to 3 $ngcm^{-2}$ (<0.5-1.6 μgL^{-1}) and from less than 0.5 to 5 $ngcm^{-2}$ (<0.5-2.2 μgL^{-1}) for the 304 and the 316 grades, respectively. Correspondingly, the released Ni quantity varied from less than 0.1 $ngcm^{-2}$ (the Ni detection limit) to 12 $ngcm^{-2}$ (<0.1-3.5 μgL^{-1}) and from 0.5 to 31 $ngcm^{-2}$ (0.2-11 μgL^{-1}) for 304 and 316, respectively. To give some perspective to these concentrations, WHO recommendations for drinking water state that Cr and Ni concentrations should not exceed 50 μgL^{-1} and 20 μgL^{-1}, respectively. Median concentrations of total Cr and total Ni in potable water in the city of Stockholm are 0.8 μgL^{-1} and 7.1 μgL^{-1}, respectively [(Avesta 1999)].
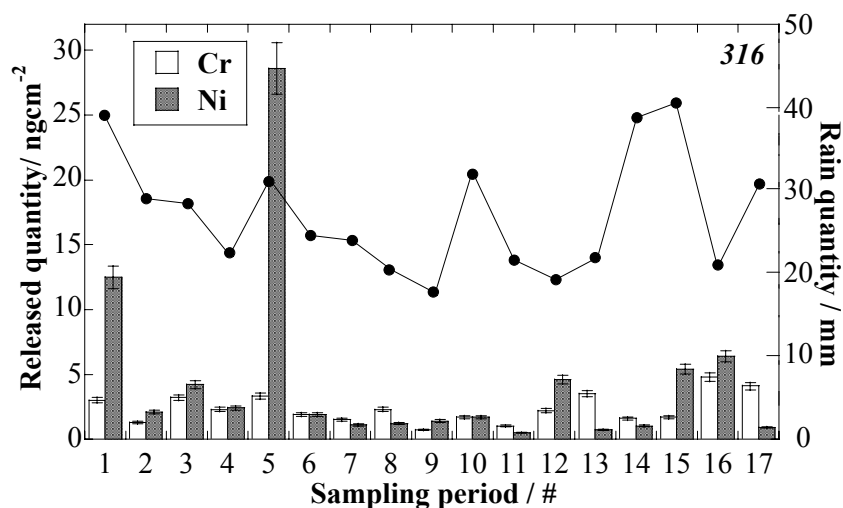

Fig. 13   Released Cr and Ni quantities and corresponding collected rain intensities during each sampling period in the first year of exposure of 304-stainless steel (upper curve) and 316 stainless steel (lower curve), respectively

The figure shows that the releases of Cr and Ni during most sampling periods were significantly higher from 316 compared to 304. This may be surprising since it is generally believed that the corrosion resistance of 316 is superior to that of 304. The 316 grade is primarily designed for chloride-rich environments, whereas the performance in low-chloride atmospheres may not fully utilize the addition of molybdenum (Mo). Higher release rates of Ni and Cr from the 316 stainless steel compared to the 304 stainless steel are clearly discerned in Fig.14, which shows the annual release rates calculated by adding the data of

each individual sampling period. The data are representative for a precipitation volume of approximately 600 mm (see Table V) impinging on panels inclined 45° from the horizontal, facing south. The yearly release rates (first year of exposure) from the grade 304 stainless steel are in the range 0.25-0.3 mgm^{-2} and 0.3-0.4 mgm^{-2} for Cr and Ni, respectively. Corresponding values for grade 316 stainless steel are 0.35-0.4 mgm^{-2} and 0.7-0.8 mgm^{-2} for Cr and Ni, respectively. No measurements of released Fe were made during the first year of exposure. To provide some perspective on these data, the annual contribution of Cr and Ni from non-polluted rainwater in Sweden is estimated to approximately 0.05 mgm^{-2} and 0.08 mgm^{-2} of land/surface area, respectively [(Walterson 1999)].
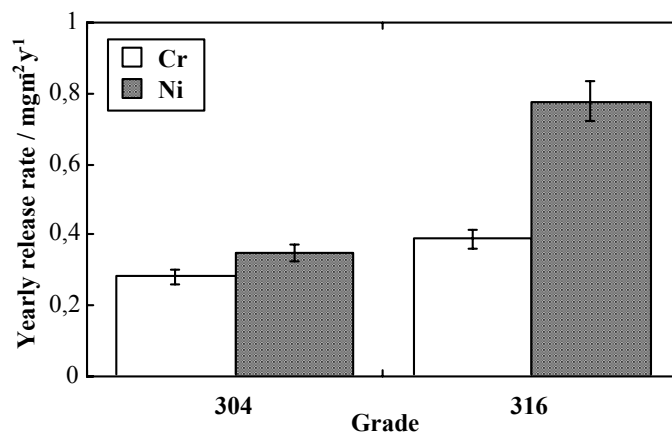

Fig. 14   Annual release rates of Cr and Ni from 304 and 316 stainless steels based on the first year of the four-year urban field exposure. Each column represents the accumulated release rate from each individual sampling period. The error bars originate from the uncertainty introduced since many concentrations were below the detection limit and, hence, may be anything between zero and a value close to the detection limit

3.2   Annual release rates of Cr, Ni and Fe from as-received stainless steel grades 304 and 316 during four years of urban field exposure

Due to passive film formation, stainless steels possess corrosion resistant properties in many liquid and gaseous environments. Other surface conditions, besides passive film properties, may also influence the corrosion resistance. Previous investigations have shown corrosion resistance to increase with increased surface smoothness [(Johnston and Pavlik 1982)]. In order to mimic realistic conditions as closely as possible, the results from this field exposure aim to reflect the situation of stainless steel with a surface finish (2B) recommended by the manufacturer to be used for roofs and facades (see 2.1.1). As a result of the high corrosion resistance of stainless steels, it must be emphasized that the released quantities of Cr and Ni are orders of magnitude lower than for other roofing materials such as Cu and Zn.

It should also be emphasized at this point that the data presented can not be used directly for environmental risk assessments. Firstly, they represent the total quantities of Cr, Ni and Fe released from stainless steels, without considering the chemical speciation or the bioavailability of each metal. Secondly, the exposure situation from which the data are generated represents a worst-case scenario. Release rates from buildings or other outdoor constructions, in which the effect of orientation, inclination or degree of building sheltering have to be integrated, are in general lower than from the present standardized exposure situation [(Odnevall Wallinder, Verbiest et al. 2000)]. However, the complex geometry of a building has shown certain areas, e.g. eaves, to corrode more severely than roofs [(Tochihara, Ujiro et al. 1996)].

Annual metal release rates were calculated based on the sum of individual sampling periods (typically 20) during each year of exposure and normalized relative to the exposed area. As a result of the limited release of Cr and Ni from the stainless steel samples, concentrations in the order of μgL^{-1} were detected in the runoff water, Fig. 15. Results from each sampling period are compiled for each element and year of exposure in box-plots for grades 304 (upper figure) and 316 (lower figure), respectively. The detection limit has been used as input for concentrations below this limit. 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.
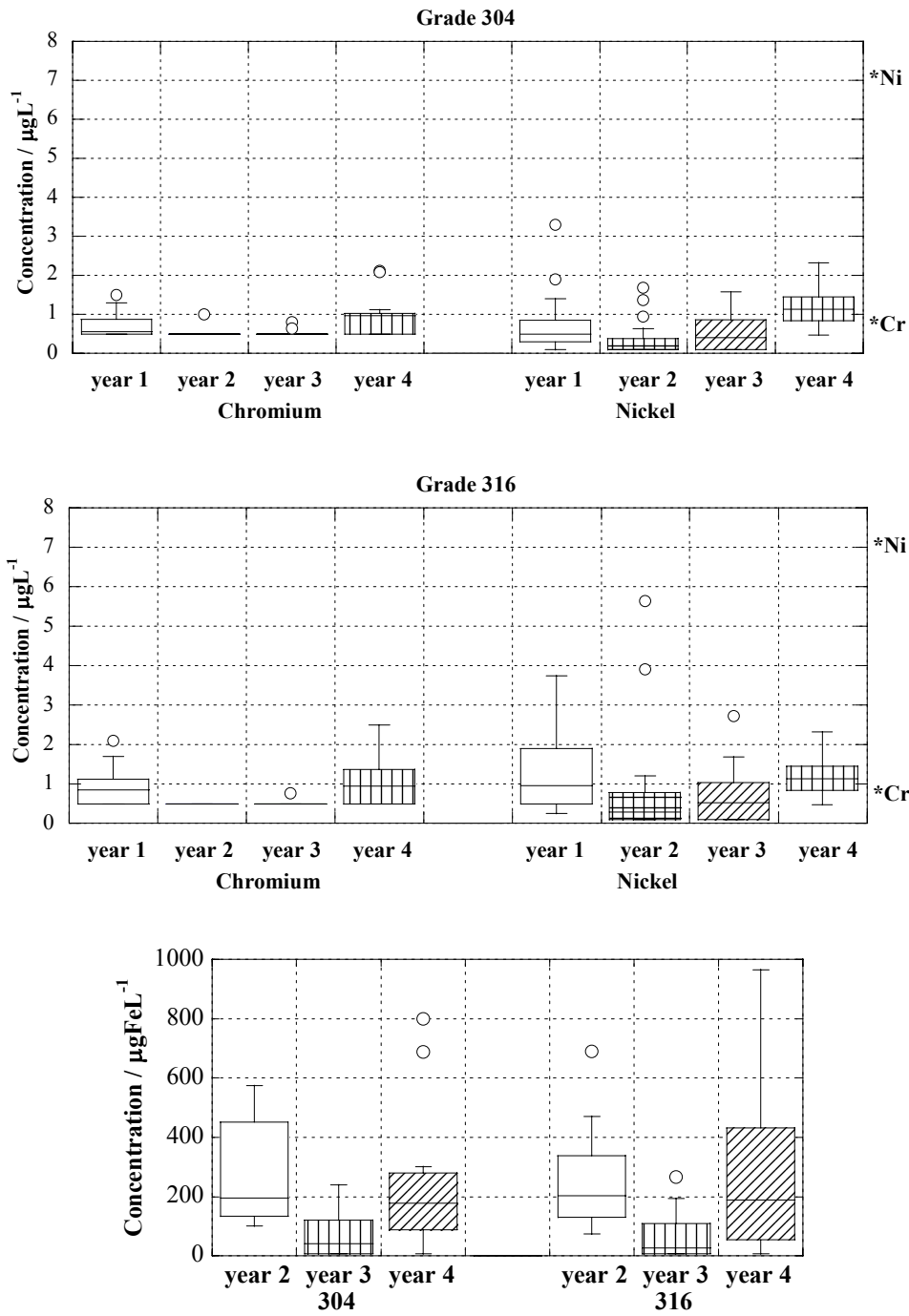
Fig. 15 *Released Cr, Ni (top and middle figures) and Fe (lower figure) concentrations during the four-year urban field exposure of 304-stainless steel and 316 stainless steel, respectively. For comparison, the asterisks for Cr and Ni mark median concentrations of Cr and Ni in potable water in the city of Stockholm*

The figures show that Cr and Ni concentrations measured in runoff water from stainless steel are comparable or lower than corresponding median values in potable water of Stockholm (0.8 µgCrL[-1] and 7.1 µgNiL[-1]) [(Avesta 1999)] and considerably lower than WHO recommendations for drinking water (<50 µgCrL[-1] and <20 µgNiL[-1]). The WHO drinking water recommendation for Fe is <100 µgFeL[-1] [(Huebers 1991)]. The results from the second, third and fourth years of exposure are consistent with those obtained during detailed investigations of the metal release rate and concentration of Cr and Ni during each sampling period during the first year of exposure, see section 3.1 and ref. [(Odnevall Wallinder, Lu et al. 2002)]. No distinct pattern between the rain quantity and metal release could be seen. Some sampling periods of equal rain quantity showed higher Cr release than Ni release, and the opposite was found for other periods. However, most sampling periods show somewhat higher concentrations of Cr and Ni from 316 compared to 304. Similar observations were made when

investigating the effect of rain pH and intensity on as-received and abraded samples [(Odnevall Wallinder, Lu et al. 2002)]. Concentrations below the detection limits (0.5 μgCrL^{-1}, 0.1 μgNiL^{-1}) were recorded in 64% and 68% of all sampling periods for Cr and in 34% and 20% of all sampling periods for Ni in runoff water from 304 and 316, respectively. Annual metal release rates were therefore calculated as intervals including both zero distribution for all sampling periods and the detection limit for all sampling periods with metal concentrations below the detection limit. All calculations also take into account an error of 7% in the analysis of metal concentration. Calculated annual metal release rates are compiled in Table VI and graphically illustrated in Fig. 16 for Cr and Ni from 304 (upper figure) and 316 (lower figure) and in Fig. 17 for Fe. The release of Fe was only measured during the second, third and fourth years of exposure.

Table VI   Annual metal release rates in mgm^{-2}year^{-1} of Cr, Ni and Fe during each year of the four-year urban field exposure

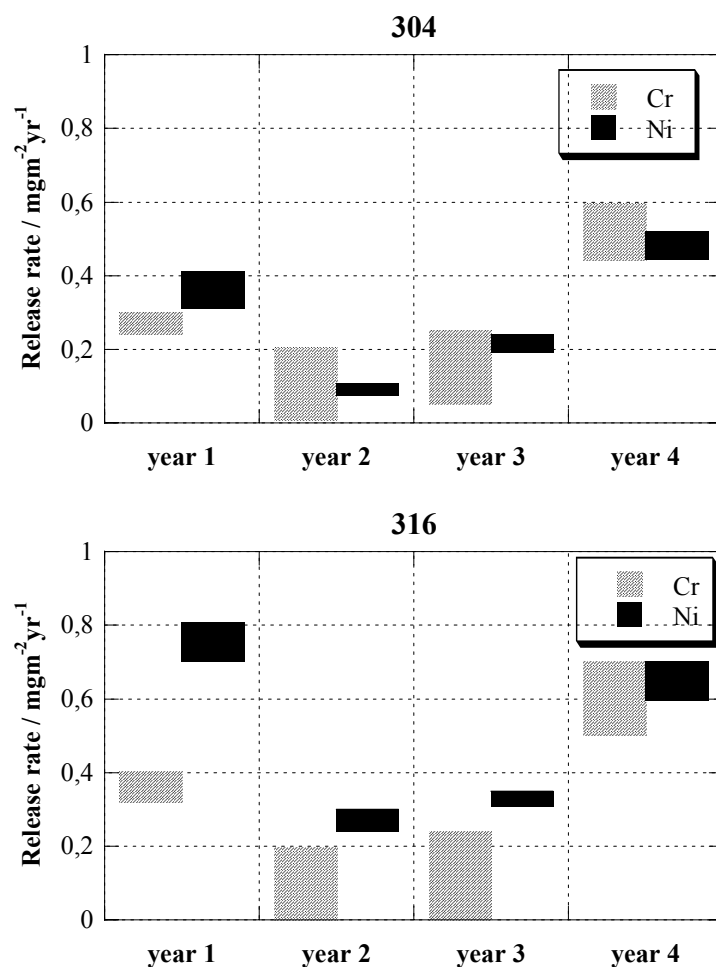| Exposure period	304			316		
	Cr / mgm^{-2}	Ni / mgm^{-2}	Fe / mgm^{-2}	Cr / mgm^{-2}	Ni / mgm^{-2}	Fe / mgm^{-2}
Year 1	0.25 - 0.3	0.3 - 0.4		0.35 - 0.4	0.7 - 0.8	
Year 2	0.0 - 0.2	0.1 - 0.12	44	0.0 - 0.2	0.25 - 0.3	45
Year 3	0.04 - 0.25	0.2 - 0.24	10	0.0 - 0.24	0.3 - 0.35	10
Year 4	0.45 - 0.6	0.45 - 0.5	140	0.5 - 0.7	0.6 - 0.7	200

Fig. 16   Annual metal release rates of Cr and Ni from stainless steel 304 (upper figure) and 316 (lower figure) during the four-year urban field exposure
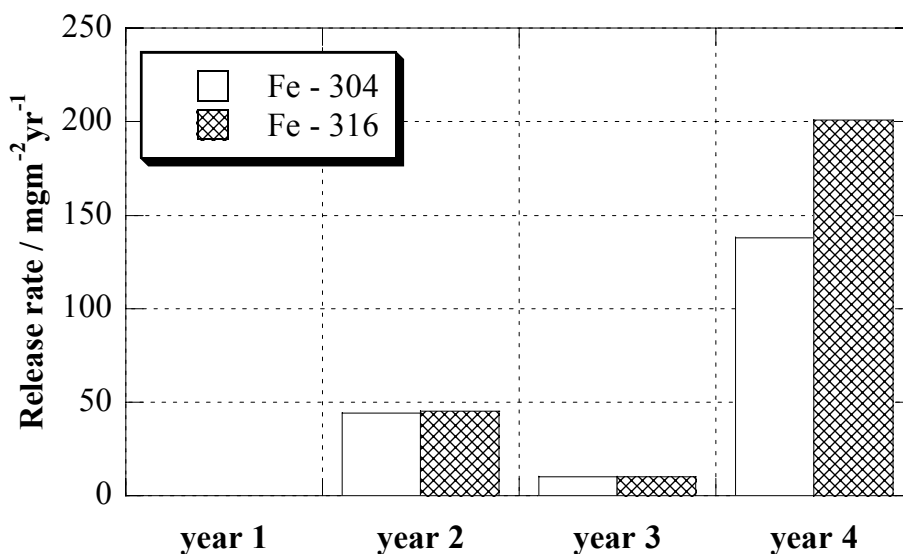
Fig. 17   Annual release rates of Fe from stainless steel 304 and 316 measured during the last three years of the four-year urban field exposure

The results show significantly higher release rates of Ni from 316 stainless steel compared to 304 for each individual year of exposure. Slightly higher rates of Cr from 316 than for 304 can be seen during the first and fourth year of exposure whereas the second and third years show similar release rates. For Fe, the release rates are comparable (2nd and 3rd year) or higher (4th year) from 316 compared to 304. In general, somewhat higher metal release rates can be seen during the first and the fourth year of exposure compared to the second and third year of exposure.

