CHEMODYNAMICS OF TRACE POLLUTANTS DURING ROOF AND STREET RUNOFF

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ABSTRACT

The fate of ionic and non-ionic organic compounds and trace metals during roof and street runoff is sensitive to their distribution between sorption onto roof and street material and suspended solids on one hand and the dissolved phase on the other hand. Using field data of runoff, suspended solids concentration and the chemical state of various trace pollutants, we try to explain the factors governing the chemodynamics and the transport behaviour during roof and street runoff.

KEYWORDS

Roof runoff, street runoff, heavy metals, organic micropollutants, rain events, suspended solids, DOC, first flush, speciation.

INTRODUCTION

We will transfer the reasoning of Chiou et al. (1985) about the sorption of non-ionic organic compounds onto soil humus and minerals to the understanding of chemodynamic behaviour of non-ionic organic pollutants on roof and street surfaces. We extend this reasoning further to hydrophobic ionizable organic chemicals (e.g. nitrophenols) and organic compounds functioning as solvatizers (DOC) (Sawhney, 1989; Rao et al., 1989). We should expect that wet surfaces of roof and street material and suspended solids, both coated with organic material, would linearly, and without competition between different solutes, uptake non-ionic organic compounds from water by solute partitioning into organic matter. However, with increasing affinity of mineral surfaces to water, adsorption of non-ionic organics on the minerals surfaces will decrease. This leads to competition between the various adsorbates in a mixture.

Dry deposition results in adsorption of vapour phase pollutants on surfaces of streets, roofs and sediments. During wetting of surfaces, fractions of the previously adsorbed non-ionic organic chemicals will desorb and partition between the organic material and the water phase. Where low organic matter content is found on street and roof surfaces, we should expect a change of activity of organic chemicals during wetting and drying cycles, because after the wetting of the surface, water will displace non-ionic organic chemicals from the mineral surfaces. As an example of hydrophobic ionizable hydrocarbons Sawhney (1989) discusses the
sorptive behaviour of phenols. Partition coefficients predicted from water solubility or octanol-water partitioning are lower than those measured in sediment-water systems. He explains this discrepancy by sorption processes of phenols by soils and sediments which are related to specific interactions, such as by H-bonds (see Fig. 1 where 2-nitrophenol has intramolecular H-bonds, and 4-nitrophenol has intermolecular H-bonds), rather than by general hydrophobic mechanisms.

Phenolic compounds with a pK<sub>a</sub> lower than the pH of roof or street runoff will dissociate, and the resulting phenolate anion has a much greater solubility than the protonated form.

Dissolved organic compounds act as cosolvents, thus decreasing sorption of organic chemicals on surfaces and decreasing the sorption coefficient. Therefore, the overall result should be an enhanced mobility of the organic chemicals when present as dissolved species within the runoff.

Liss and Slater (1974) describe the use of a two-layer model to estimate the flux of various gases across the air-water interface. The total resistance on a liquid phase basis (K<sub>j1</sub>) depends on the exchange constants k<sub>i</sub> and k<sub>s</sub> of the individual phases and the dimensionless Henry’s law constant of the gas (H):

\[ K_{j1} = k_{i1} + (H k_{s})^{-1} \]

Because of high values of H of all the volatile organic hydrocarbons we investigated, the liquid phase resistance controls the exchange (K<sub>j1»(H k_{s})^{-1}</sub>).

We plotted the distribution coefficient of the air-water system (log H) against the octanol-water partition coefficient (log k<sub>ow</sub>) in Fig. 1 for a few trace organics. The volatility increases upward and the sorption increases to the left, thus the capability of escaping the aqueous phase decreases towards the lower right.

We will select examples for the dominant chemodynamic and transport processes which affect the behaviour of organic chemicals during roof and street washoff. However, since at any time no single process acts alone, real world behaviour of organic chemicals cannot definitely be attributed to the individual contributing chemical processes.

