Determining metal origins and availability in fluvial deposits by analysis of geochemical baselines and solid–solution partitioning measurements and modelling

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Metal partitioning in floodplain deposits relative to anthropogenic and lithogenic sources.

ABSTRACT

Metals in floodplain soils and sediments (deposits) can originate from lithogenic and anthropogenic sources, and their availability for uptake in biota is hypothesized to depend on both origin and local sediment conditions. In criteria-based environmental risk assessments, these issues are often neglected, implying local risks to be often over-estimated. Current problem definitions in river basin management tend to require a refined, site-specific focus, resulting in a need to address both aspects. This paper focuses on the determination of local environmental availabilities of metals in fluvial deposits by addressing both the origins of the metals and their partitioning over the solid and solution phases. The environmental availability of metals is assumed to be a key force influencing exposure levels in field soils and sediments. Anthropogenic enrichments of Cu, Zn and Pb in top layers could be distinguished from lithogenic background concentrations and described using an aluminium-proxy. Cd in top layers was attributed to anthropogenic enrichment almost fully. Anthropogenic enrichments for Cu and Zn appeared further to be also represented by cold 2 M HNO_3 extraction of site samples. For Pb the extractions over-estimated the enrichments. Metal partitioning was measured, and measurements were compared to predictions generated by an empirical regression model and by a mechanistic–kinetic model. The partitioning models predicted metal partitioning in floodplain deposits within about one order of magnitude, though a large inter-sample variability was found for Pb.

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1. Introduction

Series of measures to increase river peak discharge capacities and actions to increase ecological quality of floodplains are currently implemented on a large scale throughout Europe and elsewhere. These actions result in more natural river and floodplain dynamics, including altered flooding frequency of floodplains. The latter affects many processes in the floodplain deposits, among which metal partitioning – and subsequently metal toxicity to biota. Flood events deposit new top-layer material, with or without newly deposited metals. Contamination risks are often expected, due to frequent exceedances of sediments quality criteria for metals. Actual risk management questions are thus to what extent:

(1) are floodplain deposits contaminated by recently deposited metals, and (2) do these locally elevated concentrations constitute a local ecological hazard? In addressing these questions, it has been observed that sometimes local (probably natural) background concentrations are higher than the risk-based maximum permissible concentrations (MPCs, e.g. Van de Meent et al., 1990). This apparent "mismatch" between risk-based environmental quality criteria and the actual situations measured in the field is problematic for risk management. Thus, there are both practical and conceptual needs for a refined, higher-tier, site-specific risk assessment, to account for site-specific conditions that determine the local mobility of metals and their availability for uptake. In this paper we address two optional items of such higher tiered risk assessment, firstly the origin of the metals and secondly the local environmental availability of metals.

Firstly, metals in floodplain deposits can originate from two types of sources: (1) lithogenic sources, resulting in sediment concentrations being related to the processes of erosion and

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sedimentation of metal-bearing geological formations upstream; (2) anthropogenic sources, that is: human activities that cause elevated metal concentrations in river waters and subsequently in floodplain deposits. Secondly, the availability of metals can vary between sites. Many studies show that total metal concentrations in sediments do not reflect the environmental availability (Allen, 1997), which is the fraction that potentially leads to accumulation in organisms (Campbell, 1995) and thus effects to them (Van Gestel, 1997). In this study we use a pragmatic definition of bioavailability, by distinguishing environmental availability ("environmental supply"), biological availability (uptake in specific species) and toxicological availability (the molecular interaction at the target site of toxic action; see Dickson et al., 1994). This study focuses on the environmental availability of metals in local substrates, with additional focus on the sources of the metals.

Various practical methods have been proposed to account for variations in environmental availability in risk assessment, many of them based on the assumption of solution-mediated exposure (Allen, 1997; Vink, 2005). Partitioning of metals between the solid and liquid phase can be measured directly, or it can be considered as being controlled by the properties of the metal itself in relation to soil/sediment properties, amongst which pH, pore water conductivity, ion concentrations, organic matter type and content and other metal-complexing ligands (Vink, 2005; Weng et al., 2002). In the latter case, measurement of these variables allows for model predictions of metal partitioning on the basis of a set of site parameters.

This paper aimed to assess in a quantitative way the source and environmental availability of metals in fluvial deposits to support higher-tier ecological risk assessment. Metal sources were distinguished according to lithogenic and anthropogenic origin (enrichment). Metals extractions were used to simulate the metal pool originating from anthropogenic origin. Metal availability in the enrichment was assessed from the solid–solution partitioning. Metal availability in the enrichment was measured in local samples, and considered according to solid–solution partitioning. Measurements were compared to the outcomes of two different partitioning models, to address model accuracy. The two selected models were an empirical regression model and a mechanistic–kinetic model. The regression models were calibrated on data from various Dutch river systems (Schröder et al., 2005). The mechanistic–kinetic model is Biochem-Orchestra (Meeussen, 2003; Vink and Meeussen, 2007). The latter model allows addressing the kinetic processes resulting from local dynamics in physico-chemical conditions, in turn associated to flooding and depth. Model results were compared to measured metal concentrations in the solid and pore water phase.