The passive film on stainless steel is believed to consist of an inner barrier oxide film enriched in Cr oxide and Fe oxides but with low Ni content, and an outer hydroxide film (mainly $Cr(OH)_3$) [(Wegrelius 1995)]. Ni is thought to be primarily enriched in the metal phase (alloy surface layer) below the passive film [(Wegrelius 1995)]. As a result of Cr enrichment in the passive film and Ni enrichment in the alloy surface layer, selective dissolution of Fe has been reported earlier during anodic dissolution and during passivation [(Olefjord, Brox et al. 1985; Olefjord and Wegrelius 1996)]. The presence of Ni and Fe in the alloy surface layer adjacent to the barrier layer suggests the presence of defects in the barrier layer, which facilitates transport of Ni and Fe through the film.

Similarities in release rates of Cr from grade 304 and 316 suggest no large differences with respect to Cr enrichment of their passive films. However, somewhat higher release rates of Ni from 316 than 304 suggest the presence of more defects in the passive film of the 316 samples used in the current study. Such defects facilitate higher Ni release.

Mass balance calculations of the dissolution of Cr, Ni and Fe from grades 304 and 316 stainless steel are presented in Table VII. The results from the second, third and fourth year show that Fe is predominantly released and that the release of Cr and Ni is considerably lower than the corresponding Cr/(Cr+Ni+Fe) ratio in the bulk alloy. This is in general agreement with previous investigations showing the dissolution kinetics of alloy constituents of stainless steel to be selective, with an enrichment of Cr in the surface film as a result [(Hultquist, Seo et al. 1987)]. A comparison between the release of Cr and Ni during each individual year of exposure shows Ni to be preferentially released compared to Cr, but still in different proportions from those of the bulk alloy composition. These results indicate that the metal release process proceeds non-uniformly in different areas of the Cr-enriched steel surface and that certain paths within the surface film near e.g. metallic inclusions, excess phases, or other defect rich regions of the surface film may act as possible areas of enhanced dissolution rates. Such paths have previously shown preferential dissolution of Fe, with Cr-enriched zones as a result [(Leygraf, Hultquist et al. 1979)]. As soon as such areas become active, the dissolution rate accelerates, which may cause variations from one sampling period to another.

Table VII   Mass balance calculations based on annual release rates of Cr, Ni and Fe from stainless steel grades 304 and 316, c.f. Table VI

Grade / exposure	Cr/(Cr+Ni)		Ni/(Cr+Ni)		Cr/(Fe+Cr+Ni)		Ni/(Fe+Cr+Ni)		Fe/(Fe+Cr+Ni)	
	bulk	%	bulk	%	bulk	%	bulk	%	bulk	%
304	67.8		32.2		18.3		8.7		73.0	
Year 1		36 - 45		55 - 64						
Year 2		2 - 60		40 - 98		0.005 - 0.41		0.18 - 0.27		99.3 - 99.8
Year 3		18 - 51		49 - 82		0.31 - 2.38		1.76 - 2.29		95.3 - 97.8
Year 4		50 - 53		48 - 50		0.32 - 0.41		0.32 - 0.37		99.2 - 99.4
316	61.1		38.9		17.2		10.9		71.9	
Year 1		27 - 34		66 - 73						
Year 2		1 - 38		62 - 99		0.007 - 0.40		0.62 - 0.66		98.9 - 99.4
Year 3		2 - 41		59 - 98		0.048 - 2.27		3.19 - 3.30		94.4 - 96.8
Year 4		45 - 49		50 - 55		0.25 - 0.33		0.31 - 0.33		99.3 - 99.4

Metal release results show that grade 316 is not superior to grade 304 in low-chloride, non-aggressive atmospheric environments. This is consistent with previous findings in which the electrochemical behavior of grade 304 in bulk rain water was compared with that of grade 316 (see section 3.5 and ref. [(Odnevall Wallinder, Lu et al. 2002)].

Differences in annual metal release rates from both grades (year 4 > year 1 > year 3 > year 2) could not be explained by differences in annual rainfall quantities (year 4 > year 3 > year 1 > year 2) (see Tables V and VI). A detailed description of the annual distribution of daily rain quantities and dry periods is given in Table VIII for each individual year during the four-year exposure.

Table VIII   Distribution of daily rain quantities and annual fraction of dry periods during each year of the four-year urban field exposure. Data are based on daily measurements of rain quantities at 6.00 am and 18.00 pm performed by the Swedish Meteorological and Hydrological Institute

Exposure period	0 – 1 mm %	1 – 5 mm %	5 – 10 mm %	10 – 20 mm %	> 20 mm %	Dry period %
Year 1	26.5	13.5	6.4	0.3	--	54
Year 2	17.2	8.6	3.0	1.2	0.1	70
Year 3	20.6	11.2	4.7	0.8	--	63
Year 4	16.2	11.9	4.1	1.7	0.3	66

Tabulated data (Table VIII) show that most daily rainfall is of low quantity, 0-1 mm, resulting in a volume that is usually insufficient for washing corrosive species, e.g. gaseous and/or particulate pollutants, completely from the surface. Days of higher rain quantity (>5 mm) are less than 7% of the total number of days over a year. No trend can be seen, suggesting that the distribution of the daily rain quantity during different years cannot explain variations in annual metal release rates. However, when examining daily rainfall quantities (unfortunately without information of the rainfall intensity or duration) during individual sampling periods of the four-year exposure period, it is clear that periods of frequent rainfall of low quantity result, in most cases, in relatively high concentrations of Cr and Ni in the runoff water, whereas relatively low concentrations of Cr and Ni are seen after e.g. most sampling periods characterized by several rain events of high rain quantity (volume), see Fig. 18.
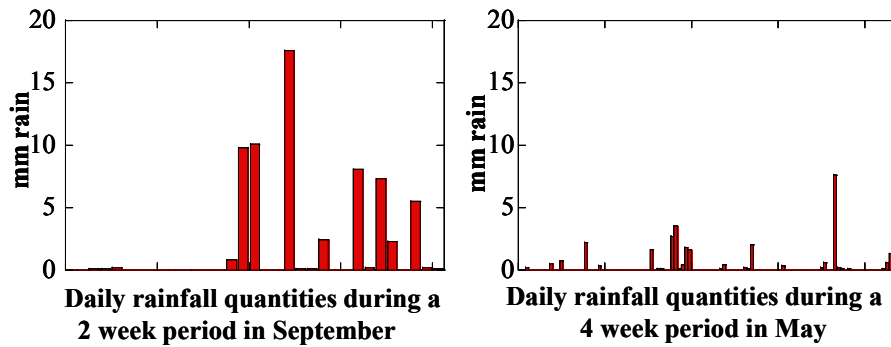
Fig. 18   *Examples of sampling periods that result in low (left figure) and high (right figure) concentrations of released Cr and Ni in the runoff water*

Hence, the higher Cr and Ni release rates are most likely caused by more regularly wet surfaces, induced by small amounts of rain at frequent intervals, persistent high humidity, fog etc. Together with corrosive deposits, e.g. dry and wet deposited pollutants, this results in a potentially more corrosive environment, since inadequate washing of the surface will occur. On the other hand, the occurrence of large rainfall volumes will wash corrosive deposits from the surface, hence reducing corrosive conditions. Temperature may also influence the corrosive conditions since evaporation of surface water occurs faster at higher temperatures. It is hence common practice that stainless steel used in outdoor constructions is regularly cleaned in order to preserve its appearance and to provide maximum corrosion resistance [(NiDI 2002)]. The frequency of cleaning depends on e.g. aesthetic requirements, the severity of the environment, the stainless steel grade and surface finish, the design, and on the rain characteristics.

3.3   Bioavailability, chemical speciation and ecotoxicity testing of metal runoff water representative of the immediate roof situation

The potential environmental effects of both Cr and Ni are strongly dependent on chemical speciation since the bioavailability of Cr and Ni is different for different species. It is hence essential to determine chemical speciation in addition to total concentrations. The most common bioavailable form of Ni in aqueous media is the free hydrated Ni(II) ion (see section 1.2). For Cr, Cr(III) is not considered to be ecotoxic due to its high complexation tendency, whereas Cr(VI) is regarded as the most toxic form of Cr. As a result of complexation with natural organic matter and inorganic constituents of the environment, the fraction of bioavailable Ni and Cr will decrease after release from a roof and during interaction with the environment.

The pH of rainwater impinging the panel surfaces was measured during the four-year exposure as well as the pH of runoff water from both stainless steel grades. The results are compiled in Fig. 19 and show a range of precipitation pH between 4.1 and 5.6 (median 4.8) and a range of runoff water pH between 3.8 and 6.4 (median 5.0) and 4.2 and 6.5 (median 5.2) from grades 304 and 316, respectively.
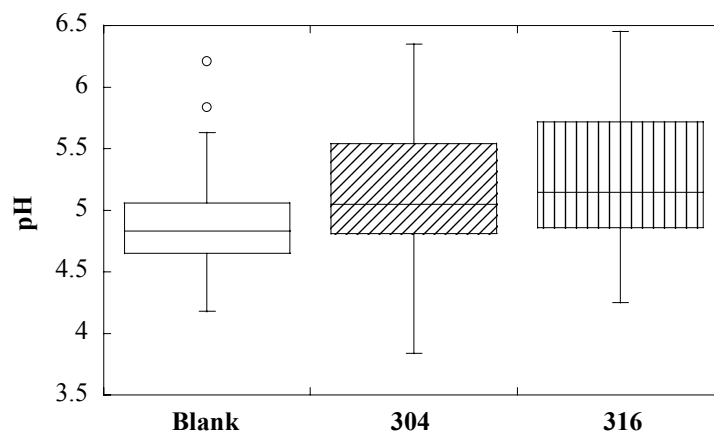

Fig. 19   *Variation in pH during sampling of rainwater from an inert surface (representing pH of natural precipitation) and of runoff water from 304 and 316 stainless steel during the four-year field exposure. Each box comprises the inner 50% of the data close to the median (shown as a line). The lines 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*

The small difference in pH between rainwater and runoff water from the stainless steel samples suggests a relatively low buffering capacity of species released from the surface film on stainless steel.

Computer modeling, using the water-ligand model MinteqA2, was performed in order to predict the chemical speciation of Cr and Ni in the runoff water. The release of Fe was not considered in the calculations since no measurements of Fe release rates were performed during the first year of exposure. However, when allowing for a concentration of Fe (both Fe(II) and Fe(III)) between 70 and 700 μgL^{-1} (representative for runoff water during the 2nd and 4th years of exposure) no effect on the chemical speciation of Cr and Ni could be seen in the model calculations. Input data for the model were the total Cr and Ni concentrations, the concentrations of sulfate and chloride and the alkalinity of the runoff water measured for three different sampling periods during the four-year exposure period. The data are compiled in Table IX. In the computer modeling, the temperature was assumed to be 22 ºC, based on the temperature at which all ecotoxicity tests were performed rather than on the actual outdoor temperature. No consideration was taken of the possible organic content of the runoff water since this was assumed to be negligible immediately after release from the stainless steel surface.

Table IX   Chemical characterization of runoff water from the sampling periods in October 1998, June 1999 and October 2000

Sampling period	Grade 304			Grade 316		
	Oct. 1998	June 1999	Oct. 2000	Oct. 1998	June 1999	Oct. 2000
Total chromium (μgL^{-1})	< 0.5	1.0	< 0.5	0.74	2.1	< 0.5
Total nickel (μgL^{-1})	0.3	< 0.1	< 0.1	0.62	0.5	0.4
pH	5.4	4.6	4.6	5.3	4.8	4.8
Chloride (mg $Cl^- L^{-1}$)	1	< DL	1	1	1	< DL
Sulfate (mg $SO_4^{2-} L^{-1}$)	8	12	7	13	6	6
Alkalinity (mgL^{-1} as $CaCO_3$)	4	4	4	2	2	4

< DL: below detection limit

During modeling calculations, it was assumed that all Cr was present as Cr(III) without any contribution from Cr(VI). The results show that, for all sampling periods, the majority of Ni (>99%) was present as the $Ni(H_2O)_6^{2+}$ in runoff water from both grades 304 and 316. A small fraction was found to be present as $NiSO_4$ (aq). For Cr, more than 98.5% was calculated to be present as the free Cr(III)-ion and the remaining fraction as $Cr(OH)^{2+}$. The assumption of the presence of small amounts of organic matter in the runoff water (0.1 mg humic $acidL^{-1}$ + 0.1 mg fulvic $acidL^{-1}$) showed a reduction of the free Ni ion concentration by a few percent and a total reduction of the Cr(III) concentration due to complexation. This illustrates the capacity of organic matter to form complexes with metals, hence affecting the potential ecotoxicity. It should be noted that even though Fe is present in the runoff water in much higher concentrations than Ni and Cr, the latter two metals have much faster complexing capacity for organic matter [(McBride 1994)].

Standard algal species ecotoxicity tests were performed to determine the acute ecotoxicity of the runoff water. Data, expressed as $72h\text{-}EbC_{50}$ values, are presented in Table X together with the corresponding Toxic Unit values (T.U.), the total concentration of Cr and Ni and the effect concentration, expressed as the concentration of Cr and Ni causing 50% algal growth inhibition ($72h\text{-}EbC50$ (μg $Cr+NiL^{-1}$)). The $72h\text{-}EbC_{50}$ value decreases with increasing ecotoxicity of the runoff water and vice versa for the T.U. value. A T.U. value below 1, or a $72h\text{-}E_bC_{50}$ value above 1000 mLL^{-1} is considered not acutely toxic. The results show that some samples of the runoff water, sampled directly after release from the stainless steel surfaces, to be slightly toxic for the algae *P. subcapitata*, with $72h\text{-}EbC_{50}$ values ranging from 625 to >1000 mLL^{-1} (<1 to 1.6 T.U.) and from 204 to 770 mLL^{-1} (1.3 to 5 T.U.) for grade 304 and 316, respectively. It should be noted that slightly toxic responses also were observed from the blank surface. These anomalies are discussed further below, and need to be evaluated further.

72h-EbC$_{50}$ values reported as higher than 1000 mLL^{-1} (<1 T.U.) are extrapolated values, with the effect concentration outside the concentration range. Please note that the EC$_{50}$ value increases with decreasing toxicity, *i.e.* a higher concentration is needed to produce the same toxic effect.

