Evaluating the Variation of Dissolved Metals on a Highway Roadside Using a Generalized Additive Mixed Model (GAMM)

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Abstract

Assessing metal-concentrations in roadside soils requires a better understanding of the extent to which they are affected by different environmental factors such as soil-texture, depth, pH, runoff concentration and precipitation Monthly data of dissolved Cd, Ni, Cr, Pb, Cu and Zn concentrations in three different roadside soils (sandy loam, gravel (0-32 mm) and a mixture of sandy loam and gravel) were measured during a two-year lysimeter field study at different depths. The data was used to assess the variation of trace elements and how they were affected by environmental factors. For data interpretation, generalized additive mixed models (GAMMs) were used to explore the complex behavior of metals in heterogeneous soils by detecting linear and nonlinear trends of metal concentrations in the soil solution. As a result, the modeling approach showed that Cd, Ni, Cr, Pb, Cu and Zn concentrations are functions of different environmental variables, which have either linear or nonlinear behavior. All investigated metals showed that pH could explain their variation. With exception of precipitation, Ni and Cr variations can nearly be explained by the same environmental factors used in this study (time, pH, infiltration volume, roadside soil type, runoff concentrations and depth). During the study period, we found that Zn variation can be explained by its nonlinear relationship with all the significant studied environmental factors. As the depth increases from the surface to 30 cm of depth, the metal concentration of Cd, Ni, Cr, Pb, and Zn increases. Surprisingly, the roadside soil consisting of gravel has the lowest organic carbon and showed the lowest median concentration of Cd, Ni, Pb, Cu and Zn at 30 cm. Moreover, the model showed that the surface runoff volume has no effect on the metal variation in the soil solution.

Keywords: metals, roadside soil, generalized additive mixed models (GAMMs), environmental factors

Capsule: We were able to explore the complex behavior of metals in heterogeneous soil systems by detecting the linear and nonlinear dynamics of metals in soil solutions.

Introduction

Road traffic has long been known to be a major source of pollutants in the environment. The worldwide growth in traffic volume (OECD, 2013) has led to increasing emission rates, which in turn result in increasing accumulation rates, especially in road dust, runoff water and in roadside soils (Monks et al., 2009; Werkenthin et al. 2014, Padoan et al. 2017). The distribution and amount of pollutants introduced in the environment is determined by different factors, such as traffic intensity (Ward, 1990; Arslan and Gizir, 2006), climatic conditions and events, vegetation cover and highway design (Barbosa and Hvitved-Jacobsen, 1999; Pagotto et al., 2001; Huber et al., 2016, Liu et al., 2016). Moreover, galvanized crash barriers, traffic control devices and road signs release a considerable amount of pollutants due to splashing and rainwater (Van Bohemen and Van de Laak, 2003; Kluge et al. 2014). The composition of traffic-derived pollutants is various and multifaceted. The most well-known pollutants emitted are carbon monoxide, nitrogen oxide, hydrocarbon, sulfur dioxide, polycyclic aromatic hydrocarbons and metals (Kayhanian et al., 2012).

Of the traffic-derived pollutants, metals are those that have the utmost importance because they are not degradable and have particularly high toxicity for plants, microorganisms, animals and humans (Wuana and Okieimen, 2011). Among other metals, Zn, Cd, Pb, Cu, Cr and Ni are the most well-known and studied metals in roadside soils (Münch, 1993; Folkeson et al., 2009; Kayhanian et al., 2012; Men et al., 2018). The metal concentrations in roadside soils decrease mostly with distance from the road edge and at increasingly greater soil depth (e.g., Harrison et al., 1985; Pagotto et al., 2001; Modrzewska and Wyszkowski, 2014; Werkenthin et al., 2014; Huber et al., 2016). The mobility of metals depends greatly on soil pH and organic matter content, as has been noted in many studies (e.g., Turer and Maynard, 2003; Walraven et al., 2014). Turer and Maynard (2003) showed a strong positive correlation between soil organic matter and certain metal concentrations. Hjortenkrans et al. (2008) estimated a mobilization of the easily exchangeable metal fraction after extreme climatic conditions, such as dry periods in connection with oxidation or intensive rain events with reducing processes. Furthermore, the application of de-icing salts in the winter often leads to higher dissolution, dispersion and leaching of organic matter in roadside soils, which in turn causes an increase in metal mobilization rates in roadside soils (Bäckström et al., 2004; Ramakrishna and Viraraghavan, 2005, Fay and Shi, 2012). High metal accumulation and leaching by the previously described processes may lead to high concentrations in roadside soil solutions (Pagotto et al. 2010; Werkenthin et al. 2014), which in turn could result in contamination of groundwater and/or receiving waters, with all the corresponding harmful effects on the environment.

From an ecological and hydrological point of view, it is therefore highly important to evaluate the of road runoff metal concentrations and soil solution concentrations of roadside environments, but this is a complex task because the transport mechanisms are potentially nonlinear. To the best of our knowledge, only a few studies have dealt with the on-site soil solution concentrations beside the affected roads and highways (Reinirkens, 1996; Dierkes and Geiger, 1999; Bäckström et al., 2004; Kocher et al., 2005; Kluge and Wessolek, 2012; Kluge et al., 2014; Werkenthin et al., 2016). All these studies used classical summary statistics to present the variability of dissolved metal concentrations in soil solutions, and they did not at all address the temporal dependencies and multivariate environmental effects.

Varied methods have been used to predict the metal concentrations in road runoff, sediments and soils. These have included classical summary statistics (Wang et al., 2013; Pal et al., 2011), regression models (Yan et al., 2013), geospatial analysis (Guo et al., 2012; Raulinaitis et al., 2012; Ignatavičius et al., 2017). Sauvé et al. (2000) collected different soil-liquid partitioning coefficients (Kd) in soils for the metals cadmium, copper, lead, nickel, and zinc, which they derived from over 70 studies of various origins. They used multiple linear regression models and showed that the Kd Coefficients are a function

of soil solution pH, -organic matter, and -total metal concentrations. However, the R^2 values of their model were low. One reason for this might be the nonlinear behavior of some metals.