This paper specifically addresses the accuracy and practical usefulness of risk assessment approaches for stakeholders, such as river basin managers. Both geogenic baseline modelling and partitioning modelling may be of help to improve river basin management. Suter (1993) distinguishes prospective risk assessment (where one can only use models to predict local impacts on the basis of exposure assessments and dose-effect knowledge), and retrospective assessments (where one can use both measurements and models to investigate the implications of an existing site contamination). The data used in this study are typical for the purpose of practical risk assessment, where options for redevelopment of contaminated areas are evaluated.

2. Material and methods

2.1. Study area

Geochemical baselines and solid–solution partitioning of metals were studied in a floodplain area, "Afferdensche en Deestsche Waarden" (ADW, The Netherlands). This area of approximately 3 km^2 is situated along the River Waal (51°54′ N, 5°39′ E;

Fig. 1). About two-thirds of this area, located between the winter and the summer dykes, is flooded periodically during high river water levels in winter and spring. On average, the period of inundation is approximately 60 days in February and March (Zorn et al., 2005). During this period new sediment material is deposited (Thonon, 2005). For the rest of the year the river banks prevent flooding, resulting in oxic conditions in the top deposit layers in these periods (Van Vliet et al., 2005). Deposit textures range from sand to sandy loam and loam (Fluvisol). The field is predominantly used as grassland, which is grazed by young cattle during the summer (Van Vliet et al., 2005; Zorn et al., 2005).

2.2. Data

We collected metal concentrations (Cd, Cu, Pb and Zn) and other characteristics (solid phase: Ca, Fe, organic matter, cation exchange capacity, clay (<2 μm) and humidity; pore water phase: Cd, Cu, Pb, Zn, pH(CaCl$_2$), dissolved organic carbon) in fluvial deposits by compiling data from different studies carried out earlier. Gathered data were uniform or made uniform regarding their units, exact locations of sampling (x–y-coordinates) and the methodology of measurement. Data on metal fractions were considered specifically. Operational methods used to determine different metal fractions, with the associated (dissolved) metal fractions, were:

- *Aqua Regia* (HNO$_3$/HCl, 3:1 microwaved) → total metal concentration;
- 2 M HNO$_3$ extraction (microwaved) → hot acid extractable fraction;
- 2 M HNO$_3$ extraction (cold) → cold acid extractable fraction;
- 0.01 M CaCl$_2$ extraction → salt-exchangeable fraction; and
- pore water collection → pore water concentrations.

For further details on data and analytical methods on deep sediment layers see Middelkoop (2000); for top layers see Van Vliet et al. (2005) and Thonon (2005). The data collected from the top layers represent 100 sampling points from Thonon (2005) and 20 sampling points from Van Vliet et al. (2005). Samples were taken from two depths, at 0 to −5 cm and −5 to −10 cm. For some sample points, multiple measurements were made, yielding a maximum of 371 data points for 120 samples (see Table 1). Samples (31) were collected from deeper layers, to a maximum of −150 cm (Middelkoop, 2000). These sediments were deposited before 1850AD. Generally, concentrations decline with depth, following a distinct gradient, and the deepest layers are considered to represent natural, lithogenic background levels (Middelkoop, 2000). To give a summary overview, the measurements for the abovementioned parameters (median values), their variation (median absolute deviation), and the total amount of data collected are given in Table 1.

2.3. Data analyses (1): distinguishing anthropogenic enrichment

In order to quantify possibly elevated local metal levels that originate from anthropogenic sources, we compared local top-layer concentrations with a so-called geochemical baseline. Changes in the mineral composition of deposits occur slowly, so we assumed that metal concentrations in deeper layers can be used for calculating background levels. A baseline model is used to describe the variation of an elements' concentration in pristine conditions, in relation to key characteristics of the parent material and underlying lithogenic processes. Although the concept of geochemical baselines is well established, it is generally agreed that no single best method to determine them exists (Reimann et al., 2002). For Dutch sediments, many studies have shown that the aluminium content, measured as Al$_2$O$_3$ of particular unaltered clayish soils, is useful as a predictor for natural background metal concentrations (Mol et al., 2001; Huisman et al., 1997; Van Gaans et al., 2007; Van der Veer, 2006). Al$_2$O$_3$ is a main component of clay-rich mineral soils and is therefore directly related to the mineral fraction. Using regression analyses, the metal concentrations of the lithogenic part of unaltered deposits can be expressed as a function of Al (Spijker, 2005; Van Gaans et al., 2007), according to Eq. (1):

$$Me = a \times Al + b + e \tag{1}$$

where Me is the measured metal concentration (mg kg^{-1}), Al the measured aluminium concentration (mg kg^{-1}), a and b are regression constants, and e is the regression error.