The explanation of the chemodynamics of trace metals during roof and street runoff is limited as we do not have sufficient information about many of the influencing factors (e.g. the kinetics of dissolution and precipitation, the thermodynamic data and ligand concentrations) necessary to estimate inorganic and organic metal complexation, metal saturation, and finally the data for computing sorption processes onto roof and street surfaces and onto suspended solids. In particular, the kinetics of partitioning of trace metals into or out of suspended solids or roof and street material is not well known.
The sorption capacity of suspended solids and roof and street surfaces primarily depends on the coating of the surfaces by amorphous oxides of Fe and Mn and by organic carbon. Further, clay minerals and amorphous Al and Si oxides act as sorbents for trace metals or they form substrates which can be coated by amorphous Fe and Mn oxides or organic carbon.

For a comprehensive treatise on the behaviour of trace metals in the hydrocycle, we refer to the monograph of Salomons and Förstner (1984).

Analogous to soils, we can expect that surfaces of suspended solids and of roofs and streets present great numbers of surface coordination sites. Normally a significant hysteresis between sorbing and desorbing trace metals is observable, resulting from the facts that the metals partly enter the solid material or diffuse into micropores or need larger endothermic energy. Thus, desorption needs more time to equilibrate than sorption.

In addition to the composition of the surfaces, the composition of the solute, too, influences the sorption behaviour of trace metals during roof and street runoff. The pH strongly influences the sorption of trace metals by hydrolysis or protonation of the ions and changes the charge of the surfaces.

With some exceptions, the complexation of trace metals by organic and inorganic ligands decreases the sorption onto surfaces and increases the mobility of the trace metals.

We are not able to predict the results of competitive behaviour of a trace metal and constituents of the solute, which potentially can adsorb at the same surface sites like the trace metal under consideration, since we generally do not know the composition of the solute and of the surfaces. Though the ionic strength affects trace metal sorption to a lesser degree than proton activity, complexation or competition, it influences metal ion activity in solution and the surface charges. Further it influences the formation of aggregates and thus sorption or desorption by increasing or decreasing the active surface area of the solid phase.

Study Area, Sampling and Chemical Analysis

For this study we selected three street sections (Herrmann et al., 1992; Kern et al., 1992) in the city of Bayreuth, five roofs within the university campus (Förster, 1990) and five experimental roofs on top of a flat roof also within the university campus (Förster, 1991). We developed automatic sampling systems (Förster, 1993; Striebel et al., 1993) which allowed us to take samples and to measure runoff, electrical conductivity and pH with high resolution. We analyzed organic micropollutants by means of solid phase and liquid/solid extraction, a cleanup step, GC and HPLC separation and ECD, MS, and fluorescence detection.

Depending on their position within the speciation scheme, we measured trace metals by means of atomic absorption spectroscopy (AAS) and anodic stripping voltametry (ASV) with or without pretreatment (e.g. ion exchange, acid digestion under

![Fig. 2. Street runoff event: plot of normalized loadings of Fluoranthene (FLT), suspended solids (SS) and DOC against normalized runoff. Bayreuth, Königsallee, July 19, 1991.](https://iwaponline.com/wst/article-pdf/29/1-2/73/113776/73.pdf)
Chemodynamics and Transport Behaviour of Trace Organic Compounds

Sorption processes. A plot of normalized loadings against normalized runoff (Fig. 2) provides evidence that, during street washoff, fluoranthene sorbed by suspended solids behaves like the suspended solids themselves, whereas the behaviour of dissolved fluoranthene can be compared with that of DOC.

However, during periods of intensive runoff, coarse particles are transported, which have a lower ratio of organic coatings to mineral surfaces and thus a lower overall sorption capacity; hence, the specific adsorption declines (see Fig. 3).

The combination of time series of temporal variations of dissolved and sorbed fluoranthene with that of DOC indicates that the ratio of dissolved to sorbed fluoranthene during street washoff can at times be considerably higher than one would predict from the high $K_{ow}$ (Fig. 1). We explain this behaviour by cosolventation by nonpolar films of mineral oil, dissolved low molecular organic substances, nitrophenols or other organic solvents (Fig. 4). We observed this behaviour in particular with non-ionic organic chemicals with very high sorption coefficients. During an event with $c(\text{DOC}) = 2 - 10 \, \text{mg} \cdot \text{l}^{-1}$, the ratio $r$ of dissolved Flt/BghiP was 7, however during another event with $c(\text{DOC}) = 27-545 \, \text{mg} \cdot \text{l}^{-1}$ the same ratio decreased to 1.