Casey et al. (2006) compared mean invertebrate metal concentration between two periods to capture the temporal trend of trace metals, using mixed models to compare sediment metal levels across years and land-use types. However, their models did not mention the nature of nonlinear patterns of trace metals. Wen et al. (2012) studied the temporal variation of dissolved heavy metal concentrations by using only the effects of rainfall events. Moreover, most previous studies did not include the influence of other environmental variables like soil properties, which could also contribute to the variability of dissolved metals in soil. Recently, Lequy et al. (2017) assessed the temporal trends of trace metal concentrations in mosses by using a generalized additive mixed model (GAMMs) approach that included the sampling protocol (sampling period, collector and moss species) to describe the variability of the concentrations in mosses. As they mentioned, it was the first attempt to analyze the temporal trend and variability of metal concentrations by using GAMMs. The authors highlighted the importance of accounting for nonlinear temporal variations in metal concentrations, but only the parameters of time, collector, and moss species were used as explanatory variables in their models.

The objective of this study is to identify the environmental data used in this study that could explain the variation of dissolved heavy metal concentrations in roadside soil solutions. To achieve this objective, we use as response variables mixed modeling on repeated measurements of concentrations over two years while basing the explanatory variables on different environmental variables such as soil properties and meteorological factors.

Material and Methods

Study area

In this study, data from a section of the Highway BAB A115 near the city of Berlin, Germany (52° 23′ 27.5″ N, 13° 09′ 42.8″ E) is selected as an example. The highway has an established speed limit of 120km/h and is surrounded by a mixed pine-oak forest stand on sandy soil beginning at a distance of about 15 m from the road. The traffic volume ranges from 63,000 to 80,000 vehicles per day, with 6-7% of them constituting heavy traffic (Fitschen and Nordmann, 2012)

Along this section, the highway is 34 m wide (including the central reservation) and has three concrete lanes in each direction. The sealed road surface has a width of 15 m in each direction and is drained across the adjacent embankment. The relative elevation of the highway is about 2 m; the longitudinal inclination is 1% and no crash barriers are installed. Annual average temperature is 8°C and precipitation is 580 mm (see also the Supplementary Data in Fig. 1.).

Highway Lysimeter

Soil solution, road runoff and climate data

At this section of the highway were installed three lysimeters of polyethylene (PE), each with a length of 150 cm, a width of 100 cm and a height of 60 cm, together with three runoff lysimeters.

The lysimeters were placed directly beside the road edge and filled with different soil materials that were recently used for embankment construction in Germany:

Sm1: Reference embankment material (surrounding topsoil of arable land) – Sandy loam

Sm2: Mixture of Sm2 with 15% of Sm1 – Gravel (0-32 mm) mixed with sandy loam

Sm3: Base course construction material from natural broken rock and sand – Gravel (0-32 mm)

The investigated embankment soils were obtained from a nearby highway construction site. The thickness of the embankment layer was 20 cm, equivalent to a soil volume of 0.3 m^3. The lysimeters had three discharges: one for collecting the surface runoff and two for collecting the soil solution at

depths of 15 cm and 30 cm (Fig.1). The water volume was measured by tipping buckets (type: V2A, UP- GmbH). Aliquots were collected as composite samples in PE vessels. The runoff lysimeter had the same surface area as the embankment lysimeters (1.5 m²); but they were only 15 cm high (length: 150 cm, width: 100 cm, height: 15 cm) and were filled with lime-free, washed pebble gravel (Ø 5.6-8 mm) to meet the road safety regulations. They had only one discharge at the bottom and were placed between the embankment lysimeters SM1-SM3 to quantify the variability of runoff quantity. Water volumes of road runoff were also measured by pre-described tipping buckets for automatic recording. In addition, a weather station was installed to measure precipitation, temperature, humidity and potential evaporation at 15 min. intervals. For more details of the lysimeter study site and construction of the highway lysimeters, please see Werkenthin et al., 2016.

Sampling of soil solution at three depths for each embankment lysimeter and runoff lysimeter was conducted once a month from November 2012 to December 2014. Samples were analyzed in the laboratory for Cadmium (Cd), Copper (Cu), Zinc (Zn), lead (Pb), Nickel (Ni), Chromium (Cr), pH, electrical conductivity (EC) and dissolved organic carbon (DOC). Part of the data (July 2013 to July 2014) is already published (Werkenthin et al., 2016).

Figure 1. Schematic sketch of the embankment lysimeter and view of the monitoring site at the Highway A115, Germany

Laboratory analysis
Dissolved concentrations of Cd, Cu, Cr, Ni, Pb and Zn were determined in the soil solution and road runoff. The samples were filtered through a 0.45 µm filter (Satorius; cellulose-acetate) and acidified with 5M HNO3 to pH < 2. All samples were measured with ICP-OES (Thermo Fisher ICAP 6000) in accordance with DIN EN ISO 11885. Limits of quantification (LOQ) were 0.09 (Cd), 0.3 (Cr), 0.8 (Cu), 0.8 (Ni), 2 (Pb) and 0.1 (Zn) µg L-1. In order to ensure good measurement quality, the maximum permissible deviation for individual metal recovery from the reference material (BRM 06C, Germany) was set to ± 8% (Kluge et al.2014).

Methodology
Nonparametric models
Monthly repeated measurements for two years on sampling lysimeters induces a structure in the data that violates the assumption of independence between samples. Therefore, we used generalized additive mixed models (GAMMs), which allow for dependence between samples and for the nonlinearity of covariants (Zuur et al., 2009). GAMMs are an extension of generalized additive models (GLMs) that allow the predictor function to also include random effects.