To construct a geogenic baseline model for the relationship between Al-content and a specific metal, the data from the deeper floodplain layers were used (Middelkoop, 2000). The least median of square method was used, which reduced the residuals on the majority of the data points. Calculation was done with R software using the least quantile of square (LQS) algorithm (R Development Core Team, 2005). After the regression analyses, the linearity assumptions of the models were tested. The domain of 98% of the variation around the resulting baseline was derived. The variation can be ascribed to different levels of clay in a sample.

Local enrichments (Me$_{enrichment}$) of Cd, Cu, Pb, and Zn were calculated by subtracting the model-based lithogenic metal concentrations from the total metal concentrations (Me) of the recently deposited top layers. These predicted, local Me$_{enrichment}$ concentrations were further considered in the studies on environmental availability (see Section 2.5).
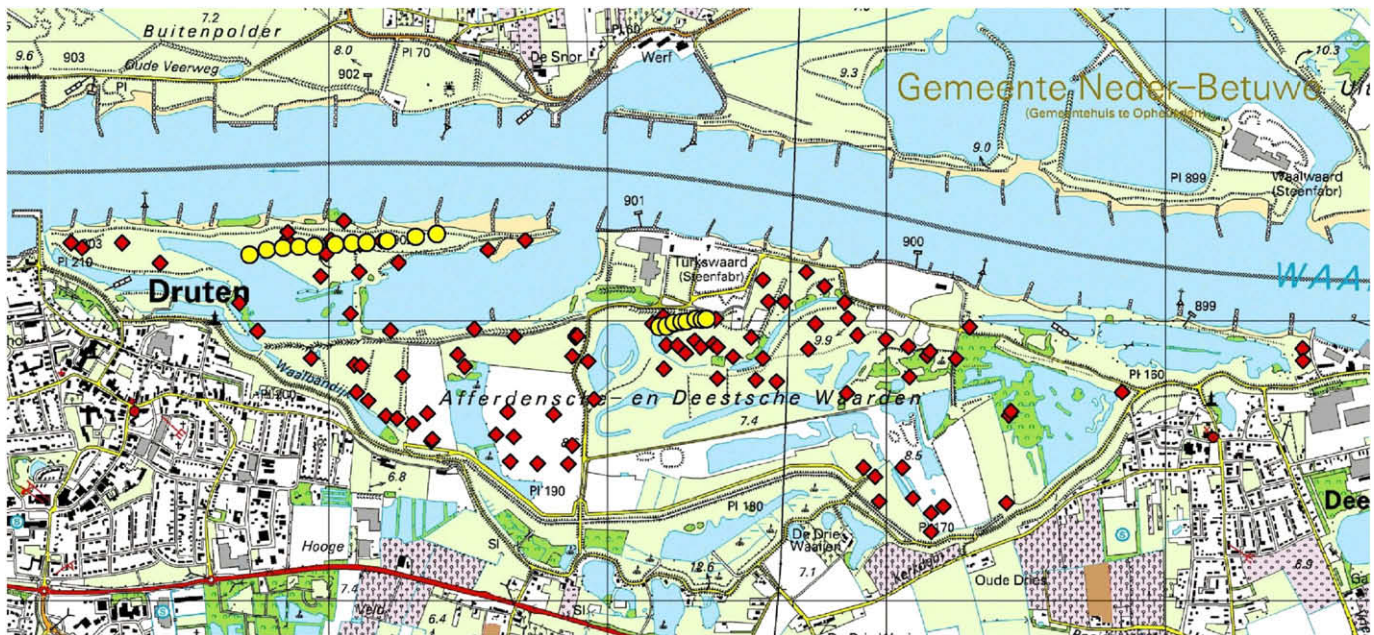
Fig. 1. Sample locations of the two studies of top-level sediments (circles from the study by Van Vliet et al. (2005), $n = 20$ sites, and squares from the study by Thonon (2005), $n = 100$ sites) in the floodplains of the Dutch River Waal (location ADW).

2.4. Data analyses (2): enrichment and top-layer extractions

Local enrichment concentrations of Cu, Pb and Zn were compared to measured, extractable concentrations (hot acid, cold acid extractions) to identify whether or not one of the measured, extractable fractions mimics the anthropogenic enrichment, and if so: which operational fraction.

2.5. Data analyses (3): model settings, data input and output

Two models were used to address environmental availability. Both models are based on conceptually different approaches to estimate partitioning, namely an empirical and a mechanistic–kinetic model. The models reflect a generic and easily applicable approach and a more site-specific and labour-intensive approach, respectively.