Table X   Total Cr and Ni concentration and 72h-EbC$_{50}$ values (in µgL^{-1}, Toxic Units and actual effect concentrations) for runoff water from 304 and 316 stainless steel collected during three sampling periods during the first two years of the four-year exposure

Sampling period	Grade 304			Grade 316			Blank Plexiglas surface		
	Oct. 1998	June 1999	Oct. 2000	Oct. 1998	June 1999	Oct. 2000	Oct. 1998	June 1999	Oct. 2000
Total Cr+Ni (µgL^{-1})	0.3 – 0.8	1.0 – 1.1	0.0 – 0.6	1.36	2.6	0.4 – 0.9			
72h-Ebc$_{50}$ (mLL^{-1})	972	625	> 1000	396	770	204	> 1000	668	520
72h-Ebc$_{50}$ (Toxic Units)	1.0	1.6	< 1	2.5	1.3	5.0	< 1	1.5	2.0
72h-Ebc$_{50}$ (µg(Cr+Ni)L^{-1})	0.3 – 0.8	0.6 – 0.7	< 0.6	0.5	2.0	0.1 – 0.2			

The actual effect concentration causing 50% inhibition ranges between 0.1 and 2 µg total Cr+NiL^{-1} for all three sampling periods. Table XI presents the results of reference toxicity tests with NiCl$_2$.6H$_2$O and K$_2$Cr$_2$O$_7$.

Table XI   Toxicity of Ni and Cr for the green algae P. subcapitata

	K$_2$Cr$_2$O$_7$ µgL^{-1} Cr(VI)	NiCl$_2$.6H$_2$O µgL^{-1} Ni(II)	
	pH 7.8	pH 6.5	pH 7.5
72h-EbC$_{50}$ for P. subcapitata	396	192	90

Reference tests using K$_2$Cr$_2$O$_7$ (Cr(VI)) as toxicant resulted in a 72h-EbC$_{50}$ of approximately 400 µgL^{-1}, which is almost 1000 times higher than measured metal concentrations in the runoff water samples. However, it should be noted that Cr in runoff water is present as Cr(III) not Cr(VI). No tests were performed with any Cr(III)-compound.

The release concentrations of Cr, Ni and Fe at the immediate situation when the runoff water leaves the surface vary in the range of <0.5-2.5 µgCrL^{-1}, <0.1-11 µgNiL^{-1}, and <8-700 µgFeL^{-1}, respectively. These values are far below reported ecotoxic concentrations (species-dependent) of Cr (32-118 000 µgL^{-1}), Ni (50-11 000 µgL^{-1}), and Fe (10,000-200,000 µgL^{-1}). [(Gauglhofer and Bianchi 1991; Sunderman and Oskarsson 1991)]. Thus, it can be expected that the observed slight toxic effects of the runoff water towards *P. subcapitata* cannot be caused by the presence of the low concentrations of Ni and Cr in runoff water. The reason for the slight toxicity cannot be explained but may be caused by some other physico-chemical component that was not measured. However, any ecotoxic effect of Cr, Ni and Fe released from the stainless steel samples can be excluded.

The sensitivity to Cr and Ni of (aquatic) organisms is clearly species-dependent. Toxic effects have been observed at concentrations as low as 32 µg CrL^{-1} for algae but rise to 118 mg CrL^{-1} for fish. For Ni, similar variations have been reported ranging from 50 µg NiL^{-1} for rainbow trout up to 11 mgL^{-1} for Fowler´s toad [(Gauglhofer and Bianchi 1991; Sunderman and Oskarsson 1991)]. Since Cr and Ni concentrations in the runoff water are far below reported concentrations causing ecotoxic effects, it can be expected that observed toxicity effects towards *P. subcapitata* in the runoff water are not due to Ni and Cr. Fe is considered to be a metal of low ecotoxicity but very little information is available on the toxic effects of Fe on aquatic microorganisms. Fe concentrations ranging from 10 to 200 mgL^{-1} have been found to be ecotoxic to plants [(Huebers 1991)]. The concentration of Fe in runoff water (<0.008-0.7 mgL^{-1}) is far below these reported ecotoxic concentrations.

It should be noted that several factors may alter the chemical speciation during a standard algal test: the dilution of the runoff water, the presence of Fe, the presence of metal-complexing components (i.e. EDTA) in the ISO medium [(ISO 1989)], an increase of pH during the test period as a result of CO$_2$ consumption, and the presence of algal cells that produce, e.g. exudates and other organic components [(Landner and Lindeström 1999)]. The present results should therefore be used with caution. In addition, since the ecotoxicity tests were conducted on runoff water samples collected immediately after being released from the roof surface, they *do not reflect the real exposure of environmental organisms*. Factors such as dilution

effects, changes in chemical speciation and bioavailability during environmental entry as well as the type and sensitivity of the receiving ecosystem (see section 4) should also be taken into consideration.

3.4 Rain parameters affecting the concentration of released Cr and Ni in runoff water from as-received and abraded 304 and 316 stainless steel - a laboratory investigation

The results from the field exposure showed relatively large variations in Cr and Ni release at a given rain quantity for both stainless steel grades and a somewhat higher release rate from grade 316 compared to grade 304. Furthermore, the proportion of release rates of Cr and Ni differs significantly from the corresponding bulk ratio. In order to explore variations in outdoor release rates and their possible dependence on rain intensity and rain pH, further investigations were performed in the laboratory with artificial rain under well-defined exposure conditions. Initial laboratory exposures were performed on as-received panels to facilitate comparisons between field and laboratory results.

3.4.1 Release of Cr and Ni as a result of various rain intensities at constant rain pH

The effect of rain intensity on Cr and Ni release rates from as-received panel surfaces is presented in Fig. 20 as stack column plots for 304 (upper figure) and 316 (lower figure) stainless steel. The results of a number of single rain events of pH 4.3 with intensities between 4 and 40 mmh^{-1} are shown in the figure. Each bar shows the individual release rate of Cr and Ni and the height of each bar represents the sum of both metals.
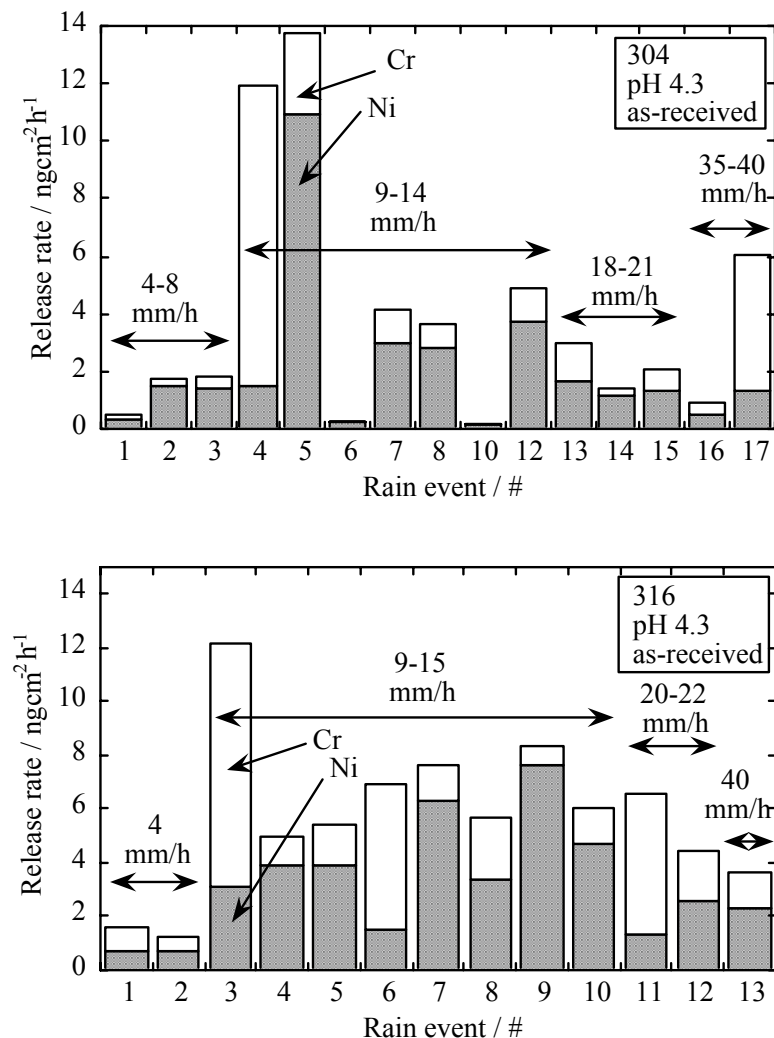
Fig. 20   *Release rates of Cr and Ni from as-received 304 (upper figure) and 316 (lower figure) stainless steel during single exposure events to artificial rain with pH 4.3 and varying intensity. Filled bars represent Ni and unfilled bars Cr*

No obvious relation between released Cr and Ni rates and rain intensity can be discerned for as-received panels. Each individual rain event shows that the release rate of Ni is sometimes faster than the Cr release rate and sometimes slower, in agreement with the field data. Most rain events also show the sum of Ni and Cr release rates to be faster from 316 than from 304 stainless steel. These trends are more clearly seen in Fig. 21 where all intensity data have been compiled into box-plots for both steel grades. 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 release rate span of the box. Outliers are displayed as individual points.

Except for a few outliers, the figure shows a tendency for Cr and Ni release rates to be somewhat faster from grade 316 compared to grade 304, and the Ni release rate to be somewhat faster than that of Cr for both grades. This is in general agreement with the field data. The median values for release rates of Cr are 0.8 ngcm^{-2}h^{-1} (304) and 1.4 ngcm^{-2}h^{-1} (316), and of Ni 1.4 ngcm^{-2}h^{-1} (304) and 3.1 ngcm^{-2}h^{-1} (316), respectively.
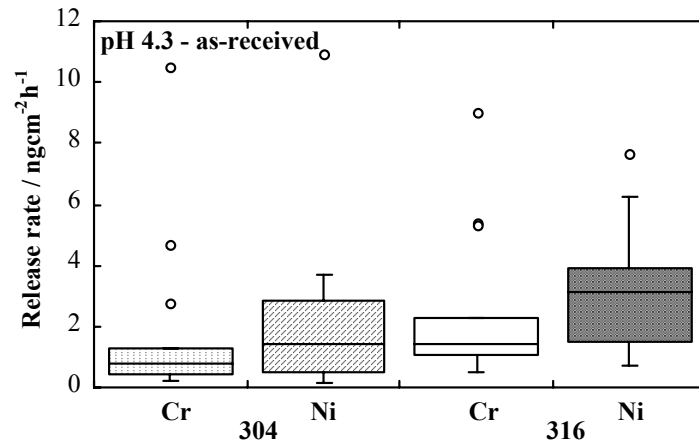
Fig. 21   Box-plot showing release rates of Cr and Ni from as-received 304 and 316 stainless steel exposed to artificial rain with pH 4.3 and varying intensity. Each box comprises the inner 50% of the data close to the median (shown as a line). The lines extending from the top and the bottom of each box mark the minimum and maximum values that fall within the median value ± 1.5 times the release rate span of the box. Outliers are displayed as individual points

The relatively large variation in release rates at similar rain intensities suggests that the extent of Cr and Ni release could depend largely on variations in the surface conditions of as-received panels. This may indicate that the dissolution of Cr and Ni proceeds non-uniformly on different areas of the steel surface. As soon as an area becomes active, the dissolution rate accelerates and this may cause variations from one rain event to another. In order to obtain a possibly more well-defined panel surface in terms of oxide layer properties, both steels were manually abraded (down to 1200 P SiC) for further laboratory investigations. Besides removing the oxide layer of as-received panels, this procedure also introduces more defects in the surface region. As previously mentioned, the surface condition may significantly influence corrosion resistance resulting in reduced corrosion resistance and increased release rates with increasing surface roughness [(Johnston and Pavlik 1982), (Wallinder, Pan et al. 1999), (Kearns, Johnson et al. 1988)]. Figure 22 compares the behavior of as-received and abraded 304 stainless steel exposed to a rain event of pH 4.3 at an intensity of 10 mmh^{-1}.
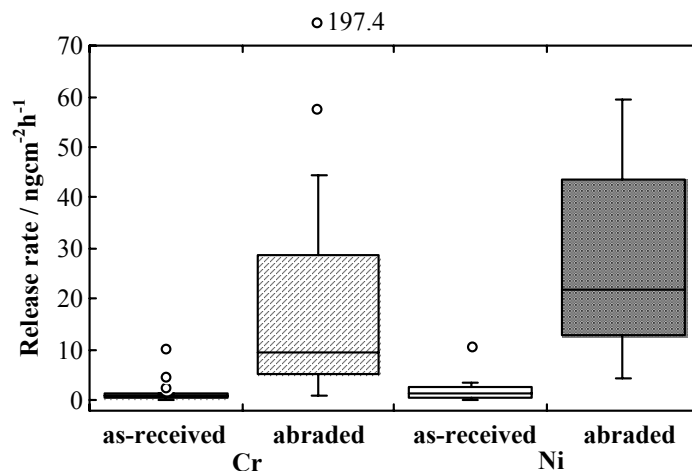

Fig.22   Box-plot showing the release rate of Cr and Ni from as-received and abraded (1200 P SiC) 304-stainless steel during artificial rain events of pH 4.3 and approximately 10 mmh^{-1}

The figure shows that as-received panels exhibit lower Cr and Ni release rates than abraded panels. Complementary XPS analyses revealed a more Cr-enriched passive film on as-received than abraded panels, Fig. 23. No Ni was detected in the top surface layer. A faster Cr-enrichment of the passive film formed on the abraded panel was also observed upon rain exposure, as compared to the as-received panel, Fig. 23. These results are in accordance with earlier conclusions that, in general, the corrosion resistance increases with Cr content of the passive film [(Wallinder, Pan et al. 1999)].
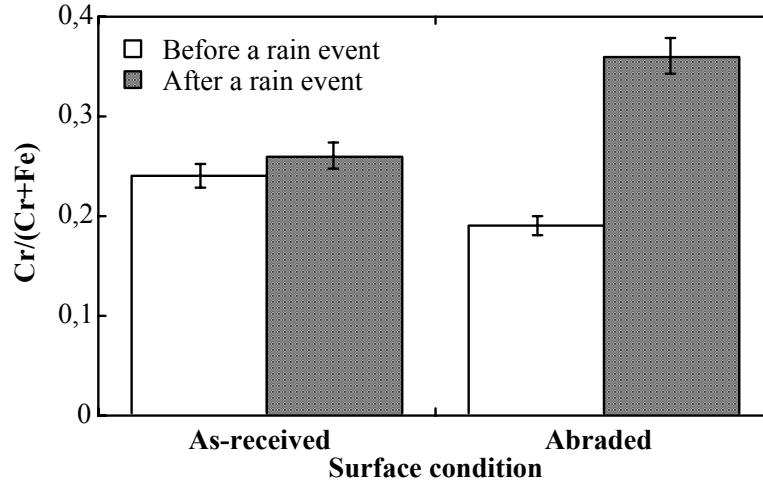
Fig. 23   Surface enrichment of Cr, as $Cr_{tot}/(Cr_{tot}+Fe_{tot})$, of as-received and abraded grade 304, before and after 4 hours of artificial rain of pH 4.3 and 10 mmh^{-1}

From this follows an expected reduction in Cr and Ni release rates. Similar behavior was observed for the 316 stainless steel.