The GAMM could be described as:

$$g(\mu_{it}) = X_{it}^T \beta + \sum_{j=1}^{m} \alpha_{(j)}(u_{itj}) + Z_{it}^T b_i$$

Where g is a link function, $X_{it}^T \beta$ is a linear parametric term with the parameter vector $\beta^T = (\beta_0, \beta_1, \dots, \beta_p)$ that includes the intercept;

$\sum_{j=1}^{m} \alpha_{(j)}(u_{itj})$ represents the smooth and nonlinear function, it is an additive term with unspecified influence functions $a_{(1)}, \ldots, a_{(m)}$; and

$Z_{it}^T b_i$ contains the cluster-specific random effects.

If no linear component is included, the model is considered to be nonparametric. A model whose predictions consist of both linear and unspecified nonlinear functions of predictor variables is considered to be a semi parametric model.

For GAMM, we used the metal concentrations (log scale) as a response variable and the following predictors as fixed effects: time (represented by a numeric vector from 0 to 743 days after 2012-11-21); EC (microSiemens/cm); pH; rainfall (mm); soil temperature (C°); ; infiltration (l); soil moisture (mm-3/mm-3); surface runoff volume (l); and runoff concentration (microgram/l). The factors of soil type (Sm1, Sm2, and Sm3) and soil depth are also included as fixed effects. While the random variables refer to the points at which the repeated measurements were taken. These points are identified by the combination of soil depth and soil type. Visual inspection of residual plots did not reveal any major deviations from homoscedasticity or normality. Specifically, the metal data was log-transformed to meet the demand for residual normality and homoscedasticity. In all the models, the time covariant was kept to adjust time trends, even when this predictor was not significant.

In the first run of the model, we hypothesized that the response of metal concentrations would have nonlinear relationships with the predictors, as we mentioned above. Using the GAMMs of the MGCV package (Wood, 2006) implemented in R version 3.3.0 (R Core Team, 2017), the GAMM model for the first run could be expressed as:

$$
\left.
\begin{aligned}
form &= as.formula(\log(metal\ concentraion)) \sim (time\ ) \\
&+ materila * depth + s(EC) + s(pH) + s(precipitation) \\
&\quad + s(soil\ temperature) + s(infiltration_{15cm}) \\
&\qquad + s(infiltration_{30cm}) + s(soil\ moisture) \\
&+ s(surface\ runoff\ volume) + s(runoff\ concentratoin) \\
\\
mod &< -gamm4(form, data, random = \sim(1/ID))
\end{aligned}
\right\} \quad (1)
$$

where ID refers to the point where we obtain the sample from either the runoff or the soil solution according to the soil type and depth. The s() represents the spline functions that allow the curve to bend in order to describe the observed metal data. We also hypothesize that the metal variation is explained by the depth for each soil type. Therefore, we show in the model the interaction between soil type (material) and depth.

The p-value is used to determine which nonlinear relationship in model (1) can be considered linear and which explanatory variables should be excluded from model (1). When these processes are accompanied by a decrease in the Akaike information criterion (AIC), then the model is preferred. We choose the model when the lower AIC is obtained with significant explanatory variables (Burnham and Anderson, 2004).

Results

Descriptive analyses of the dissolved concentrations at the different highway embankments

The raw data of the dissolved soil solution concentrations of the three embankment soils and the runoff concentrations during the measurement period is presented in fig. 2. The concentrations at 30 cm depths of the three different embankment soils often show higher ranges than at shallow depths (Fig. 2).

The soil solution concentrations of SM1 show the highest range at 15 cm and decrease at 30 cm, while the concentration range at SM2 increases with depth (Tab.1). The median dissolved metal concentrations in soil solution are highest in the SM1 embankment at soil depths of 15 and 30 cm when compared with SM2 and SM3, with the exception of Cd (Tab. 1). SM3 has the lowest median metal concentration at 30 cm, except for Cr, where it is slightly higher than SM2. The runoff concentrations of Pb, Cd and Ni are mostly lower than the concentrations in the soil solution at 15 and 30 cm of the three different embankment soils (Fig. 2), but they are nearly in the same range for SM2 and SM3.

The metal concentrations of all lysimeters at 30 cm show an increase during the wintertime, whereas the concentrations decrease in spring before increasing again in summertime (Fig.2). Comparing the three different embankment soil types, the SM1 embankment soil type seems to react as a source for these metals.

Table 1.: Median, min and max dissolved metal concentrations for three embankment soils at three different depths during the measurement period

The descriptive analysis mentioned above visually confirms the existence of variation in metal concentration according to soil type and depth over time. To understand these metal variations and the influence of other environmental factors, an advanced statistical method will be used: the generalized additive mixed model (GAMM), which we are going to explain in the following sections.

Figure 2. Raw data of the dissolved soil solution concentrations of the three different embankment soils and the runoff concentrations during the measurement period

Effects of environmental factors on metal variations according to GAMM

An assessment of the effects from environmental factors on the variation of dissolved metals at the roadside was conducted for each metal by selecting the best GAMM for each one. The significance analysis of the model shows the explanatory variables for each metal to be the following: **time for** Cr, Cu, Pb, Ni and Zn; **pH** for Cd, Cr, Cu, Pb, Ni and Zn; **depth** for Cd, Cr, Pb, Ni and Zn, **EC** for Cd and Cu; **precipitation** for Cu, Ni and Zn; **soil type** for Cr, Cu and Ni; **soil temperature** for Pb; **soil moisture** for Zn; **infiltration** for Pb, Ni, Cu, Cr and Cd; and **runoff concentration** for Ni and Cr (Table 3). For all metals, the model showed no significance in the interaction between soil type and depth. Moreover, the surface runoff volume could not explain the metal variation in the soil solution.