2.5.1. Model 1

The empirical models can be used to predict solid–solution partitioning of a metal based on statistically derived regression functions. The empirical models were derived from data collected in various Dutch floodplains (Schröder et al., 2005). The regression models were calibrated with 194 samples collected from 48 different floodplains from eight different Dutch river systems. These models assign an important role to DOC in the solid–solution partitioning of individual metals. From the study of Schröder et al. (2005) it was concluded that the empirical models accurately described the partitioning of metals in Dutch floodplain deposits, that is: the training set.

2.5.2. Model 2

The mechanistic–kinetic model Biochem-Orchestra (Meeussen, 2003; Vink and Meeussen, 2007) applies time and space dynamic calculations, based on mechanistic considerations on metal behaviour. The model contains modules for precipitation and dissolution of solids, based on an extended database of mineral components with up-to-date thermodynamic constants for the ferro/ferric and sulphur/sulfide minerals. Electrolyte strength of the pore water solution was adapted to EC-measurements. For speciation in the aqueous phase, the model normally uses the NICA DONNAN approach, adapted from Kinniburgh et al. (1996), to address sorption to dissolved organic matter. Speciation was, however, not specifically considered in this study. Calculations accounted for CO_2-diffusion. For the comparison with the output of the other models, we calculated with a scenario at which the water level was at -0.2 m, pH = 7.3 constant with depth; $[PO_4] = 0.02$ mol kg^{-1}; $[SO_4] = 0.01$ mol L^{-1}. To allow for comparison between model predictions and point measurements, the model was run to generate dissolved metal concentrations predicted at a depth of -10 cm, thus under oxic conditions, and likewise measured values for this depth were used. As an illustration, the scenario for three case studies is given for cadmium in Fig. 2.

Total metal concentrations of the top-layer samples, from which the lithogenic part was subtracted, were used as data for the environmental availability modelling. So, metal partitioning was addressed using calculated data on the anthropogenic part only ($Me_{enrichment}$, mg kg^{-1}).

A total of 131 data points for the 120 sampling sites in the ADW contained sufficient parameters, and were separately used, to yield sample-specific model predictions of metal pore water concentrations with the empirical model (model 1). Similar predictions were made with the mechanistic model (model 2) for three data points. The input data that were used for the latter purpose were the 5th percentile,

Table 1
Summary characteristics of the ADW top-layer samples used for modelling

	Ca_s (mg/kg) ($\times 1000$)	Cd (mg/kg)	Cu_s (mg/kg)	Pb_s (mg/kg)	Zn_s (mg/kg)	Fe_s (mg/kg) ($\times 1000$)	OM	CEC
Median ± MAD	25.6 ± 15	3.0 ± 0.5	53 ± 9	91 ± 22	302 ± 64	25 ± 7	10 ± 4.5	17 ± 5
Min	4.2	0.3	3	12	72	8	0.3	8.7
Max	47.4	5.6	110	180	656	58	26	35
n	111	136	136	136	136	111	371	51
	Clay (%)	Cd_{pw} (µg/L)	Cu_{pw} (µg/L)	Pb_{pw} (µg/L)	Zn_{pw} (µg/L)	pH cacl$_2$	DOC (mg/L)	Humidity (%)
Median ± MAD	28 ± 3	0.4 ± 0.2	31 ± 11	0.7 ± 1	28 ± 9	7.4 ± 0.2	32 ± 7	27 ± 13
Min	1	0.1	15	0.1	11	6.7	19	1
Max	36	2.0	73	6	89	7.6	45	67
n	137	57	57	57	57	54	57	85

Samples were taken from a depth of 0 to -10 cm, implying oxic conditions. Data given as median ± MAD. Total metal concentrations are determined using a concentrated HNO_3 destruction, for Ca *Aqua Regia* destruction was used. Both methods simulate "near-total metal" concentrations (mg/kg dry wt). Metal concentrations in the pore water are reported in µg/L. $n =$ Number of data points as collected from the 120 samples.
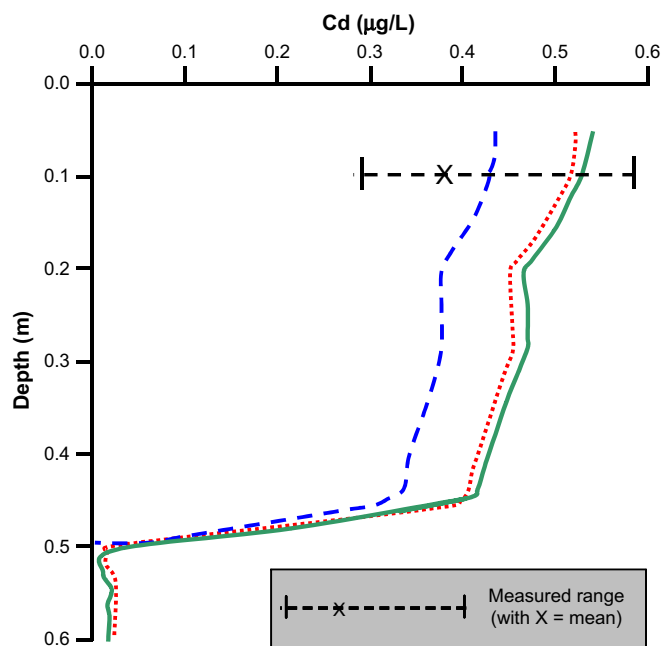
Fig. 2. Illustration of three Biochem-Orchestra scenario analyses of pore water concentrations of cadmium based on measured total Cd concentrations, the mineralogical composition of the deposit and the local redox conditions of the sites (pH = 7.3 constant with depth; $[PO_4]$ = 0.02 mol/kg; $[SO_4]$ = 0.01 mol/L). Scenario calculations can be compared with the point measurements at −10 cm. The crosses depict the field measurements.