Because the surface condition has a large influence on the Cr and Ni release rates, abraded panels of 304 were used to investigate whether the rain intensity could influence the metal release rate from this type of surface condition. As seen in Fig. 24, the Cr and Ni release rates from abraded 304 stainless steel, like those for the as-received surface condition (Fig. 20), seem to be largely independent of rain intensity. Similar results were obtained for as-received 316 stainless steel (Fig. 20). No investigation was made on the effect of intensity on abraded surfaces of grade 316. The data shown in Fig. 24 furthermore suggest the Ni release rate from abraded panels to be faster than the Cr release rate for different rain intensities, in agreement with findings for as-received panels.
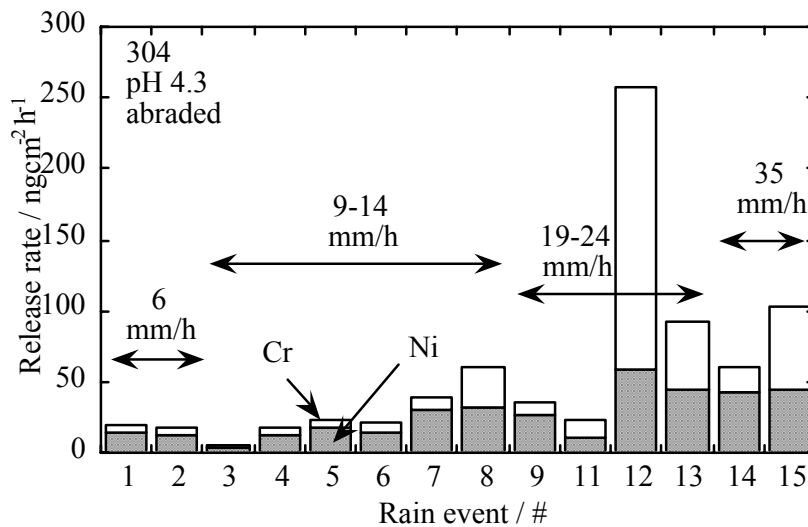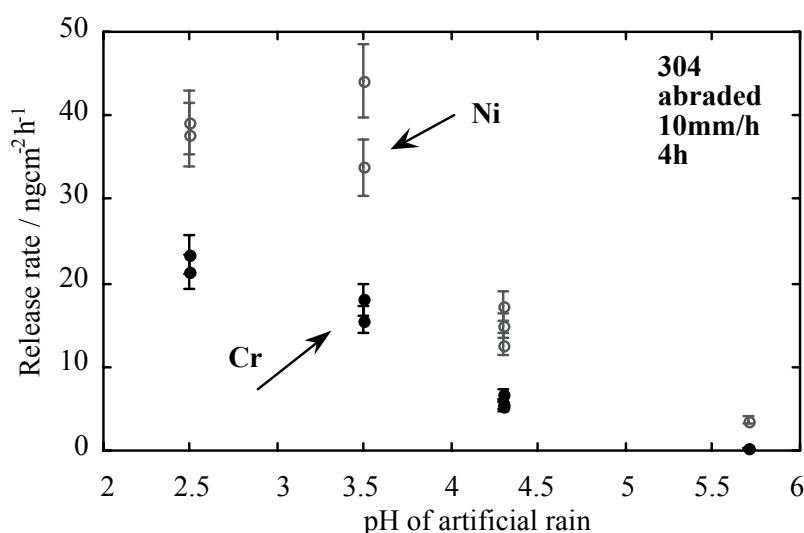

Fig. 24   Release rates of Cr and Ni from abraded 304 stainless steel during single artificial rain events of pH 4.3 and varying intensity

3.4.2 Release of Cr and Ni as a result of variations in rain pH at constant rain intensity

Having established that rain intensity under present conditions has no direct influence on release rate of Cr and Ni, the effect of rain pH on release rate was investigated. The results from abraded 304 stainless steel are displayed in Fig. 25. The investigation was performed at a fixed rain intensity of 10 mmh^{-1} impinging the panel surfaces during 4 hours of continuous artificial rain with pH varying from 2.5 to 5.7. It is evident that both Cr and Ni exhibit increasing release rates with decreasing pH, in agreement with previous findings [(Avesta 1999).]. Compared to the rate obtained at pH 4.3, the release rate of Cr is approximately 10 times lower at pH 5.7 and approximately three times higher at pH 3.5, and is further increased at pH 2.5.The release rate of Ni is 3-4 times lower at pH 5.7 and 2-3 times higher at pH 3.5. Again, the release rate of Ni is higher than that of Cr.

Fig. 25   Release rates of Cr and Ni from abraded 304 stainless steel during single artificial rain events of intensity 10 mmh^{-1} and varying pH

The Cr release rates at the lowest pH may be compared with previously reported absolute Cr dissolution rates from Fe18Cr and Fe18Cr3Mo single crystals in 0.5 M H_2SO_4 [(Leygraf, Hultquist et al. 1979)]. Under steady-state conditions in the passive potential range, Cr dissolution rates were measured ranging from around 5 to 50 ngcm^{-2}h^{-1}, in reasonably good agreement with the present results. The study indicated that the dissolution of Cr, Fe and Mo might proceed non-uniformly on different areas of the steel surface. Non-metallic inclusions and excess phases may be regarded as possible areas with enhanced dissolution rates. As soon as such areas become active, the dissolution rate accelerates and this may cause variations from one rain event to another. In all, variations in natural rain pH and in steel surface conditions, rather than variation in natural rain intensity, may explain differences in metal release rates between different rain episodes (Fig.13). However, other processes may also be responsible for or contribute to those differences. As has previously been shown to be the case for Cu and Zn, the length of dry and humid exposure periods combined with variations in the composition of dry and wet natural deposition of corrosive species may also have an effect on the metal release rate [(He 2000)].

3.5 Electrochemical behavior of 304 and 316 steel in bulk rainwater

Since grade 316 stainless steel is generally considered to have superior corrosion resistance to 304 stainless steel in most chloride rich environments [(Avesta 1999)], the corrosion resistance of the two steel grades was examined in bulk solution using artificial rain. The aim was to investigate whether the same corrosion behavior could be seen in relatively low-aggressive solutions of low chloride content (see section 2.1.3). Figure 26 illustrates the results for both the as-received and the abraded 304 and 316 stainless steel. The results are given as the mean values of triplicate measurements. It is clear that the corrosion potential is increased and the corrosion rate decreased for as-received panels compared to abraded panels as a result of thicker passive films. However, no significant difference can be seen in polarization resistance between the two grades, being approximately 1.0×10^5 Ωcm^{-2}, in each case. These results show that the corrosion resistance of grade 316 stainless steel is not superior to 304 stainless steel in low-aggressive solutions of low chloride content.
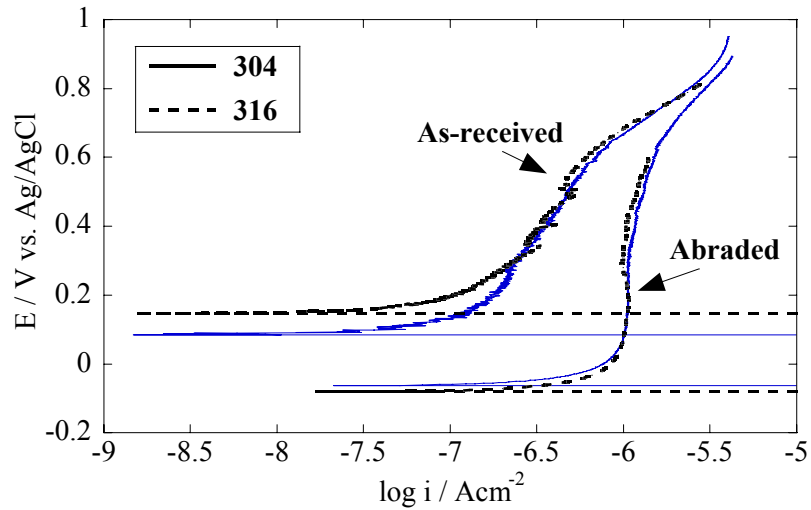
Fig. 26   Potentiodynamic polarization curves (obtained in artificial rain solution, scan rate 10 mVmin[-1]) typical for as received and abraded 304 (filled line) and 316 (dotted line) stainless steel

3.6   A comparison of metal release rates of Cr, Ni and Fe from alloys (stainless steel grades 304 and 316) and pure metals (Cr, Ni, Fe)

Previous sections have focused on the release of Cr, Ni and Fe from stainless steel alloys of two different grades (304 and 316). The results have shown the metal release rate into rainwater to be non-proportional to the corresponding metal content of the stainless steel and Fe to be preferentially released from the surface of both 304 and 316 stainless steels. Cr and Ni are also released from both grades, however at rates orders of magnitude lower than Fe (see Table VI). The primary aim of this part of the study was to show the difference in release rates of Cr, Ni and Fe between stainless steel alloys and pure metals under identical exposure conditions.

Results from this study for the stainless steels are consistent with previous findings showing somewhat higher release rates of Cr and Ni from as-received 316 compared to as-received 304 and significantly higher release rates of Fe for both 304 and 316, Fig. 27. Similar release rates of Fe were determined for 304 and 316, also in agreement with field data (Table VI). Abraded panels show the same tendency for the two grades but with significantly higher release rates, Fig. 28.
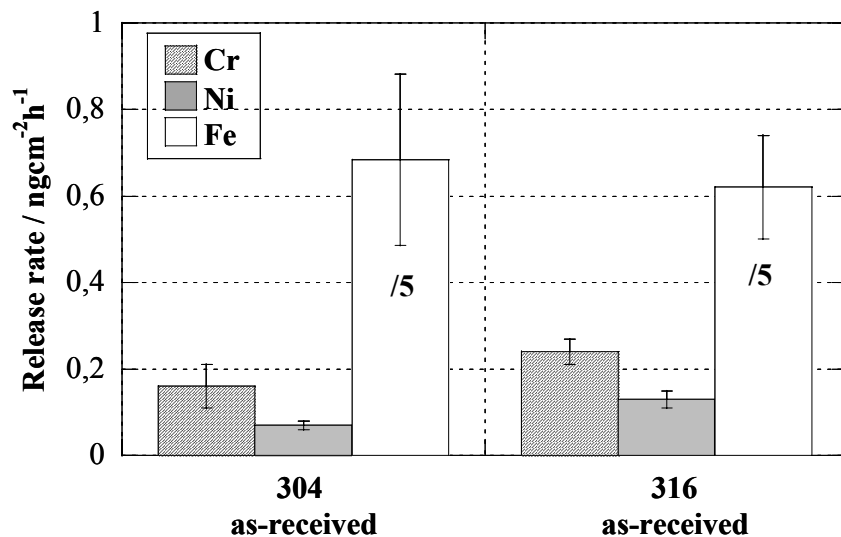

Fig. 27   Release rates of Cr, Ni and Fe (ngcm[-2]h[-1]) from as-received 304 and 316 stainless steel after 8 hours of continuous rain (pH 4.3, intensity of 4 mmh[-1])

Fig. 28   Release rates of Cr, Ni and Fe (ngcm⁻²h⁻¹) from abraded 304 and 316 stainless steel after 8 hours of continuous rain (pH 4.3, intensity of 4 mmh⁻¹)
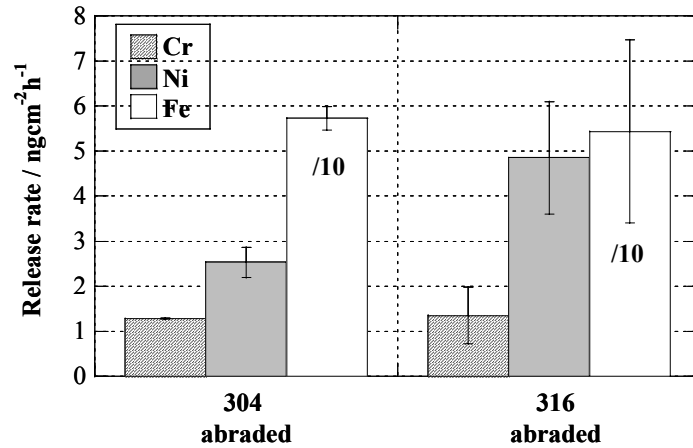
The release rates of Cr, Ni and Fe were continuously measured from stainless steel alloys and from pure metals during eight-hour rain episodes. A first flush effect with somewhat higher metal release rates during the first rain volumes impinging the surfaces was followed by more constant release rates during subsequent rain volumes for all materials, except pure Fe, Figs. 29-31. Fe is an exception most probably due to the formation of voluminous and weakly adherent corrosion products ("rust").
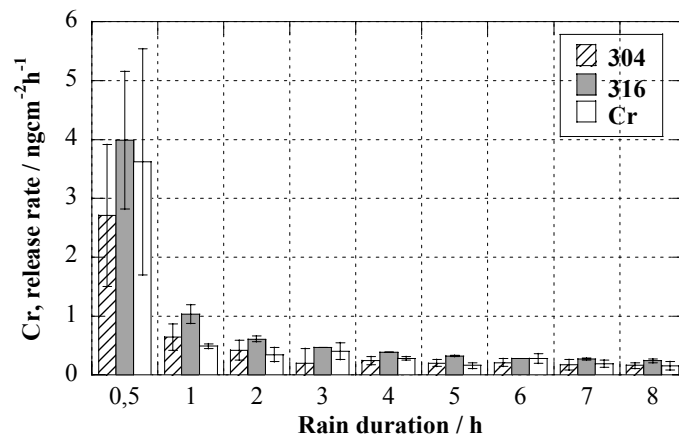
Fig. 29   Release rates of Cr (ngcm⁻²h⁻¹) from as-received stainless steel (grade 304 and 316) and pure electrolytic Cr during an eight-hour rain episode of constant pH (4.3) and intensity (≈4 mmh⁻¹

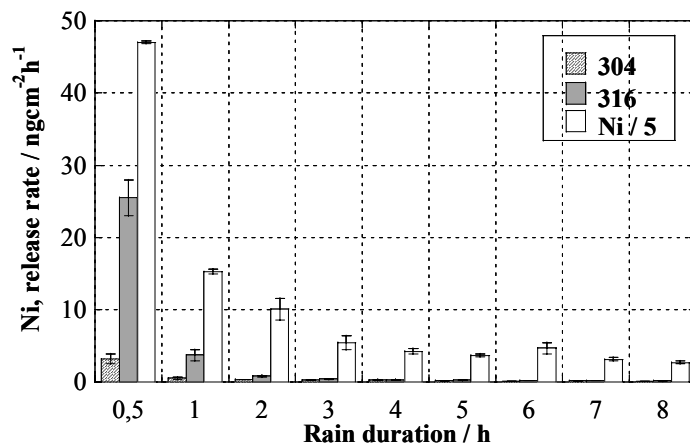*Fig. 30   Release rates of Ni (ngcm⁻²h⁻¹) from as-received stainless steel (grade 304 and 316) and pure Ni during an eight-hour rain episode of constant pH (4.3) and intensity (≈4 mmh⁻¹)*
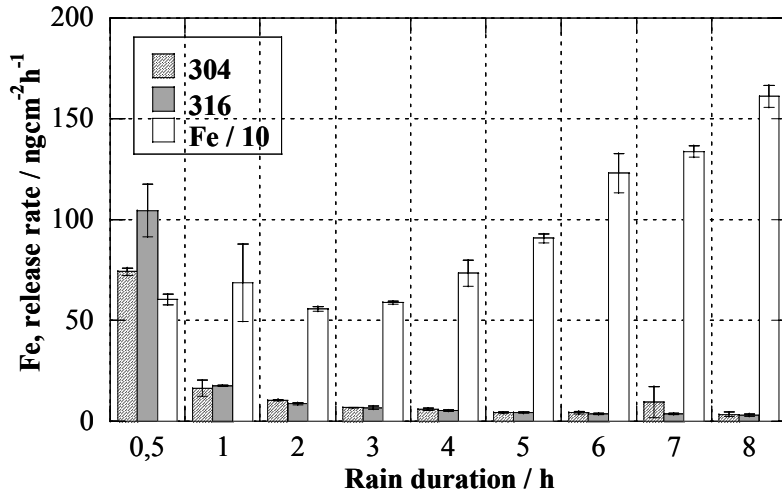
Fig. 31   Release rates of Fe (ngcm⁻²h⁻¹) from as-received stainless steel (grade 304 and 316) and pure Fe during an eight-hour
rain episode of constant pH (4.3) and intensity (≈4 mmh⁻¹)

A comparison between metal release rates from as-received alloys and pure metals was made after two and eight hours of continuous rain.