The following provides more details about the how the explanatory variables could explain the metal variation investigated in this study over the experiment period.

Figure 3: Explanatory variables of GAMMs on the metal concentrations at the investigated embankment soils

<u>*Time*</u>

Taking into account that the constructed embankment needs time to settle, we observed that the concentrations of Cu and Cr somehow decreased linearly after two years of the field experiment when compared with the initial concentrations (Tab. 2). This might be an effect of leaching from the soil matrix (see Tab.3 and Fig.3). On the other hand, the time variable showed a nonlinear effect on the dissolved Pb and Zn concentrations in the soil solutions of the roadside embankments. Pb and Zn have higher solution concentrations at the beginning and lower ends of the sampling period (Fig. 3). In this study, only the Cd variation could not be explained by the time variable.

Table.2: Metal concentrations of the embankment soils at the beginning of the field study

<u>*pH*</u>

The pH shows linear effects on Cu and Cr concentrations. It is generally agreed that pH is the key factor that affects concentrations of soluble and plant-available metals (Brallier et al., 1996). The metal solubility in soils is inclined to increase at lower pH and decrease at higher pH values, as has been demonstrated in numerous laboratory studies (Tills and Alloway, 1983, Sanchez-Camazano et al., 1994 and Rieuwerts et al., 1998), but this is only partially true for our data, which was generated from a lysimeter field study. We can see in Table 3 that the coefficients of Cr and Cu with pH are positive. The Cu concentrations increase with increasing pH within the range of 6.5 to 9.0. This finding could be explained by soluble metal-organic complexes forming above pH 6 (Brümmer et al. 1986). The organic matter preferably immobilizes Cu in soils. The solid and dissolved fraction of organic matter can substantially affect mobility (Temminghoff, 1997). A calculation by Tipping and Woof (1990) shows that increasing soil pH by 0.5 units could lead to an increase in approximately 50% in the mobilized organic matter. We therefore assume that increase in the Cu increasing with the pH is related to enhanced leaching of DOC. Sauvé et al. (2000) showed that total Cu, pH, and DOC are the most significant variables controlling Cu solubility in soils. Adsorption of Cr characteristically decreases with increasing pH due to the decrease in the positive surface charge of the soils (Rai et al., 1986; Zachara, 1989; Khaodhiar et al., 2000). Moreover, the influence of pH on the concentrations shows a nonlinear trend for Cd, Zn, Ni and Pb (Fig. 3). In the case of Cd, no changes in the concentrations were observed when pH ranges between 7.0 and 8.2. The concentrations of Pb decrease with increasing pH. Brümmer et al. (1986) showed the strong relationship between Pb concentrations and soil pH. They described a strong decrease in soil solution concentrations with increasing pH. The correlation was even higher when the concentrations were higher. The Ni concentrations decrease sharply when the pH value is higher than 8.5 (Fig. 3). This may be associated with the start of the hydroxide precipitation reactions with the Ni^{2+} and $NiOH^+$ species (Sen Gupta and Bhattacharyya, 2006). Zn decreased drastically under

alkaline conditions and then increased after pH > 8, because soluble metal-organic complexes are formed in this pH range (Brümmer et al. 1986).

It is interesting to see that metals which have a nonlinear relationship with pH also have a nonlinear relationship with the time covariant. pH varies over the year due to rainfall events. Häring et al. (2017) reported that water quantity significantly affected pH over time.

*Table 3: Best selection GAMMs for each element according to AIC including its coefficient estimates for linear and non-linear (nl), with: Time(T), depth (D), EC (E), pH (P), humidity (H), soil material (S), evapotranspiration (Ev), runoff concentration (R), precipitation (Pr), soil temperature (St), soil moisture (sm). s() refers to spline function (non-linear), i15 and i30 are infiltration rates at 15 cm and 30 cm respectively. The term **n.l.** refers to non-linear relationship.*

Precipitation

The increase in Cu and Ni concentrations with precipitation (Tab. 3 and Fig. 3) might be explained by temporal and spatial variations of dissolved organic carbon (DOC) in runoff water and higher rates of microbial decomposition of organic compounds. High pH (in our study 6-9) and DOC increases the mobility of Cd, Ni, and Zn (Impellitteri et al., 2002). Orlović-Leko et al. (2009) and Pan et al. (2010) reported strong seasonal variations of organic carbon in rainwater samples and explained these findings through a combination of different climatic conditions, i.e.: the amount of precipitation, temperature, humidity, site specific parameters and proximity to anthropogenic and/or biogenic emission sources. Only Zn shows nonlinear behavior with the amount of rainfall. Runoff concentrations of Zn increase during intensive rainfall events (Fig. 2). Explanation: Metal road installations such as crash barriers are generally galvanized with Zinc. Due to corrosion by rain and spray water, Zn in particular as well as Cd and Cu are released into roadside soils (Dierkes and Geiger, 1999; Barbosa and Hvitved-Jacobsen, 1999; Kluge and Wessolek, 2012. They all reported higher Zn concentrations in runoff and soils as a result of the corrosion of crash barriers.