the geomean value and the 95th percentile value of the concentrations in the total data set, which together give a summary view on model results for the whole data set. Both models were used to predict the local, dissolved metal fractions in pore water ($\mu g\,L^{-1}$); the geomean and variability were calculated. The performance of both models was compared with actual pore water concentrations measured in top-layer field samples. Overlap of variances in model predictions with measured data was considered to indicate model accuracy. When no overlap of the variances could be determined, differences are reported as orders of magnitude.

3. Results

3.1. Geochemical baseline and anthropogenic enrichments

Robust baseline model regressions were obtained for Cu, Pb and Zn, not for Cd (Fig. 3, Table 2).

The residuals from the regression models were normally distributed. The standardised residual scale for the majority of the points was in the range of 2.5 standard deviations of the error term (Table 2). Outliers were detected for Zn and Pb (4), and Cu (5) and were excluded from the analyses. Data points were considered outliers if their value was larger than the 75th percentile plus five times the interquartile range (IQR, Tukey test).

As an example, the derivation of the local anthropogenic enrichment for Zn is given in Fig. 4: the baseline measurements for Zn are much lower than the top-layer total concentrations. Anthropogenic enrichment per sample can be calculated on the basis of subtraction. This type of analysis can thus show whether metals likely are of natural, lithogenic origin, or result from anthropogenic enrichment, or a mixture of both sources. A similar distinct separation between the baseline, including the variability around the baseline value, and the top-layer concentrations was also observed for Pb and Cu.

The baseline concentrations for Cd were close to the detection limit, with a maximum of 0.85 times those of the top-layer concentrations. This small difference resulted in extra variance and a marginal covariance with Al. Therefore, the resulting regression model for this metal performed poorly, and was thus rejected
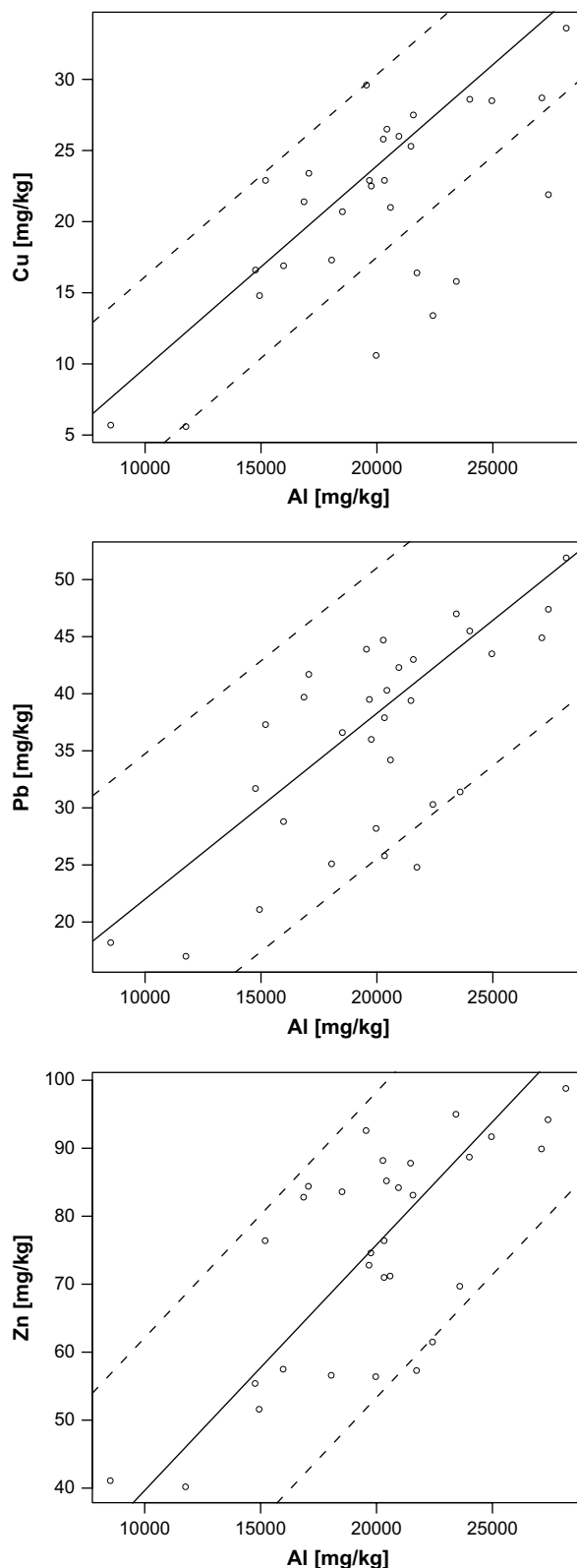