**Fig. 3.** Temporal variation of specific concentrations of sorbed fluoranthene (Flt) and benzo(ghi)perylene (BghiP), suspended solids (SS), and runoff (Q) during street runoff. Bayreuth, Königsallee, July 14, 1991.

**Fig. 4.** Temporal variation of dissolved (diss.), particulate (part.), fluoranthene (Flt) and DOC during street runoff. Bayreuth, Königsallee, July 14, 1991.

**Fig. 5.** Concentrations of $\gamma$-HCH during roof washoff from pantiles and fibre cement.
During dry weather, γ-HCH (Lindane®) deposits on roofs and streets from the gaseous phase. During wetting of the surface, this organic compound, which is only weakly adsorbed by minerals (lg \( K_d < 2 \)) and has a solubility of \( S = 15 \mu\text{mol/l} \), will readily desorb, and during the course of a runoff event will adopt concentrations of the feeding rainfall. Thus, at onset of rain, roofs with a higher inner mineral surface, like fibre cement, exhibit a considerably higher concentration of γ-HCH in surface roof washoff than does the rain (Fig. 5).

Because of their high solubility (Fig. 1) nitrophenols, as an example of hydrophobic ionizable hydrocarbons, are easily mobilized during street washoff. Nitrophenols with intermolecular H-bonds or \( pK_a < \text{pH} \) (like 4-nitrophenol in our example - \( pK_a = 7.1 \)) show a marked first flush effect (Fig. 6). By contrast, the transport of nitrophenols adsorbed onto suspended solids is in most cases below the limit of determination and in general negligible. During times of intensive rainfall the concentrations of nitrophenols in street washoff decrease, caused by dilution and lower contribution by dissolution. Near the end of a rain event, however, concentrations in washoff are controlled by concentrations in rainfall. Further, during summer events with low runoff, warm street surfaces cause evaporation with the increase of nitrophenol concentrations. During strong street washoff the more mobile 4-nitrophenol reaches a state of supply limit considerably earlier than the less soluble and mobile 2-nitrophenol.

**Transport across the water-air interface.** Due to high Henry's law constants and low octanol-water partition coefficients \( K_{ow} \), deposition of volatile chlorinated hydrocarbons (Fig. 1) from vapor phase on street and roof surfaces and sorption onto mineral or organic surfaces are negligible. Thus, the concentrations of this class of non-ionic organic hydrocarbons in roof and street runoff are governed by their concentrations in rainfall, and as a result the deviation of their normalized loadings from the normalized runoff is very low.

**Photochemical reactions.** Comparing the concentrations...
Fig. 8. Thermodynamic speciation of Cu, Pb, and Cd in street runoff samples with low and high concentration.
Chemodynamics of trace pollutants

Species distribution: chemical speciation. Using two examples of chemical speciation, a meltwater and a rain runoff event (Fig. 9), we want to emphasize that the species distribution, and thus sorption and transport behaviour, may change considerably between and within runoff events. During a meltwater event with high ion concentration ($\kappa_\text{H} = 36.000 \, \mu S \, cm^{-1}$), Cu was transported in equal portions in dissolved and particulate phases. The contribution of dissolved Cu was high when compared with other events. About a third of the dissolved Cu is ASV-labile bound, and this portion cannot be increased by UV-radiation. Equally, the portion of chelax-labile metals does not increase. Thus, the Cu species which is not labile bound probably exists in colloidal form. The rain runoff resulted from a weak rain event, and thus the concentration of suspended solids (SS>12 µm and <12 µm), and dissolved Cu. Bayreuth, Königsallee, July 14, 1991.

Fig. 9. Chemical speciation of Cu in meltwater and rainwater runoff samples, Meranierring, Bayreuth.

Fig. 10. Concentrations of particulate Pb in roof runoff, May 18, 1988.

Fig. 11. Temporal variation of concentrations of Cl-, suspended solids (SS>12 µm and <12 µm), and dissolved Cu. Bayreuth, Königsallee, July 14, 1991.