EC

The variable EC shows linear effects on the soil solution concentrations of Cd. This is easily explained by the strong increase in EC concentrations in runoff and the extended time during the winter period the when the soil solution was exposed to de-icing salts (Fig. 2). The presence of high Cl concentrations leads to a strong decrease in the adsorption of Cd ions in soils (Doner, 1978; Boekhold et al., 1993; Lumsdon et al., 1995). The strong influence of salt concentration on the mobilization of metals has already been observed by many other authors dealing with the topic of road runoff and roadside soils (e.g., Bauske & Goetz, 1993; Amrhein and Strong, 1990, Amrhein et al., 1992; Bäckström et al., 2004, Ramakrishna and Viraraghavan, 2005). Li et al. (2015) determined an extensive mobilization of Cd soil leachate by salts, accounting for about 21% of the total Cd in the soil. Bauske & Goetz (1993) examined concentrations of Cd and Zn that had increased by a factor of 20 in highway soil solutions during the utilization of de-icing salts in winter. Salimi et al. (2015) found that the Cl- ion formed complex ions with Cd to CdCl+, CdCl3-, and CaCl4-. The application of Cl- might dissolve the adsorbed soil Cd to form complex ions.. The regular relationship between EC and metals concentration is positively linear. In this study, the GAMM model shows a nonlinear relationship between EC and Cu (Fig xxx). The use of road salt may result in an increased mobilization of Cu due to complexion with chloride ions (Doner, 1978; Lumsdon et al., 1995). An increase in soluble Cu by extraction tests with calcium magnesium acetate solutions has been reported by Elliott and Linn (1987).

The nonlinear findings here between Cu and EC also agree well with Makarychev et al. (2013). They used a conductometric and potentiometric titration of water extracts (Cu, Al and Pb). A nonlinear dependence of electrical conductivity on water extracts was observed with the added concentration of metals. They explained their findings by metal organic complexes forming with the participation of metal ions. Our results show that the highway runoff in wintertime combined with high amounts of road de-icing agents (high EC) might lead to a higher release of sorbed metals from the organic matter of the SM1 and SM2 (Fig.2;Tab.2).

Depth

The positive coefficients of Cd, Cr, Ni and Pb at greater depth indicate an increase in the concentration with soil depth, and the negative coefficient of Zn indicates a decrease in Zn concentration with soil depth (Table 3 and Fig. 3). Cd is the most mobile metal in soils because a large proportion is associated with easily exchangeable and carbonated chemical fractions, as several studies have pointed out (Harrison et al., 1981; Gibson and Farmer, 1984; Chlopecka et al., 1996).

Soil Type

The coefficients in Table 3 indicate how much the concentrations of Cr, Cu and Ni decrease from Sm1 to Sm2 and from Sm1 to Sm3. This is because the Sm1 has higher organic matter than Sm2 and Sm3 (Table 2), and thus the dissolved Cu concentrations are higher as we explained above. Cu in soils is known to be dominant in the organic and residual phases (Harrison et al., 1981, Gibson and Farmer, 1984; Hamilton et al., 1984; Ramos et al., 1994; Ma and Rao, 1997).

The results in Table 3 regarding soil material agree well with the results found by Turer et al. (2003). They concluded that the mobility of Ni and Cr appears to be controlled by the original soil material rather than by anthropogenic sources.

Infiltration volume

There is a negative relationship between Cd, Cu, Ni and Pb and the infiltration volume (Tab. 3 and Fig. 3). Pb was largely associated with particles (90%), as reported in the previous study on the same data (Werkenthin et al., 2016). The dilution could be one reason for a decrease in dissolved Pb concentrations with infiltration volumes at 15 cm.

Soil temperature

The soil temperature has a significant nonlinear effect on the Pb, the concentration of Pb increases from 0 to 15 with an increase in temperature and then decreases (Fig. 3). A decrease in dissolved Pb at higher temperatures could be explained by Cornu et al. (2016), who found that the affinity that dissolved organic matter (DOM) has for metals was indeed suspected to increase with soil temperature.

Runoff concentration

Runoff concentration has a nonlinear effect on the dissolved Cr and Ni concentrations (Fig.3). The concentrations increase sharply at the beginning, and then continue to increase but slowly. The pH and ionic strength (the total ion concentration in the solution) affect the Ni adsorption. Scheidegger et al. (1996) observed an increasing Ni adsorption at pH values lower than 7, with a decrease in the ionic strength. At pH > 7.0, Ni adsorption also seems to be affected by the ionic strength. This finding could explain the nonlinear relationship that Ni and Cr have with runoff concentration. Moreover, as Turer et al. (2003) reported that soil material has a significant effect on dissolved Ni and Cr, the runoff concentrations of dissolved Ni and Cr affect the mobility of dissolved Ni and Cr in roadside soils.

In general, the results show that time and pH explanatory variables have the most significant effects on the variation of dissolved metal concentrations in the soil solutions studied here. Regarding the issue of choosing an adequate embankment soil that provides enough safety and metal retardation to prevent groundwater contamination, GAMM allows distinguishing between three roadside soil types in order to establish which has the best possible retardation. The model demonstrated that the embankment soils with higher OM show higher dissolved soil solution concentrations of Ni and Cr than the embankment soils with lower OM. Therefore, the OM content of the embankment soils affect the solubility of Ni, Cr and Cu, because they are mostly bounded at the OM fraction and thus might be more easily remobilized. The higher Cu concentrations in our study might be due to the higher initial concentrations of the soil at the time when we began setting up the field lysimeter experiment (Table 2). Moreover, the runoff concentrations do not significantly affect Cd, Pb, Cu and Zn concentrations in the soil solution; only the Ni and Cr concentrations in runoff correlated with the dissolved Ni and Cr concentrations in roadside soil solutions. In addition, the modeling approach shows that the metal variation can be explained by the depth: as the depth increases from 0 to 30 cm, the concentration of dissolved metals increases (Fig. 3). Table 1 shows that, with the exception of Cr, the SM3 at 30 cm depth has the lowest concentration of dissolved metals.

Our model results mostly agree with other studies that used controlled laboratory experiments to investigate individual metal behaviors. Furthermore, partially higher Ni, Pb and Cr concentrations in soil solutions at increasing soil depths suggest that a metal translocation occurs from the upper to the lower horizons within the soil profiles, thus leading also to the assumption that transport hot spots exist.

Conclusions

This study assesses the effects of different environmental factors on the variation of dissolved metals in roadside soils. Monthly data of dissolved Cd, Ni, Cr, Pb, Cu and Zn in the soil solution concentrations of three different roadside soils were measured at different depths over a two-year period in a lysimeter field study.