Consistent with previous findings, grade 316 shows somewhat higher release rates of Cr compared to the 304 grade, Fig. 32. Pure Cr shows somewhat lower release rates than the alloys. This is probably related to a denser and less defect-rich Cr oxide/hydroxide film on the pure metal surface compared to the alloy surfaces. The low release rates of Cr and the relatively small variation in results between the alloys and the pure metals is due to the presence of a passive Cr oxide/hydroxide film on all surfaces, acting as a barrier for corrosion and metal release, Fig. 33.
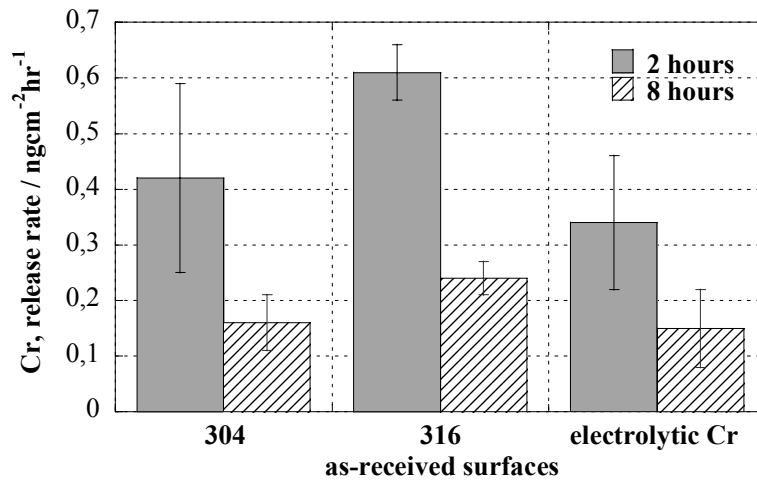

Fig. 32   Release rates of Cr (ngcm⁻²h⁻¹) from stainless steel (grade 304 and 316) and pure electrolytic Cr after 2 and 8 hours of rain
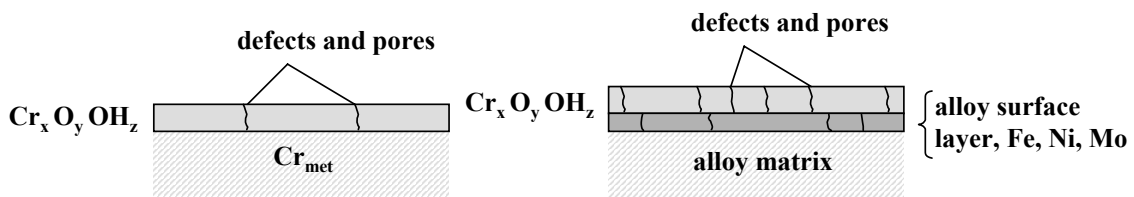*(pH 4.3, intensity 4 mmh⁻¹)*

Fig. 33   Schematic illustration of the surface layer on pure Cr and stainless steel

More Ni is released from 316 compared to 304, Fig. 34, in agreement with previous findings (Table VII). Ni is preferentially released compared to Cr (Fig. 31) but in a different proportion compared to the bulk alloy composition (Table VII). In addition, substantially more Ni is released from the pure Ni surface compared to the alloyed surfaces. This is related to the formation of highly defective surface films on Ni that are easily removed [(MacDougall and Graham 1995)]. In the case of the stainless steel, Ni has to pass the Cr-enriched passive film that acts as a barrier for metal release, hence reducing the Ni release rate, Fig. 35.
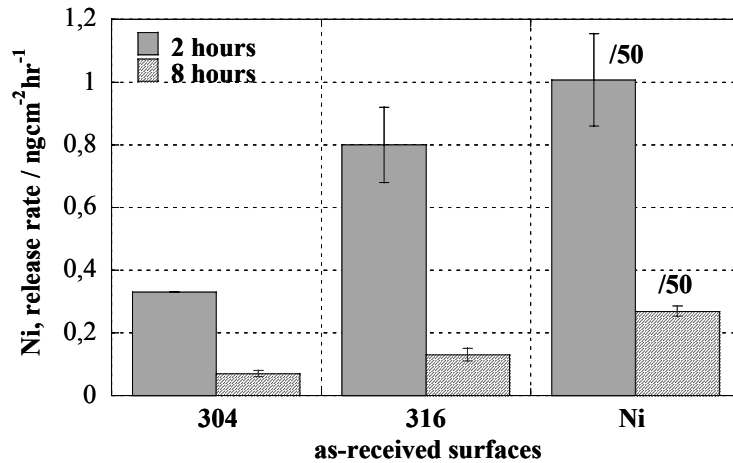

Fig. 34   Release rates of Ni ($ngcm^{-2}h^{-1}$) from stainless steel (grade 304 and 316) and pure Ni after 2 and 8 hours of rain (pH 4.3, intensity 4 mmh^{-1})
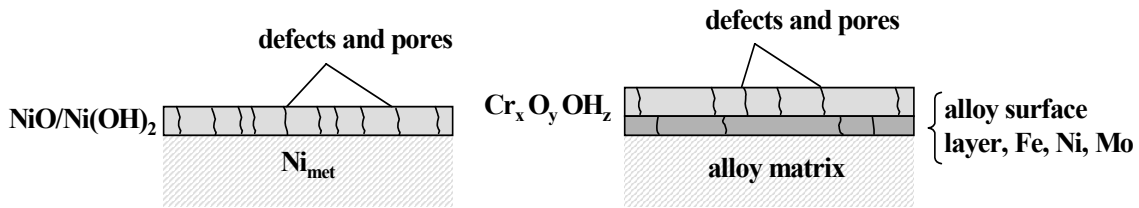

Fig. 35   Schematic illustration of the surface layer on pure Ni and stainless steel

For Fe, no large differences in release rates can be seen between the two stainless steel grades, Fig. 36. This is consistent with field data (Table VI). Substantially more Fe is released from the pure Fe surface compared to the alloyed surfaces. This is related to the insufficient passivation of Fe with an oxide film that is relatively highly susceptible to chemical dissolution, whereas, in stainless steel, Fe, similar to Ni, has to pass the passive film, Fig. 37 [(MacDougall and Graham 1995)].
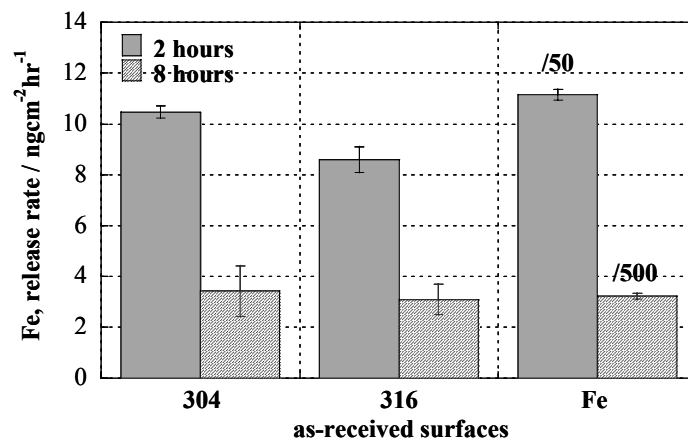

Fig. 36   Release rates of Fe ($ngcm^{-2}h^{-1}$) from stainless steel (grade 304 and 316) and pure Fe after 2 and 8 hours of rain (pH 4.3, intensity 4 mmh^{-1})
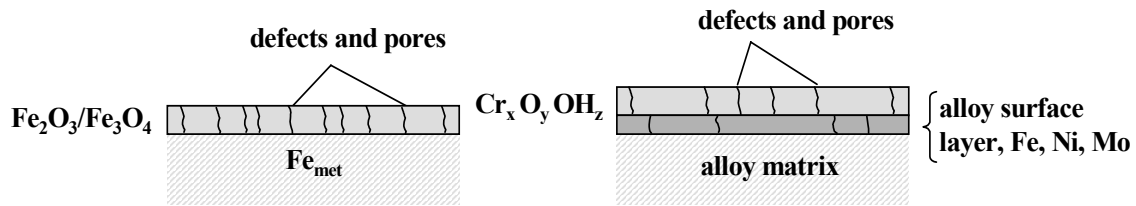
Fig. 37 Schematic illustration of the surface layer on pure Fe and stainless steel

In all, the investigation shows the release rates of Ni and Fe from stainless steel alloys (304, 316) to be quantitatively different from those observed with the pure metals, but similar for Cr. The similarity in results for pure Cr and stainless steel is related to the presence of a Cr-enriched passive film on both surfaces. The presence of the passive film on stainless steel reduces the release rates of Ni and Fe compared to the release rates from the pure metals. The results are summarized in Table XII, which also includes calculated release rates of Cr, Ni and Fe from stainless steel based on the weight fraction of each metal in the alloy multiplied by the pure metal release rates. The calculation has been done to show the large discrepancy in such calculated release rates when compared with actual release rates of each metal from stainless steel. This type of calculation is commonly made within the framework of environmental risk assessment of metals and is, of course, highly erroneous.

Table XII Compilation of hourly measured metal release data (after 2 and 8 hours of continuous rain on pure metals and stainless steel (grade 304 and 316)) and the difference in data when using the weight fraction of a metal in the alloy to calculate metal release rates from release rates of pure metals

Metal / exposure time	304 18.3% Cr, 8.7% Ni, 73% Fe			316 17.2% Cr,10.9% Ni, 71.9% Fe			Cr	Ni	Fe
	ng/cm^2h^{-1} measured		ng/cm^2h^{-1} calculated*	ng/cm^2h^{-1} measured		ng/cm^2h^{-1} calculated*	ng/cm^2h^{-1} measured	ng/cm^2h^{-1} measured	ng/cm^2h^{-1} measured
Cr $_{2h}$	0.42 ± 0.17	>	0.06 ± 0.02	0.61± 0.05	>	0.06 ± 0.02	0.34 ± 0.12		
Cr $_{8h}$	0.16 ± 0.05	>	0.03 ± 0.01	0.24 ± 0.03	>	0.02 ± 0.01	0.15 ± 0.07		
Ni $_{2h}$	0.33 ± 0.00	<<	4.4 ± 0.6	0.80 ± 0.12	<<	5.5 ± 0.8		50.3 ± 7.4	
Ni $_{8h}$	0.07 ± 0.01	<<	1.2 ± 0.1	0.13 ± 0.02	<<	1.5 ± 0.1		13.5 ± 0.8	
Fe $_{2h}$	10.5 ± 0.2	<<	406 ± 8	8.6 ± 0.5	<<	400 ± 8			557 ± 10
Fe $_{8h}$	3.4 ± 1.0	<<	1177 ± 40	3.2 ± 0.6	<<	1159 ± 39			1612 ± 55

* calculated as the alloy percentage times the pure metal release rate

3.7 Conformity between field and laboratory data

In order to check the validity of the artificial rain, we compared the Cr and Ni release rates obtained under natural and laboratory exposure conditions. The annual precipitation volume during this investigation was 500 mm, the number of days with precipitation around 175, out of which approximately 100 days were characterized by a precipitation quantity of ≥1 mm. Because the rain intensity in the interval investigated exhibits no significant influence on Cr and Ni release rates, the annual precipitation quantity of 500 mm can be said to be equivalent to 100 days with a daily average rain period of one hour and a rain intensity of 5 mmh^{-1}, i.e. altogether 100 rain hours per year.

By using the median release rates of Cr (0.8 ngcm^{-2}h^{-1} (304) and 1.4 ngcm^{-2}h^{-1} (316)) and of Ni (1.4 ngcm^{-2}h^{-1} (304) and 3.1 ngcm^{-2}h^{-1} (316)) obtained from the as-received stainless steel panels in artificial rain (c.f. Fig. 21), yearly release rates of 0.8 mgCrm^{-2} and 1.4 mgNim^{-2} are expected for the 304 stainless steel. Correspondingly, yearly release rates of 1.4 mgCrm^{-2} and 3.1 mgNim^{-2} are expected for the 316 stainless steel. These calculated release rates, based on artificial rain, are somewhat higher, but still of the same order of magnitude as the observed release rates obtained in natural rain (c.f. Table VI). This slight discrepancy is expected when considering that the outdoor exposure situation is much more complicated than the laboratory exposure with a single rain event of constant rain composition and pH. As a result of climatic fluctuations between different sampling periods, the natural outdoor rain pH varies typically between 4.1 and 5.8, whereas the release rates in artificial rain were based on pH 4.3. Taking the effect of rain pH into account, (c.f. Fig. 25) the release rate of Cr should be reduced by a factor of 4-5 and that of Ni by a factor of 2-3. This would result in calculated yearly release rates of approximately 0.2 mgCrm^{-2} and 0.6 mgNim^{-2} for the 304 stainless steel and 0.4 mg Crm^{-2} and 1.3 mgNim^{-2} for the 316

stainless steel. These calculated values are in excellent agreement with the field data (c.f. Fig. 16, Table VI) and show that the artificial rain can be used successfully to simulate the effect of various rain parameters on the release rates of Cr and Ni from stainless steel.

3.8 *Conclusions*

Quantitative data on metal release rates of Cr, Ni and Fe from two different stainless steel grades have been determined during four years of urban exposure in Stockholm, Sweden. Work has been performed to determine the chemical speciation of Cr and Ni in the runoff water, the retention of these metal species in two different soil types and the potential ecotoxic effect on algae of metals released from stainless steel in the environment. The effects of individual rain parameters, including pH and intensity have been investigated in parallel laboratory exposures simulating outdoor rain conditions. The laboratory system has also been used to demonstrate differences in release rates of Cr, Ni and Fe from alloys and pure metals exposed under identical conditions.

The following main conclusions can be drawn from this investigation:

- Yearly metal release rates from grade 304 stainless steel into rain water runoff range from 0.2 to 0.6 mg Cr m^{-2}, 0.1 to 0.5 mg Ni m^{-2}, and 10 to 140 mg Fe m^{-2}, partly as a result of variations in yearly rainfall quantities
- Yearly metal release rates from grade 316 stainless steel into rainwater runoff range from 0.2 to 0.7 mg Cr m^{-2}, 0.3 to 0.8 mg Ni m^{-2}, and 10 to 200 mg Fe m^{-2}.
- Ni is generally released at a higher rate than Cr from both stainless steel grades.
- Fe is preferentially released into the runoff water at approximately the same rate from both stainless steel grades.
- The proportion of release rates between Cr and Ni (<1) differs significantly from the corresponding bulk ratio (>1.5).
- The chemical speciation of Cr and Ni in the runoff water is predominantly as Cr(III) (>98.5%) and Ni(II) (>99%), respectively. Computer modeling predicts the presence of organic material in the runoff water to substantially reduce the Cr(III) concentration. For Ni, the reduction is small.
- The actual concentrations of Cr and Ni in runoff water are far below reported ecotoxic concentrations of Cr (32-118,000 μgL^{-1}) and Ni (50-11,000 μgL^{-1}).
- The concentration of Fe in runoff water (<8-700 μgL^{-1}) is far below reported ecotoxic concentrations of Fe (10,000-200,000 μgL^{-1}).
- Surface conditions have a major influence on the metal release rates. The release rates of Cr and Ni are significantly faster from an abraded surface compared to an as-received surface.
- The release rates of Cr and Ni are somewhat faster from the 316 steel than from the 304 steel, in abraded as well as as-received surface condition.
- No significant difference in polarization resistance can be seen between the 304 steel and the 316 steel in bulk solution of artificial rainwater.
- No direct effect of rain intensity on metal release rate could be discerned for as-received surfaces.
- The release rate of Cr and Ni from abraded surfaces increases significantly with decreasing pH.
- A first flush effect with somewhat higher metal release rates during the first rain volumes impinging the stainless steel surfaces was followed by more constant rates during subsequent rain.
- The release rates of Ni and Fe from stainless steel are significantly lower than rates from the pure metals.
- Similar release rates of Cr are seen from stainless steel alloys and the pure metal as a result of the presence of a Cr-rich passive film on both surfaces.
- Release rates determined during laboratory exposures in artificial rain exhibit excellent agreement with release rates determined during field exposures in natural rain.

4 Soil column simulation of reactions occurring between Ni and Cr in runoff water and soil

A possible environmental effect of Cr- and Ni-containing runoff water was simulated by evaluating the retention capacity of soils with different characteristics, the concentration and chemical speciation of Cr and Ni in percolate water (runoff water after contact with soil) and also the possibility of mobilizing Cr and Ni retained within the soil. In this way, different environmental effects, such as possible accumulation and toxicity to organisms and plants in soil, leaching to groundwater and also toxicity to aquatic life were considered. The results are presented in the following sections.