Chemodynamics and Transport Behaviour of Trace Metals

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Metal speciation by means of thermodynamic equilibrium. Computations (Fig. 8) reveal that the separation into free dissolved and inorganic metal complexes cannot be related to the general status of contamination of a runoff sample. Rather, the separation depends on the availability of the complexing ligands. Cu tends to complex with chloride and sulphate as well as with hydroxide and carbonate. As a result, we observe, in the 'high contamination case,' a significant complexation by chloride and sulphate caused by the availability of these anions and a low pH = 6.2. This low pH caused a low carbonate and hydroxide complexation and a high concentration of free Cu. On the other hand, low chloride and sulphate concentrations and a high pH = 7.6 in the 'low contamination case' shift the species distribution to a dominant carbonate and hydroxy-complexation.

The species distribution of Pb is caused by the same governing factors. However, the distribution is reduced to sulphate and hydroxide complexes, which are related to contamination and pH, respectively, and to free dissolved Pb.

In case of Cd, only chloride and sulphate complexes and free Cd are of importance. Thus, the species distribution is clearly related to the availability of chloride and sulphate caused by contamination.

In most cases concentrations of the three metals are below saturation. Only in the 'low contamination case' did we...
compute a weak oversaturation \((SI = +0.1)\) of free Cu against CuO. This oversaturation may be a computational or experimental artifact caused by neglect of monovalent Cu ions, neglect of organic ligands or inclusion of colloidal Cu which passed the filter. Thus, we cannot refute the hypothesis that the concentrations of dissolved trace metals are governed by competitive reactions between adsorption equilibria related to adsorption sites and dissolved complexes.

**Influence of Different Roof Materials on Transport Behaviour**

Quek and Förster (1993) investigated the pollutant load in runoff from five roofs with different materials and slopes (between 15° and 30°), and one flat roof. During the runoff event presented (see Fig. 10) the mean concentrations of suspended solids in runoff related to that of rain \(C_{\text{SS, min}} = 17 \text{ mg dm}^{-3}\) were: tar felt roof 260%, pantile roof 210%, fibre cement 280%, zinc sheet roof 400%, and a flat gravel roof 26%. During the first 0.25 mm of runoff, the concentrations of particulate Pb differ greatly. We explain this by different amounts of dry deposition before onset of rain and different washoff efficiency of suspended solids caused by roof roughness and resistance to flow rather than pH-variation (\(\Delta \text{pH} < 0.5\) during the event).

**Chemodynamics of Cu and Pb During a Street Runoff Event**

Figs. 11 to 14 depict the temporal variations of various Cu and Pb fractions. We observe a well marked coherence between the temporal variation of coarse suspended solids and the concentration of Cu bound to those solids. However, the maximum concentration of coarse suspended solids does not coincide with the maximum concentration of coarse particle bound Cu. It is evident that during peak washoff of coarse suspended solids, these were only weakly contaminated. More clearly, this can be shown with the temporal variation of the specific content (mass of metal/mass of SS) of Pb and Cu in coarse suspended solids (Fig. 14), where we observe a concentration minimum after 3 hours at the time of peak runoff. In general, the specific Cu content decreased; particles with higher contamination were preferentially washed off. Further, at the time of the second concentration peak of coarse suspended solids, we do not observe a change in specific content. Thus, at this time a higher washoff of particles leads to a proportional increase in particle bound copper. The washoff of Cu bound to fine suspended solids follows their washoff with, however, a distinctly higher specific content at the beginning. The concentration of dissolved Cu decreases with time in the same way as \(\text{Cl}^-\) and electrical conductivity which show conservative behaviour.

The temporal variation of Pb bound to coarse suspended solids resembles that of Cu. However, we do not observe a general decrease of specific Pb content as for Cu. Dissolved Pb and Pb bound to fine particles show a temporal variation similar to that of \(\text{Cl}^-\) or electrical conductivity and fine suspended solids, respectively. Thus, these temporal variations are similar to those of Cu. However, during this event dissolved Pb concentrations were extraordinarily high. During other runoff events, dissolved Pb concentrations were fairly constant and in the range of the determination limit of \(c = 2.4 \text{ nmol l}^{-1}\).

The specific contents of trace metals on fine particles are greater than for coarse particles. However, considering the far greater surface area of the small particles, this difference in concentration is surprisingly low.

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REFERENCES