Generalized Additive Mixed Models (GAMMs) have been used to interpret the multiple data derived from a lysimeter field study at a roadside. The chosen approach enabled us to explore the complex behavior of metals in heterogeneous soil systems by detecting the linear and nonlinear dynamics of metals in soil solutions.

Regarding the EC, the GAMM model allows us to show only a nonlinear relationship between EC and Cu. Generally, metal solubility tends to increase at lower pH and decrease at higher pH values. However, this is only partly true for our data, which are gained from a lysimeter field study. The GAMM model results show only that Cu and Cr soil solution concentrations have a positive linear relationship with pH. In our case, the modeling approach showed that pH and soil material composition play the most important roles in terms of metal release in roadside soil. The study shows that variations of metal concentrations can be explained by the depth: as the depth increases from the surface to 30 cm, the metal concentrations increase, with SM3 having the lowest median of dissolved concentrations of Cd, Ni, Pb, Cu and Zn at 30 cm. In our case, SM3 has the lowest content of organic carbon and is the most effective embankment material for reducing soil water pollution from dissolved metal concentrations. This is a surprising finding, because existing recommendations suggest using twenty or more centimeters of thick topsoil with a high ratio of organic carbon to ensure high sorption capacity for infiltrated runoff. The highway runoff in wintertime and high amounts of road de-icing agents might lead to a higher release of sorbed metals from the organic carbon of the SM1 and SM2 when combined with higher amounts of organic matter.

One interesting matter shown by the model is that the surface runoff volume does not affect the metal variation in soil solutions.

Using the GAMM for interpreting heterogeneous roadside soil solution data has two main strengths. First, the mixed part of the model takes into account the dependencies in the data. This is because our measurements were repeated and thus induced a structure in the data that would violate the assumption of independence between samples. Second, due to the nature of the irregular fluctuations of metal concentrations over time, polynomials fail to describe the observed curvature in the data. By including smoothing functions for the explanatory variables, e.g., spline functions, the additive part of the model allows the curve to bend in order to describe the observed data.

Overall, when using GAMM to analyze environmental data such as soil solution concentrations at the field scale, it gives a strong advantage to assessing the variation of metal translocation that is affected by different environmental factors.

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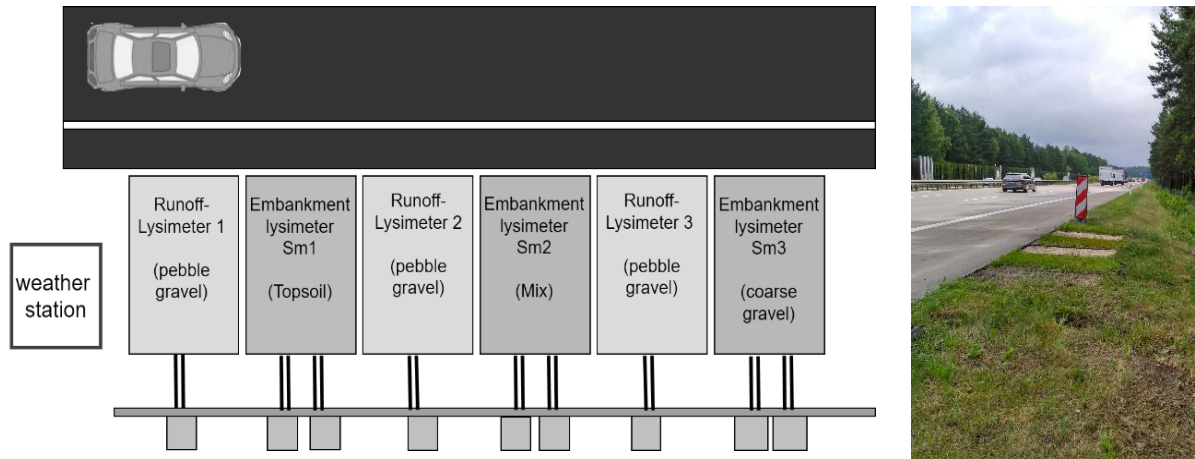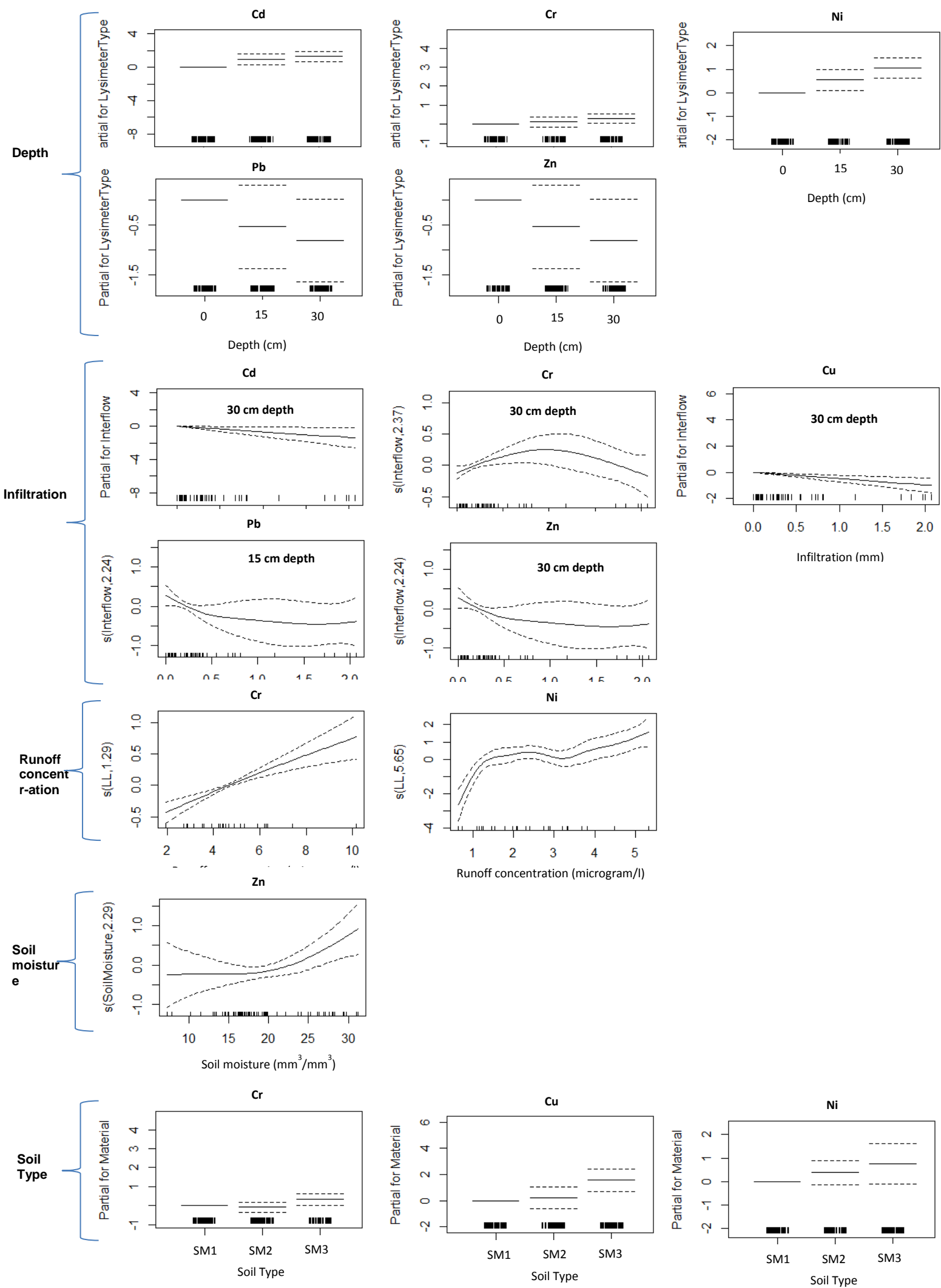
Figure 1. Schematic sketch of the embankment lysimeter and view of the monitoring site at the Highway A115, Germany