4.1 Retention capacity of soil for Cr and Ni in runoff water

Two different soils, OECD and Rosenlund (see section 2.1.2) were evaluated in the study. The retention capacity was determined by introducing artificial runoff water containing Cr (7 µgL^{-1}) and Ni (14 µgL^{-1}) to each soil column. These concentrations are approximately ten times higher than those found in real runoff water from stainless steel (section 3.1). The higher concentrations were used in order to be sure of being able to detect Ni and Cr in the percolate water since the high reactivity of metals towards retention sites in soil was expected to decrease the concentrations markedly. The retention capacity of each soil is defined as the percentage of introduced Cr and Ni that has reacted with the soil, and hence not found in the percolate water. The concentration of these metals in the percolate water arises from a combination of introduced Cr and Ni in the runoff water and from natural leaching of the initial metal content of each soil. The initial metal content has its origin in weathered minerals as well as from dry deposition from the atmosphere. The "natural leaching" from each soil was evaluated in parallel with the retention studies by using artificial rainwater without any added Cr or Ni. The concentration of naturally leached Ni and Cr compared to the total metal concentrations of the percolate water after artificial runoff water interaction is illustrated in Fig. 38 for the OECD soil and in Fig. 39 for the Rosenlund soil.
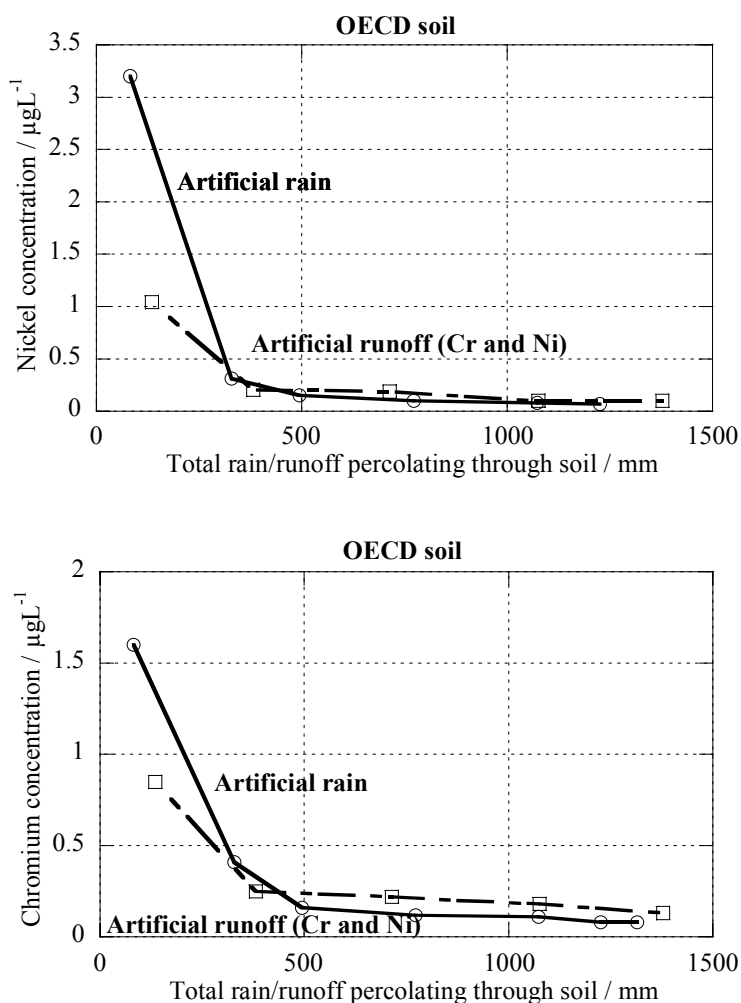

Fig. 38   OECD soil: Ni (upper figure) and Cr (lower figure) concentration in percolate water during a continuous exposure of the soil systems to artificial rain (with no Ni and Cr) compared to artificial runoff water containing Ni and Cr

Natural leaching accounts for most, if not all, Ni found in the percolate water from the OECD soil (upper curve). In the case of Cr (lower curve), somewhat higher concentrations are reached for artificial runoff water compared to natural leaching, but still natural leaching accounts for approximately two thirds of the Cr concentration in the percolate water. The first samplings in artificial rain compared to artificial runoff water could not be performed at the exact same solution volume. As a result, a direct comparison in concentrations of the first samplings cannot be made. The mobilization of Cr and Ni due to mobile organic species is very pronounced during the initial stage of exposure. This is illustrated in Fig. 40 showing the mobile organic species (TOC) in percolate water as a function of exposure. As TOC decreases, the Cr and Ni concentrations in percolate water decrease.
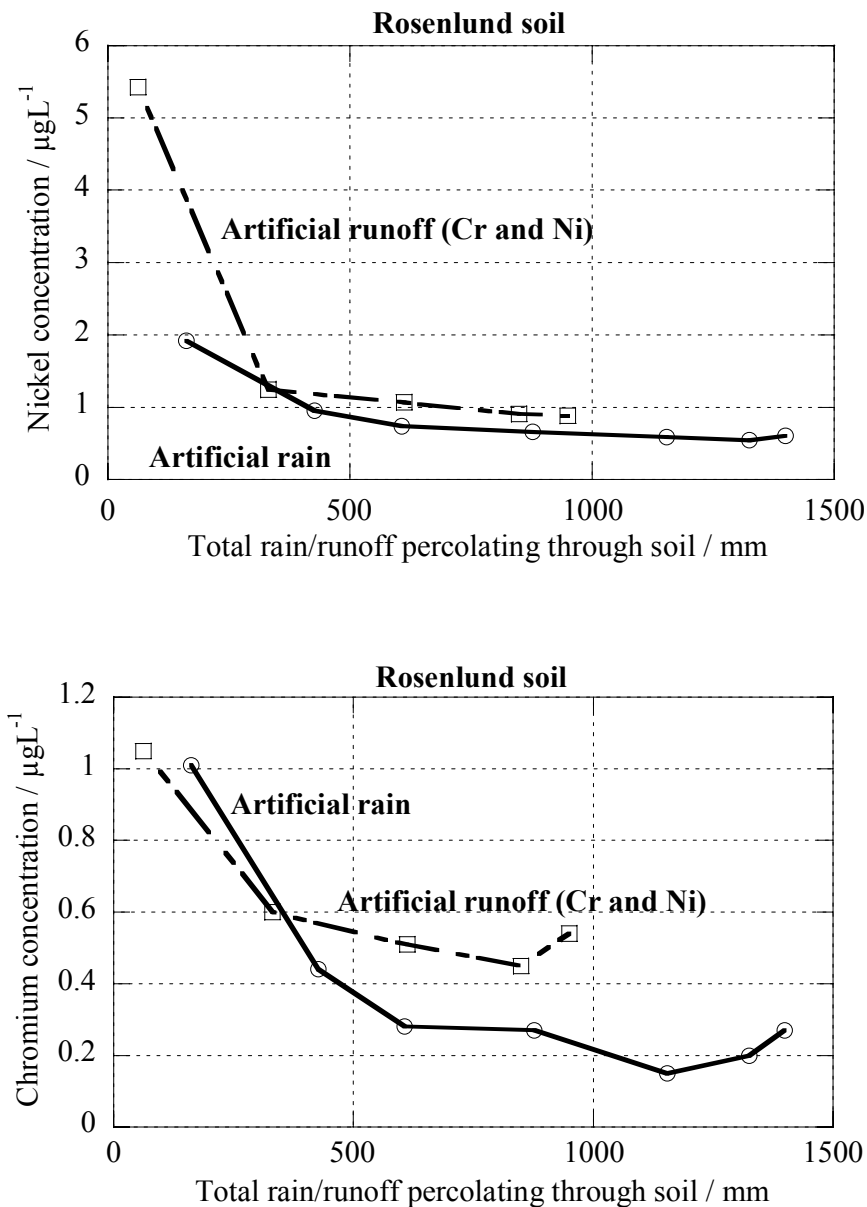

Fig. 39   Rosenlund soil: Ni (upper figure) and Cr (lower figure) concentration in percolate water during a continuous exposure of artificial rain compared to runoff water containing Ni and Cr to the soil system

Somewhat higher concentrations in the percolate water can be seen for both Ni (upper curve) and Cr (lower curve) when using artificial runoff compared to artificial rain in the Rosenlund soil. The reason for the significant effect of Cr and Ni leaching during the first 500 mm of exposure is probably that the natural content of Cr and Ni in the soil is complexed to organic matter, some complexes being small enough to become mobilized by a precipitation event, while introduced Ni and Cr (as in the case of real runoff water) is in ionic form and thereby very reactive towards retention sites in the soil.
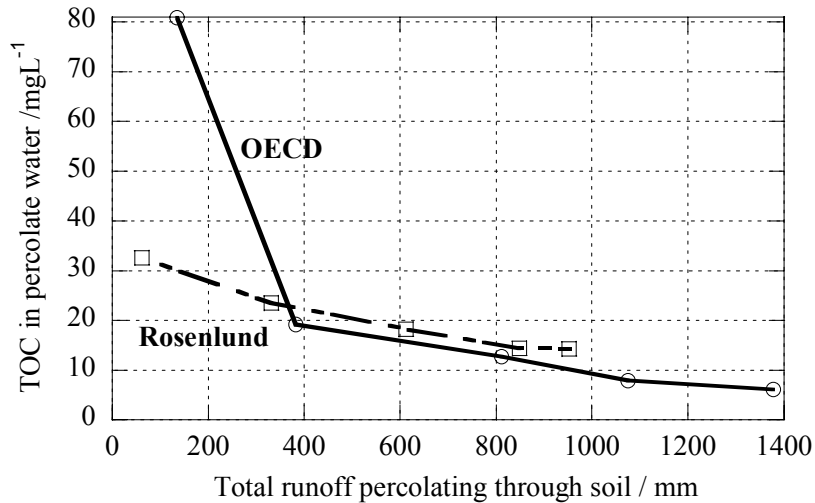
Fig. 40   TOC concentration in percolate water for both soils investigated

Despite the fact that the investigation was performed with approximately ten times higher Cr and Ni concentration compared to real runoff water from stainless steel, the results show that the very low concentrations of Ni and Cr of the percolate waters would not result in any relevant difference when comparing artificial rain interactions with soil to values of runoff interactions with soil. When comparing the retention capacity of the two soils as the percentage of the introduced Cr (7 µgL^{-1}) and Ni (14 µgL^{-1}) that has reacted with the soil it is therefore important to keep in mind that the metal concentration in percolate water is the sum of natural leaching of metals from the soil itself and metals due to the runoff water interaction. Natural leaching has a large effect during the first rain or runoff water quantity percolating through the soil but diminishes with increasing time and rain/runoff quantity. The results of soil retention capacity calculations are given in Figs. 41-42. The lower retention capacity of Ni and Cr seen during the first ~ 300 mm of runoff exposure is explained by the presence of mobile organic compounds in the soil. These organic compounds form complexes with Cr and Ni and, due to their very small size they become mobile in the flow of rainwater and could hence be found in the percolate water. The initial content of small organic compounds is thereafter diminishing (see Fig. 40) which results in an increased retention capacity of the soils. The lower retention capacity of the Rosenlund soil compared to the OECD soil is probably best explained by its lower pH, resulting in more protons in the soil competing with Cr and Ni for retention sites in the soil, as well as less negative surface charge attracting cations such as Cr(III) and Ni(II).
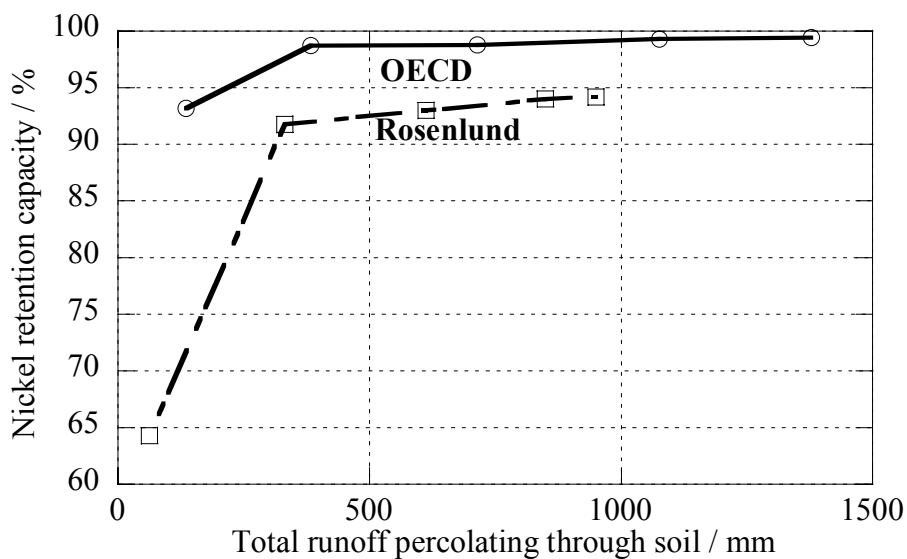

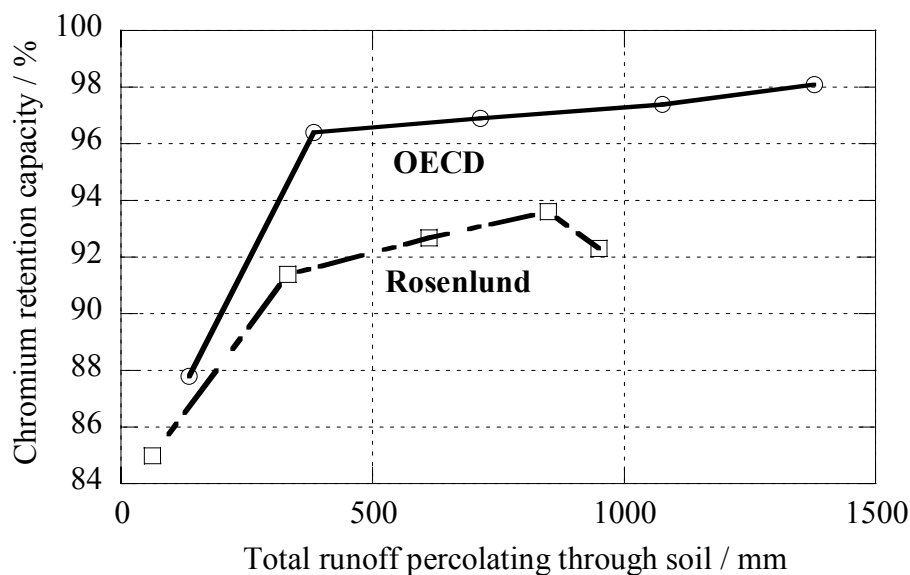*Fig. 41   Ni retention capacity of the OECD and the Rosenlund soil*

Y-axis label: Chromium retention capacity / %
X-axis label: Total runoff percolating through soil / mm

Labels: OECD, Rosenlund

Fig. 42   Cr retention capacity of the OECD and the Rosenlund soil

The Ni retention capacity varied between 93 and 99% for the OECD soil and between 65 and 95% for the Rosenlund soil. For Cr, the retention capacity varied between 88 and 98% for the OECD soil and between 85 and 94% for the Rosenlund soil. When natural leaching is taken into account, the OECD soil has a retention capacity of about 99% for Ni and 98% for Cr introduced via artificial runoff water during a continuous exposure to approximately 1200 mm of rain, i.e. 2.5 years of exposure in Stockholm. For the Rosenlund soil, which is regarded as a low retention soil, a somewhat lower retention capacity was indeed obtained with about 95% for Ni and 94% for Cr during 950 mm rain, i.e. 2 years of exposure in Stockholm.

Differences in soil characteristics result in somewhat different retention capacities, but even the Rosenlund soil with an expected low retention capacity has a high ability for retaining Cr and Ni during the simulated time-period (2-2.5 years of exposure in Stockholm). In reality, the introduced concentrations of Cr and Ni would represent a 20-year outdoor exposure.

4.2   Can Cr and Ni retained in soil become mobilized in the future?

Extractability of metals from soil is influenced by physical factors (e.g. pH, organic constituents, redox potential) and biological factors (e.g. plant species variability, microbial activity). Extractable Ni concentrations in soils, measured by treating soil samples with solutions of potassium chloride, ammonium acetate, acetic acid, or ethylenediamine tetraacetate (EDTA), usually range from less than 0.01 to 2.6 mg $Nikg^{-1}$ and are correlated with the Ni concentrations found in plant crops (0.05 to 5 mg $Nikg^{-1}$ dry weight) [(Sunderman and Oskarsson 1991)]. Cr concentrations found in plants range typically from 0.5 mg $Crkg^{-1}$ for grains of winter rye to 23 mg $Crkg^{-1}$ for spinach [(Gauglhofer and Bianchi 1991)].