Fig. 3. Scatter plots of measured Al concentrations versus those of the metals Zn, Pb and Cu (all in mg/kg total concentrations) in deeper layers of the ADW, deposited before 1850AD. The straight line is the robust regression line using the LQS algorithm. The dotted line marks the domain between the dashed lines, which covers 98% of the data.

(Table 2). For simplicity, Cd baseline concentrations were assumed to be negligible as compared to the Cd concentrations in the top-layer, and field measurements were thus all attributed to anthropogenic enrichment.

Table 2
Regression parameters of metal baseline models (see Fig. 2) for floodplain deposits of the Dutch River Waal, location ADW, and summary statistics (median ± mean absolute deviation)

	Regression			Summary statistics			
	a	b	e	r (base)	Base	Enriched	Total
Zn	3.2	8.3	9.8	0.59	64 ± 10	245 ± 60	236 ± 113
Pb	1.6	5.6	5.3	0.78	34 ± 5	56 ± 22	130 ± 57
Cu	1.4	−4.4	2.9	0.89	20 ± 4	34 ± 8	38 ± 20
Cd	1.2	2.6	0.5	0.38[a]	2.2 ± 0.1	0.8 ± 0.5	1.9 ± 0.6

For details on regression see Eq. (1). Summary statistics give the concentration ranges of the different geogenic layers. r = The robust correlation coefficient calculated according minimum covariant determinant (MCD) method.

[a] Regression is rejected.

3.2. Variability of anthropogenic concentrations and extractable fractions

Variances in anthropogenic enrichments between samples were found for all metals. The cumulative enrichment over all samples is given at a percentile scale (Fig. 5, *x*-axis).

The variances in Cu enrichment concentrations were lowest compared to the other metals. Predicted Cu enrichments correspond best with the cold acid extractable fractions up to the 70th percentile. Above the 70th percentile, both the cold and the hot acid extraction methods over-estimated the Cu enrichment. For Pb, the extractions did not relate well to the enrichments; the extraction methods both over-estimated the enrichment, the hot acid extract more than the cold acid extract. Zn enrichment corresponded best with the cold acid extractable Zn fractions. The hot acid extractions over-estimated the enrichments for Zn. The derivation of a baseline for Cd was not successful, and total Cd concentration was considered to be total enrichment. For this reason Cd is not further presented.

3.3. Availability modelling and model comparisons

Since the measurements of dissolved fractions were limited to the top-layer samples and were not made for the samples
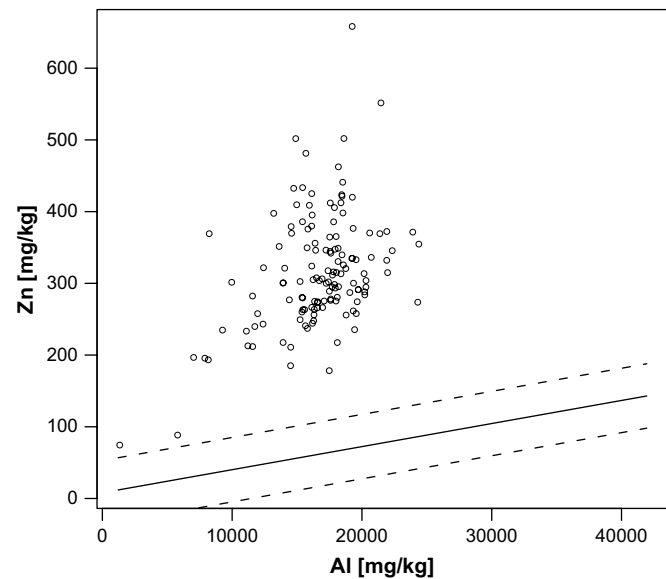