Figure 2. Raw data of the dissolved soil solution concentrations of the three different embankment soils and the runoff concentrations during the measurement period
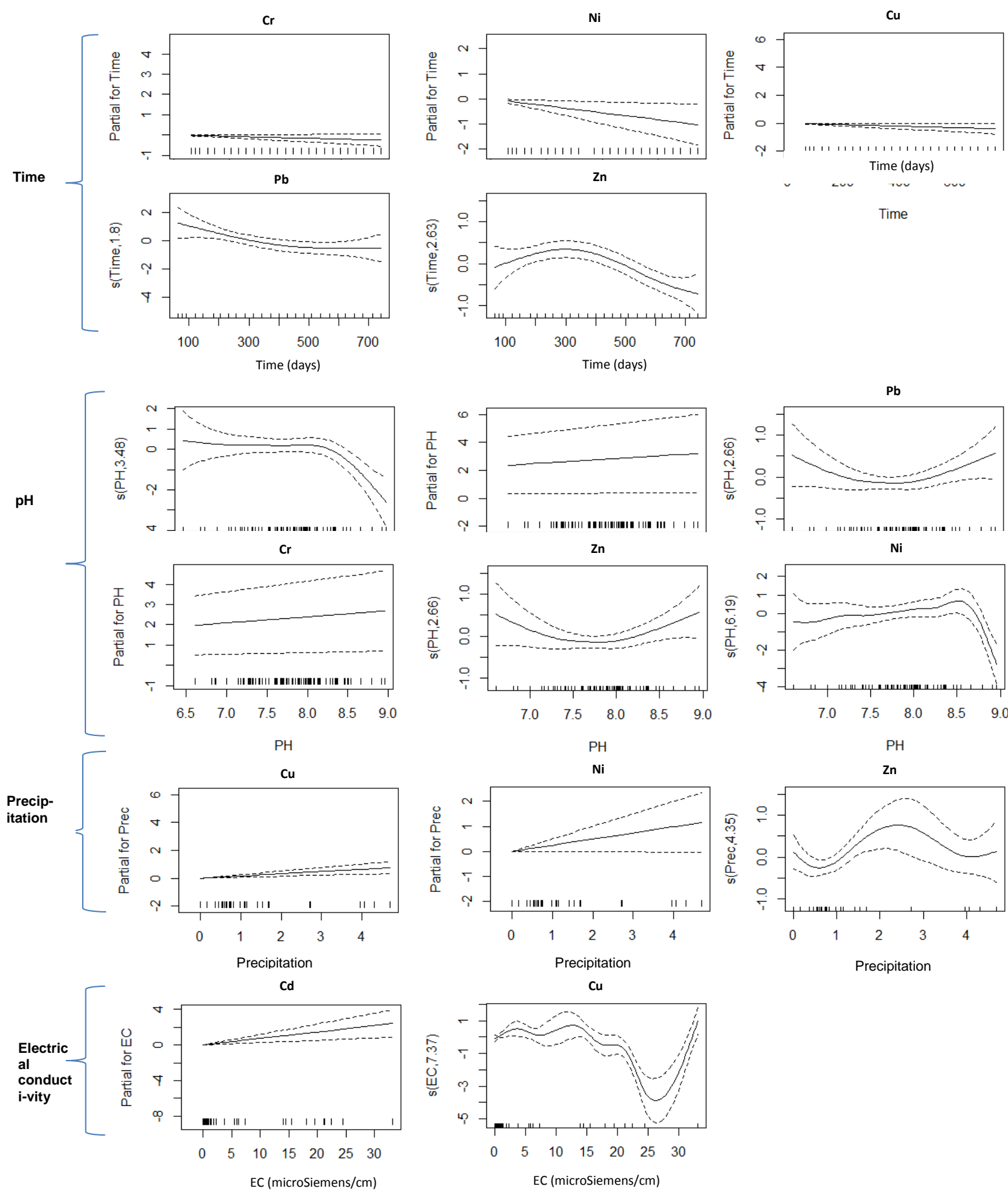
Depth