Two different extractions were performed within this study in order to evaluate where, within the soil column, Cr and Ni were retained after exposure to artificial runoff water containing Cr and Ni, and how easily the retained metals could become mobilized. The total amount of Cr and Ni that was added to the soil in the runoff water (7 µgCrL^{-1} and 14 µgNiL^{-1}) during the total time-period of the percolation study was 8 µg Cr and 17 µg Ni for the OECD soil (corresponding to a total introduction of 0.145 mg$Crkg^{-1}$ and 0.309 mg$Nikg^{-1}$ dry weight soil) and 6 µg Cr and 11 µg Ni for the Rosenlund soil (corresponding to a total introduction of 0.109 mg $Crkg^{-1}$ and 0.200 mg $Nikg^{-1}$ dry weight soil). After exposure, each soil core was divided into 7 segments from which three segments were selected for extractions, numbered 1, 2 and 7, being soil from top layers 1 and 2, and soil from the bottom of the column 7, respectively. Two extractions were performed in sequence starting with artificial rainwater followed by EDTA (see section 2.5). The results are presented in Table XII and Figs. 43-46, as milligrams of extracted Cr and Ni per kilogram soil from each soil segment.

Extraction with artificial rainwater (defined in section 2.1.3) was performed in order to evaluate whether retained Cr and Ni could be released/mobilized from the soil during a precipitation event. As has been shown previously, part of the natural Cr and Ni content found in the soils becomes mobile during exposure to a precipitation event (see section 4.1). A comparison between concentrations of Ni and Cr in extracted solutions with artificial rain is made in Table XII.

Table XII   *Ni and Cr concentrations in different soil segments extracted with artificial rain*

Soil	OECD		Rosenlund	
	Ni ($\mu g L^{-1}$)	Cr ($\mu g L^{-1}$)	Ni ($\mu g L^{-1}$)	Cr ($\mu g L^{-1}$)
Top layer (1)	1.2	1.0	4.9	1.3
Top layer (2)	0.6	0.7	3.2	1.0
Bottom layer (7)	0.4	0.7	2.4	0.9

When comparing individual soil segments for both soils, the top layer 1 of both the OECD and the Rosenlund soil show somewhat higher concentrations of both Ni and Cr than the lower layers. Assuming that retained Cr and Ni would be equally mobilized wherever retained within the soil column, this suggests that most Cr and Ni is retained within the top layer 1 i.e. the reaction between Cr and Ni and soil is very fast. Top layer 2 and the bottom layer of the OECD soil would then represent natural leaching of the soil for both Ni and Cr. Similar observations can be seen for Cr in the Rosenlund soil whereas Ni seems to become mobilized from both top layers 1 and 2. The concentrations of mobilized Ni and Cr are well below the introduced Ni and Cr concentrations (i.e. 7 $\mu g CrL^{-1}$ and 14 $\mu g NiL^{-1}$) and also well below the WHO drinking water recommendations for maximum concentrations (50 μg NiL^{-1} and 20 μg CrL^{-1}) [(Avesta 1999)].

EDTA extraction of Cr and Ni from soil gives an estimate of more strongly bonded metals retained in the soil and is often used to predict how available the metals are for potential plant uptake. In Fig. 46, the mobilization of Ni in the Rosenlund soil is shown, to be higher from top layer 1 compared to deeper layers. This suggests a fast reaction between Ni in runoff water and the soil system. A somewhat slower reaction can be deduced for the OECD soil, in which mobilized Ni also was found in the top layer 2 of the soil column (Fig. 44). Unexpectedly, more Cr was extractable from the top layer 2 of the OECD soil and from the bottom layer of the Rosenlund soil compared to the top 1 and 2 soil layers (Figs. 43 and 45). This implies slower reaction kinetics and that Cr is not so rapidly retained in contact with soil.
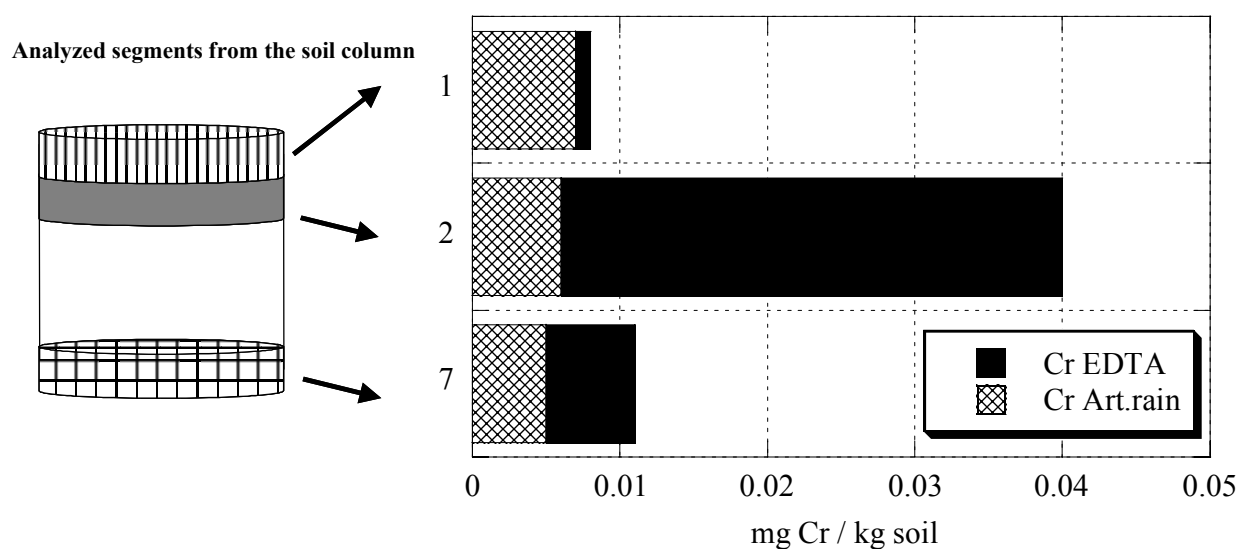

Analyzed segments from the soil column

Fig.43   *Portion of Cr extracted from the OECD soil using artificial rain and EDTA after exposure to artificial runoff water containing Cr and Ni*
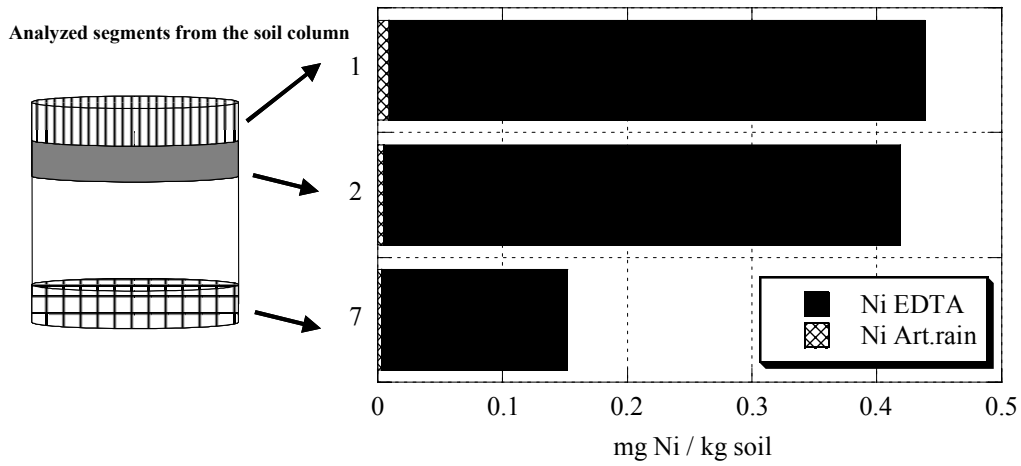
Fig. 44   *Portion of Ni extracted from the OECD soil using artificial rain and EDTA after exposure to artificial runoff water containing Cr and Ni*

Fig. 45   *Portion of Cr extracted from the Rosenlund soil using artificial rain and EDTA after exposure to artificial runoff water containing Cr and Ni*

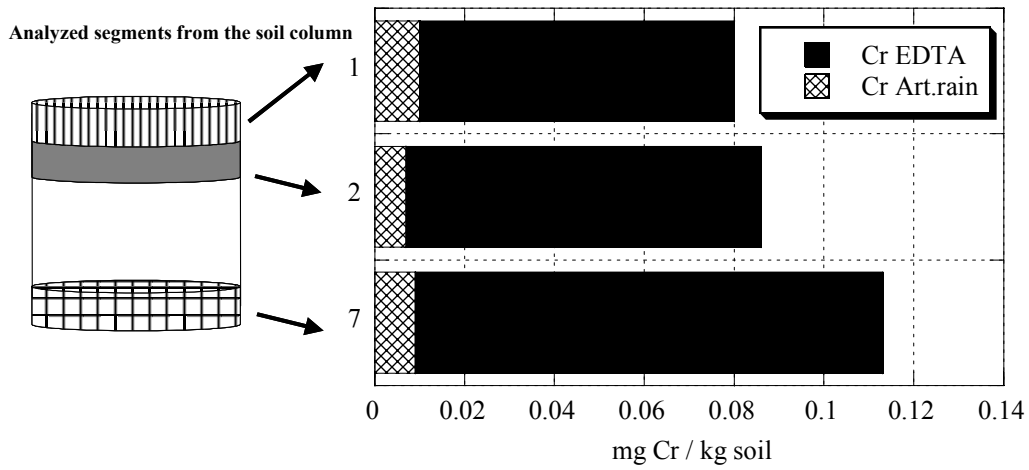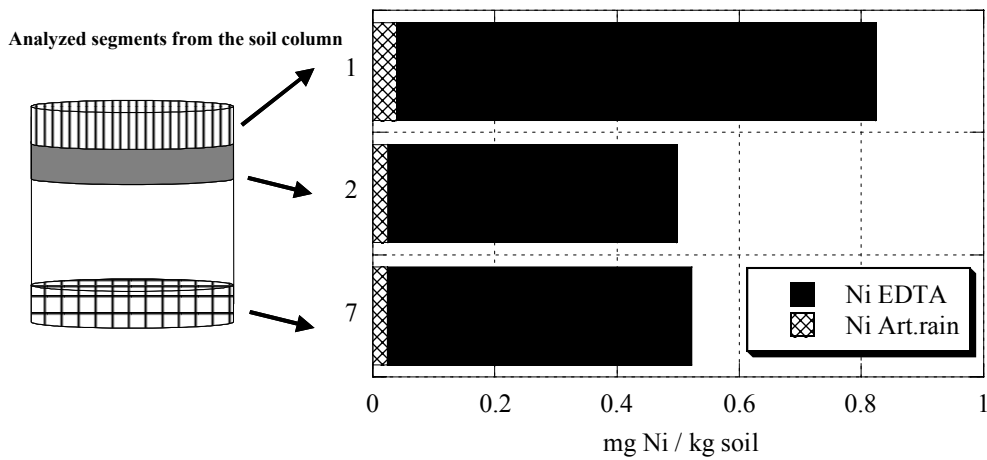*Fig. 46*   *Portion of Ni extracted from the Rosenlund soil using artificial rain and EDTA after exposure to artificial runoff water containing Cr and Ni*

The results show that most Cr mobilized by rain is from the top soil layer whereas Ni can also be released from lower soil layers. Strongly bonded Cr and Ni are also released from lower soil layers. The overall picture suggests a fast initial reaction between the metals and soil, causing a retardation of the metal transport to lower soil layers. Once Cr and Ni reach the lower soil layers, more strongly bonding reactions can occur.

Estimated toxic levels for plants have been reported as total concentrations of 75-100 mg Crkg^{-1} dry weight and 100 mg Nikg^{-1} dry weight [(Walterson 1999)]. Another report [(Gauglhofer and Bianchi 1991)] shows no damage to plants at Cr concentrations in the soil of up to 500 mg Crkg^{-1} dry weight soil. Recent publications have evaluated EC$_{50}$ values for invertebrates ranging from 604-892 mg Crkg^{-1} dry weight for Cr and 275-476 mg Nikg^{-1} dry weight for Ni [(Gauglhofer and Bianchi 1991; Lock and Janssen 2002a; Lock and Janssen 2002b)]. These concentrations are much higher than the total dose added to the soils during the exposure period (0.11-0.14 mg Crkg^{-1} and 0.20-0.31 mg Nikg^{-1} dry weight soil). In a real runoff situation this would be a result of 20 years of exposure.

In conclusion, most Cr and Ni introduced during the soil percolation study were retained in the soil. Extraction showed that most Ni was found in the top soil layer, implying a very fast reaction between Ni in runoff water and soil, while a somewhat slower reaction between Cr and soil was apparent. Some of the retained Cr and Ni can become remobilized during a rain event, but the concentrations are close to those found for natural leaching from the soils. Aging of the soil, resulting in reactions causing strong bonding between metals and soil with time, would result in even stronger retention of Cr and Ni with time than seen in these experiments.

4.3   Conclusions

The retention capacity of Cr and Ni of a low retention capacity soil (Rosenlund) and a standard soil (OECD) has been investigated in controlled laboratory simulations to illustrate reactions occurring with metal containing runoff water (Ni, Cr, Fe) from roofs of stainless steel and soil systems. Investigations have also been made to determine the strength of metal retention and the possibility for future mobilization.

The following main conclusions have been drawn:

- High retention capacities of Cr and Ni can be seen for both soil systems, being >98% Cr and >99% Ni for the OECD soil and >94% Cr and >95% Ni for the Rosenlund soil, simulating 2 to 20 years of exposure. The somewhat lower retention capacity of the Rosenlund soil is mainly explained by its lower pH increasing the competition between protons and metals for retention sites.
- Most Ni is retained in the top surface layer of the soils, which implies a fast reaction between Ni in runoff water and soil. A somewhat slower reaction was apparent for Cr.
- Some of the retained Cr and Ni can become remobilized during a rain event, but the concentrations are close to those found for natural leaching from the soils. Most Cr and Ni are strongly bonded to the soil.