Fig. 4. Illustration of the baseline model for Zn using Al as proxy (domain with median estimate of the baseline and are covering 98% of the data) and the total metal concentrations measured in top layers (dots) as derived in the studies of Thonon (2005).
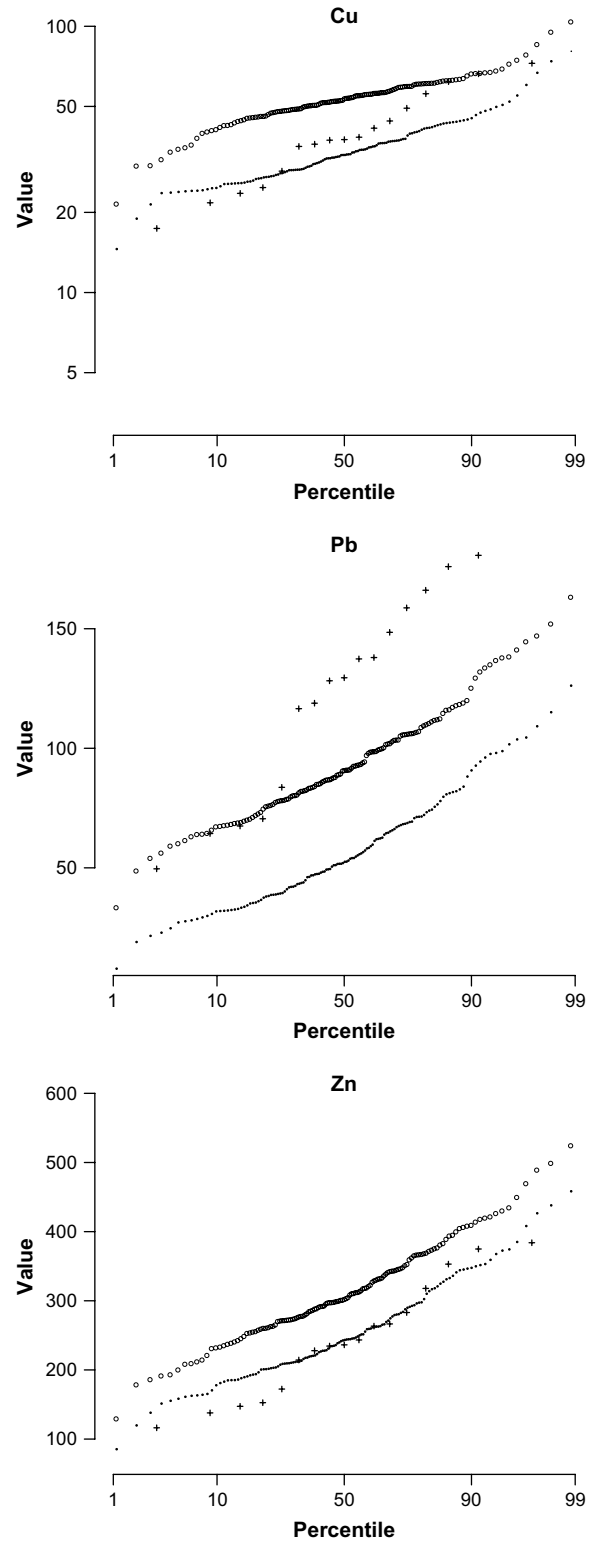

Fig. 5. Cumulative frequency plots of calculated anthropogenic enrichments (dots) and of measured hot (circles) and cold (plusses) 2 M HNO₃ extracts.

of the lithogenic background study by Middelkoop (2000), we were unable to analyse the dissolved metal fraction in the natural background. It was assumed that natural backgrounds do not significantly contribute to the concentrations measured in the extracts, based on the assumption that metal fractions of lithogenic origin are known to be firmly bound to or

incorporated in the mineral lattice. Hence, the input data for the partitioning calculations made with the two models were the metal fractions that were calculated as having an anthropogenic origin. The dissolved concentrations as calculated from these data using the model 1 were thus plotted against the measured pore water concentrations for all samples, results being depicted in box-plots (Fig. 6). Results obtained by model 2 are similar in kind to the pattern shown in Fig. 2 and also plotted against measured pore water concentrations (Fig. 6).

The two models performed differently regarding the metal concentrations they predicted in the solution phase. Dissolved Cu concentrations calculated by the empirical model gave good agreement with the field sample measurements; the variances showed overlap. Calculated Cu concentrations with Biochem-Orchestra were between 5.2 and 6.5 μg L^{-1} at a -10 cm depth. These calculated values underestimated the measured Cu concentration in the field. Dissolved Pb concentrations as measured in the field showed a large variation. The calculated Pb concentrations calculated by both models showed Pb-pore water concentrations within the same order of magnitude as the measured values. All results were between the measured geomean concentration and the lower 90-percentile level. Dissolved Zn concentrations as calculated by the empirical model gave good agreement with the measured dissolved concentrations. Calculated dissolved Zn concentrations using the mechanistically model gave overestimation of the actual concentration measured in the field. Measured pore water concentrations of Cd were in the same order of magnitude as the calculated concentrations generated by both models.