Cd

Cr

Ni

Pb

Zn

Depth (cm)

Depth (cm)

Depth (cm)

Infiltration

Cd

30 cm depth

Cr

30 cm depth

Cu

30 cm depth

Pb

15 cm depth

Zn

30 cm depth

Infiltration (mm)

Runoff concentr-ation

Cr

Ni

Runoff concentration (microgram/l)

Soil moisture

Zn

Soil moisture (mm^3/mm^3)

Soil Type

Cr

Cu

Ni

Soil Type

Soil Type

Soil Type

Figure 3: Explanatory variables that explain the variation of dissolved metal concentration used in GAMM

Table 1.: Median, min and max dissolved metal concentrations for three embankment soils at three different depths during the measurement period

	Depth (cm)	Cd	Cr	Cu	Ni	Pb	Zn
SM1	**0**	0.13 (0.01-0.53)	3.360 (1.33-15.03)	15.88 (7.55-45.70)	1.40 (0.71-4.97)	0.80 (0.01-3.80)	30.35 (6.55-233.90)
	15	0.15 (0.01-0.66)	4.55 (1.31-12.75)	35.85 (7.10-163.40)	2.60 (0.01-24.97)	3.80 (0.30-52.80)	24.45 (4.45-387.55)
	30	0.30 (0.01-4.06)	7.01 (0.1-19.05)	73.60 (9.60-393.60)	3.94 (1.38-35.20)	11.20 (0.01-59.84)	42.40 (9.50-96.65)
SM2	**0**	0.10 (0.01-1.75)	4.77 (1.90-9.20)	16.90 (5.55-123.20)	1.80 (0.01-8.10)	1.02 (0.01-3.80)	41.55 (17.40-151.35)
	15	0.14 (0.01-0.55)	4.23 (1.20-12.06)	13.43 (6.70-50.30)	2.53 (0.01-22.42)	0.74 (0.01-5.10)	25.18 (5.95-72.30)
	30	0.22 (0.01-1.34)	4.12 (1.30-18.15)	6.55 (0.10-26.36)	3.20 (0.01-16.32)	1.89 (0.01-8.20)	6.60 (0.20-49.30)
SM3	**0**	0.08 (0.01-0.36)	3.60 (0.71-13.31)	12.50 (7.10-44.90)	1.80 (0.82-10.73)	0.57 (0.01-4.50)	27 (6.40-412.10)
	15	0.30 (0.01-2.15)	3.65 (1.59-13.55)	13.90 (4.50-83.80)	3.88 (0.01-50.60)	2.25 (0.01-9.50)	12.30 (3.75-55.95)
	30	0.30 (0.01-1.75)	3.61 (1.25-24.60)	11.80 (3.35-90.70)	5.82 (1.09-29.10)	2.27 (0.01-9.90)	10.70 (0.45-95.55)

Table.2: Metal concentrations of the embankment soils at the beginning of the field study

	Cd	Cr	Cu	Ni	Pb	Zn	pH	C org
mg*kg-1							-	M.%
Sm1	< 0.2	5	20	<5	25	33	7.67	0.88
Sm2	< 0.2	< 5	5	5	5	19	7.57	0.40
Sm3	< 0.2	< 5	11	6	13	30	7.63	0.13

Table 3: Best selection GAMMs for each element according to AIC including its coefficient estimates for linear and non-linear (nl), with: Time(T), depth (D), EC (E), pH (P), humidity (H), soil material (S), evapotranspiration (Ev), runoff concentration (R), precipitation (Pr), soil temperature (St), soil moisture (sm). s() refers to spline function (non-linear), i15 and i30 are infiltration rates at 15 cm and 30 cm respectively. The term **n.l.** refers to non-linear relationship and the empty cells refer to be not significant with the metal variation.

	Cd	Cr	Cu	Ni	Pb	Zn
	Fixed effect: s(T)+s(P)+D+H+E+i30 Random effect: 1/S_D	Fixed effect: T+P+D+S+Ev+s(R)+s(i30) Random effect: 1/S_D	Fixed effect: T+P+S+s(E)+Pr+s(H)+ i30 Random effect: 1/S_D	Fixed effect: s(T)+s(P)+D+S+Pr+s(R)+i30 Random effect: 1/S_D	Fixed effect: s(T)+s(P)+D+s(St)+i15 Random effect: 1/S_D	Fixed effect: s(T)+s(P)+D+s(Ev)+s(Pr)+s(sm)+s(i30) Random effect: 1/S_D
(Intercept)	0.6416	-0.8517	1.137	1.040	-0.9389	3.511
Time		-0.0003	-0.0005	-0.0014	n.l.	n.l.
EC	0.0721		n.l.			
pH	n.l.	0.2983	0.3587	n.l.	n.l.	n.l.
Precipitation			0.1595	0.2457		n.l.
Soil.temperature					n.l.	
Infiltration_15cm					-0.0638	
Infiltration_30cm	-0.6792	n.l.	-0.4817	-0.4432		n.l.
Soil.moisture						n.l.
SurfaceRunoff						
Runoff.concentration		n.l.		n.l.		
Soil.materialSm2		-0.397	-1.332	-0.3761		
Soil.materialSm3		-0.3162	-1.566	-0.7541		
Depth15	0.9511	0.1228		0.5519	1.411	-0.5298
Depth30	1.273	0.2924		1.046	1.851	-0.8094