5 General conclusions

A multidisciplinary research project, combining corrosion science, ecotoxicology and soil science, has been implemented in a four-year urban field investigation and in parallel laboratory investigations. The aim of the field investigation has been mainly to provide quantitative data on metal release rates of Cr, Ni and Fe from two grades of stainless steel (304, 316), commonly used for roofing and other outdoor applications and to address the issues of chemical speciation, bioavailability and potential ecotoxicity of released metals. The aim of the laboratory investigations has been two-fold, on one hand to investigate the effect of individual rain parameters (pH, intensity, amount) on the metal release rates and show differences between alloys and pure metals; and, on the other hand, to illustrate how metal-containing runoff water may interact with the environment, in this case soil, by determining the retention capacity of Cr and Ni in soil systems and the potential for future mobilization. The main conclusions drawn from this investigation are illustrated in Fig. 47.
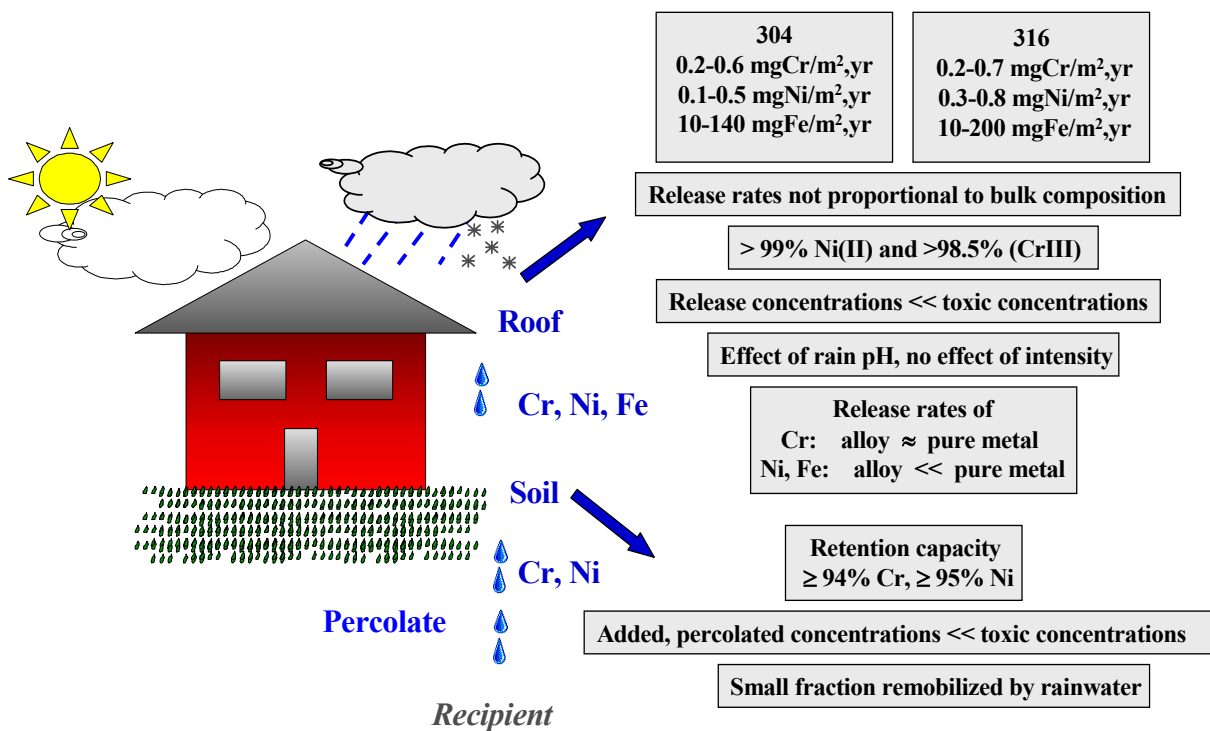

304
0.2-0.6 mgCr/m^2,yr
0.1-0.5 mgNi/m^2,yr
10-140 mgFe/m^2,yr

316
0.2-0.7 mgCr/m^2,yr
0.3-0.8 mgNi/m^2,yr
10-200 mgFe/m^2,yr

Roof

Cr, Ni, Fe

Release rates not proportional to bulk composition

> 99% Ni(II) and >98.5% (CrIII)

Release concentrations << toxic concentrations

Effect of rain pH, no effect of intensity

Release rates of
Cr: alloy ≈ pure metal
Ni, Fe: alloy << pure metal

Soil

Cr, Ni

Retention capacity
≥ 94% Cr, ≥ 95% Ni

Percolate

Added, percolated concentrations << toxic concentrations

Small fraction remobilized by rainwater

Recipient

Fig. 47   *Main conclusions from the multidisciplinary research project*

6   Acknowledgements

We acknowledge the financial support of The Swedish Steel Producers' Association (Jernkontoret), Stockholm and EUROFER, Brussels.

M. Sc. Hoshyar Rada at the Swedish Pulp and Paper Research Institute (STFI), Stockholm, is highly appreciated for performing the GF-AAS-analyses and Åsa Gustafsson at the Dep. of Analytical Chemistry for ICP-AES measurements.

Finally, we are grateful for the help from Dr. Wenle He and Lic. Camilla Karlén for maintenance of the test exposure site, to Dr. Jinshan Pan for invaluable expertise on electrochemical measurements and to Dr. Jianshu Lu for performing for studies of the effect of individual rain parameters in the laboratory.

7   References

Allison, J. D. and Brown, D. S. (1991). MINTEQA2/PRODEFA2, "A Geochemical Assessment Model for Environmental Systems":.

Asami, K. and Hashimoto, K. (1996). "Surface analytical study of atmospheric corrosion of stainless steel." 13th International Corrosion Congress, paper 038, Melbourne, Australia.

Avesta (1999). "Avesta Sheffield Corrosion Handbook." 8th Ed, ISBN 91-630-8118-0.

Baker, E. A. and Lee, T. S. (1990). "Long-term atmospheric corrosion behaviour of various grades of stainless steel in rural, industrial, and marine environments." Corrosion testing and evaluation: Silver Anniversary Volume, ASTM STP 1000, R. Baboian and S.W. Dean, eds., American Society for Testing and Materials, Philadelphia, 177

Bertling, S., Odnevall Wallinder, I.,Leygraf, C. and Berggren, D. (2002a). "Environmental Effects of Zinc Runoff from Roofing Materials - A New Multidisciplinary Approach." Outdoor and Indoor Atmospheric Corrosion, ASTM STP 1421, H.E. Townsend, Ed., American Society for Testing and Materials, West Conshohocken, PA, p.200.

Bertling, S., Odnevall Wallinder, I., Leygraf, C. and Berggren, D. (2002b). "Immobilization of copper in runoff water from roofing materials by limestone, soil and concrete." 15th International Corrosion Conference, Granada, Spain, paper 044.

Brady, D., Letebele, B. Duncan, J.R., and Rose, P.D. (1994). Water SA **20**: 213.

Castle, J. E. and Qiu, J. H. (1990). "The application of ICP-MS and XPS to studies of ion selectivity during passivation of stainless steel". J. Electrochemical Soc. **137**(7): 2031.

Cervantes, C., Campos-Garcia, J. Devars, S., Guitiérrez-Corona, F., Loza-Tavera, H., Torres-Guzmán, J.-C., and Moreno-Sánchez, R. (2001). "Interactions of chromium with microorganisms and plants". FEMS Microbiology Reviews **25**: 335.

Chiba, A., Sakakura, S., Kobayashi, K., and Kusayanagi, K. (1997). "Dissolution amounts of nickel, chromium and iron from SUS 304, 316 and 444 stainless steels in sodium chloride solutions." J. Mat. Sci. **32**: 1995.

Cramer, S., Carter, J. P., Linstrom, P.J., and Flinn, D.R. (1988). "Environmental effects in the atmospheric corrosion of zinc." Degradation of metals in the atmosphere, ASTM STP 965, S.W. Dean and T.S. Lee, Eds., American Society of Testing and Materials, Philadelphia: 229-247.

Di Toro, D. M., Kavvadas, C. D., Mathew, R., Paquin, P.R., and Winfield, R.P. (2001). "The persistence and availability of metals in aquatic environments." International Council on Metals and the Environment, Ottawa, Ontario, ISBN 1-895720-36-2.

Duke, J. M. (1980). Nickel in the Environment. J. E. Nriagu. New York, John Wiley & Sons.

Fendorf, S. E. (1995). "Surface reactions of chromium in soils and water." Geoderma **67**: 55-71.

Florence, T. M., Staober, J. L., and Ahsenullah, M. (1994). "Toxicity of nickel ores to marine organisms." The Science of the Total Environment **148**: 139-155.

Frink, C. R. (1996). "A Perspective on Metals in Soils." Journal of Soil Contamination **5**(4): 329-359.

Gauglhofer, J. and Bianchi, V. (1991). Metals and Their Compounds in the Environment. Occurrence, Analysis, and Biological Relevance: Chromium, Merian, E., Ed., VCH New York.

Graedel, T. E. (1987). "Copper patinas formed in the atmosphere-II. A qualitative assessment of mechanisms". Corrosion Science **27**: 721.

Granat, L. (1990). Swedish Environmental Protection Agency No. 3942 (in Swedish).

He, W. (2000). "Corrosion rates and runoff rates of copper and zinc as roofing materials. - A combined field and laboratory study". Lic. Thesis., KTH, Royal Institute of Technology, Stockholm, Sweden, ISBN 91-7170-527-9.

He, W. (2002). "Atmospheric Corrosion and Runoff Processes on Copper and Zinc as Roofing Materials". Doctoral Thesis, Royal Institute of Technology, ISBN 91-7283-364-5.

He, W., Odnevall Wallinder, I. and Leygraf, C. (2001a). "A comparison between corrosion rates and runoff rates from new and aged copper and zinc as roofing material". Water, Air and Soil Pollution, Focus **1**: 67.

He, W., Odnevall Wallinder, I. and Leygraf, C. (2001b). "A laboratory Study of Copper and Zinc Runoff during First Flush and Steady-State Conditions". Corrosion Science **43**: 127-146.

He, W., I. Odnevall Wallinder, I. and Leygraf, C. (2002a). "Runoff Rates of Zinc - a Four-Year Field and Laboratory Study". Outdoor and Indoor Atmospheric Corrosion, ASTM STP 1421, H.E. Townsend, Ed., American Society for Testing and Materials, West Conshohocken, PA, p.216.

Heidersbach, R. H. (1987) Marine Corrosion. Metals Handbook, Corrosion ASM International. Vol. 13.

Hindak, F. (1990). "Pseudokirchneriella subcapitata Korshikov." F. Biologicke Prace **5**: 209.

Huebers, H. A. (1991). Metals and Their Compounds in the Environment. Occurrence, Analysis, and Biological Relevance: Iron. E. Merian, Ed. New York, VCH. **II.14**.

Hultquist, G., Seo, M., Leitner, T., Leygraf, C., and Sato, N. (1987). "The dissolution behaviour of iron, chromium, molybdenum and copper from pure metals and from ferritic stainless steel." Corrosion Science **27**(9): 937.

ISO8565 (1992). Metals and Alloys- Atmospheric corrosion testing - General requirements for field tests, International Organization for Standardization, Geneva, Switzerland.

ISO (1989). ISO 8692, Water Quality - Fresh water algal growth inhibition test with Scenedesmus subspicatus and Pseudokirchneriella subcapitata., International Organisation for Standardisation, Geneva, Switzerland.

Johnston, M. J. and Pavlik, P. J. (1982). Atmospheric Corrosion: Atmospheric corrosion of stainless steel. W. H. Ailor. New York, John Wiley &Sons**:** 461 (Chapter 32).

Jonsson, E. (1999). "Retention of heavy metals in Soil". Report ISSN 1102-1381, Swedish University of Agricultural Sciences, Uppsala.

Karlén, C., Odnevall Wallinder, I., Heijerick, D., Leygraf, C., and Janssen, C.R. (2002). "Runoff rates, Chemical speciation and Bioavailability of Copper Dispersion from Naturally Patinated Copper Roofs"." Environmental Pollution, **120**(3): 691-700.

Karlén, C., Odnevall Wallinder, I., Heijerick, D., Leygraf, C., and Janssen, C.R. (2001). "Runoff rates and ecotoxicity of zinc induced by atmospheric corrosion". The Science of the Total Environment **277**(1-3): 169-180.

Kearns, J.R., Johnson, M.J., and Pavlik, P.J. (1988). "The corrosion of stainless steels in the atmosphere". Degradation of Metals in the Atmosphere, ASTM STP 965. S. W. Dean and T. S. Lee, Eds., American Society for Testing and Materials, Philadelphia**:** 35-51.

Khangaroth, B. S. and Ray, P. K. (1987). "Correlation between heavy metal acute toxicity values in Daphnia magna and fish." Bulletin of Environmental contamination and toxicology, **38**: 722.

Landner, L. and Lindeström, L. (1999). Copper in society and in the environment., Swedish Environmental Research Group (MFG), ISBN 91-630-7932-1.

Leygraf, C. and Graedel, T. E. (2000). Atmospheric Corrosion, John Wiley & Sons, New York, ISBN 0-471-37219-6.

Leygraf, C., Hultquist, G., Olefjord, I., Elfström, B.-O., Knyazheva, V.M., Plaskeyev, A.V., and Kolotyrkin, Y.M. (1979). "Selective dissolution and surface enrichment of alloy components of passivated Fe18Cr and Fe18Cr3Mo single crystals". Corrosion Science 19: 343.

Lock, K. and Janssen, C. R. (2002a). "Ecotoxicity of nickel to Eisenia fetida, Enchytraeus albidus and Folsomia candida." Chemosphere 46: 197-200.

Lock, K. and Janssen, C. R. (2002b). "Ecotoxicity of Cr(III) to Eisenia fetida, Enchytraeus albidus and Folsomia candida." Ecotoxicity and Environmental Safety 51: 203-205.

MacDougall, M. and Graham, M. J. (1995). Corrosion Mechanisms in Theory and Practice. Marcus, P. and Oudar, J. Eds., New York, Marcel Dekker Inc., chapter 5, p.143.

Madoni, P. (1994). "Acute toxicity of lead, chromium and other heavy metals to ciliates from activated sludge plants." Bulletin of Environmental Contamination and Toxicology, 53: 420-425.

Madoni, P. (2000). "The acute toxicity of nickel to freshwater ciliates." Environmental Pollution, 109: 53.

McBride, M. B. (1994). Environmental Chemistry of Soils, Oxford University Press, Inc., ISBN 0-19-507011-9.

NiDI (2002) Stainless Steel in Architecture, Building and Construction: Guideline for Corrosion Prevention, Report no. II 024, NiDI Nickel Development Institute.

NIDI (1989). Technical manual for the design and construction of roofs of stainless steel sheet, NiDI publication No.12 006.

NiDI (2000). "Ecotoxicitiy of nickel-containing substances", ENV-2, NiDI Ni Development Institute.

NiDI (2002). Guidelines for Corrosion Prevention.

Odnevall, I. and Leygraf, C. (1997). "A study of copper runoff in an urban atmosphere." Corrosion Science 39(12): 2039.

Odnevall, I., Verbiest, P., He, W., and Leygraf, C. (1998). "The influence of patina age and pollutant levels on the runoff rate of zinc from roofing materials." Corrosion Science 40(11): 1977.

Odnevall Wallinder, I. and Leygraf, C. (2001). "Seasonal variations in copper corrosion rate and runoff rate in an urban and a rural atmospheric environment." Corrosion Science 43(12): 2379.

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

Odnevall Wallinder, I., Verbiest, P., He, W., and Leygraf, C. (2000). "Effects of exposure direction and inclination on the runoff rates of zinc and copper roofs." Corrosion Science 42(8): 1471.

OECD (1984). Earthworms, Acute Toxicity Tests, Report 207, OECD, Organisation for Economic Coorporation and Development, Paris, France.

OECD (1984). OECD, Algal growth inhibition test. Guideline No. 201, OECD Guidelines for Testing of Chemicals, Organization for Economic Cooperation and Development, Paris, France.

Olefjord, I., Brox, B., and Jelvestam, U. (1985). "Surface composition of stainless steel during anodic dissolution and passivation studies by ESCA". J. Electrochemical Soc. 132(12): 2854-2861.

Olefjord, I. and Wegrelius, L. (1996). "The influence of nitrogen on the passivation of stainless steels". Corrosion Science 38(7): 1203-1220.

Pacyna, J. F. and Nriagu, J. (1988). Chromium in the natural and human environments, Vol 105, Nriagu, J., Nieboer, E., Eds, Wiley & Sons, New York.

Ross, H. B. (1986). "The importance of reducing sample contamination in routine monitoring of trace metals in atmospheric precipitation." Atmospheric Environment 20(2): 401.

Sunderman, F. W. J. and Oskarsson, A. (1991). Nickel. Metals and Their Compounds in the Environment. Occurrence, Analysis, and Biological Relevance. E. Merian. New York, VCH. II.22.

Tipping, E. and Hurley, M. A. (1992). "A Unifying model of Cation binding by Humic substances". Geochimica et Cosmochimica Acta 56: 3627-3641.

Tochihara, M., Ujiro, T., Yazawa, Y., and Satoh, S. (1996). "Atmospheric corrosion of stainless steel used for the eaves of buildings." Materials Performance: 58-62.

UN/ECE (1997). UN/ECE International programme on material including historic and cultural monuments, Rep. No 21.

Wallinder, D., Odnevall Wallinder, I., and Leygraf, C. (2003). "Influence of surface treatment of 304L stainless steel on atmospheric corrosion resistance in an urban and a marine environment." Corrosion 59(3): 220-227.

Wallinder, D., Pan, J., Leygraf, C., and Delblanc-Bauer, A. (1999). "EIS and XPS study of surface modification of 316LVM stainless steel after passivation." Corrosion Science 41: 275.

Walterson, E. (1999). Chromium, nickel and molybdenum in the society and the environment, Swedish Environmental Research Group.

Wegrelius, L. (1995). "Passivation of Austenitic stainless steel". Doctoral Thesis, Dep. of Engineering Metals, Chalmers University of Technology, Göteborg, Sweden.

Verbiest, P., Waeterschoot, H., Racek, R., and Leclerq, M. (1997). "A study of runoff and corrosion rates of rolled zinc sheet in different exposures". Prot. Coat. Europe 47.

Zysset, M. and Berggren, D. (2001). "Retention and Release of Dissolved Organic Matter in Podzol B Horizons: Column and Batch Studies". European Journal of Soil Science 52: 409-421