4. Discussion

4.1. Assessing and using lithogenic concentrations

This paper shows that metal concentrations in top-layer deposits of the ADW site are elevated compared to the lithogenic concentrations. Concentrations of Cu, Zn and Pb in the top layers were around two- to fivefold higher than the natural, lithogenic background. A similar phenomenon has earlier been shown for sediments of the major lakes in The Netherlands, for which human activities have similarly resulted in a two- to fourfold increase as compared to natural metal levels (Vink and Winkels, 1994; Winkels et al., 1993). Results in riverbank sediments in Belgium and Luxembourg also showed pollution-related depth profiles related to a history of past human activities (Swennen and Van der Sluys, 1998, 2002).

River basin management, as regulatory obligation under, e.g. the European Water Framework Directive, and specifically risk management, may benefit from an approach that discriminates between these two sources of metal loads. The pragmatic argument is that when there is no anthropogenic enrichment, but only natural background, clean-up operations would be redundant, despite the possible presence of risks and adverse effects of the existing concentration levels.

In the context of criteria-based assessment of environmental quality, when a toxic compound can have increased lithogenic concentrations, the general concept of the maximum permissible concentration (MPC) can be extended. For example, with an adapted local value that is composed of the maximum permissible addition (MPA, in concentration "value" equal to the MPC) plus the
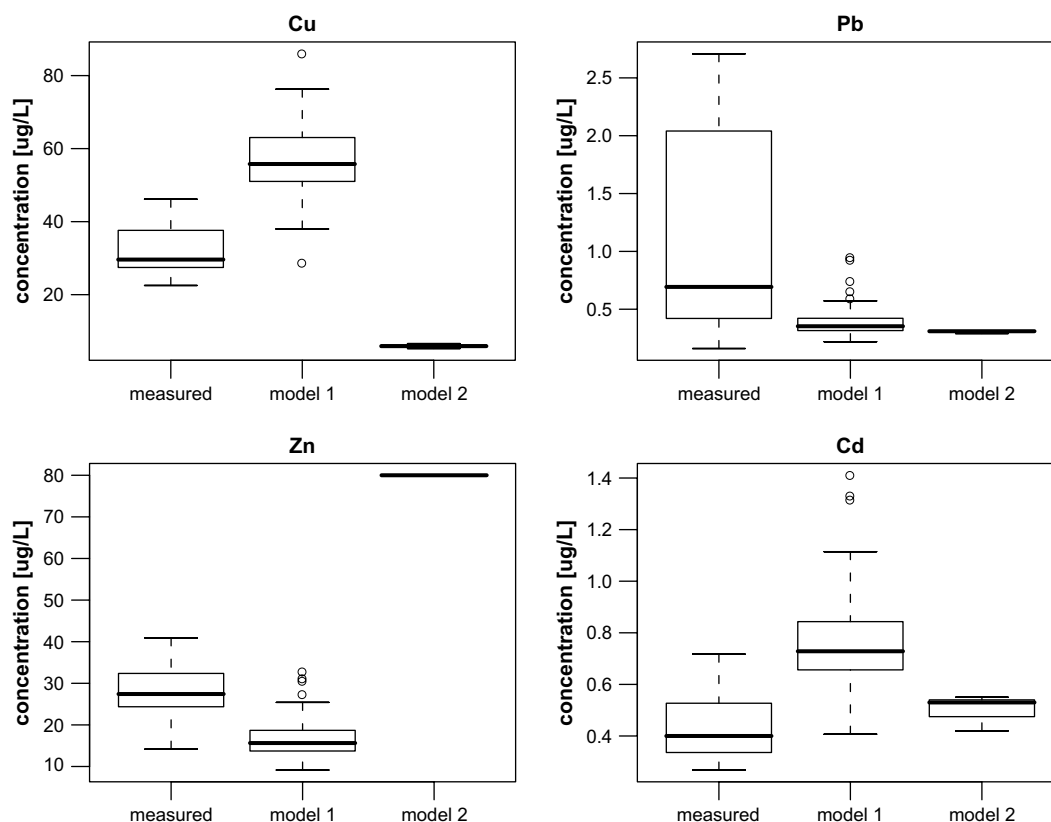

Fig. 6. Comparison of pore water concentrations measured in the field (first box plot) and calculated with the empirical functions (model 1) and with Biochem (model 2) using the calculated enrichment.

local natural background concentration, according to the so-called concept of the 'added risk approach' (Struijs et al., 1997). This type of amendment to the standard protocols for criterion-based site assessments implies that one can take into account a concept like 'metalloregion'. Such metalloregions are not only considered in terrestrial environmental risk assessment, but also in aquatic risk assessments, e.g. in the (draft) EU-Risk Assessment Reports on Zn (European Union, 2008). Nevertheless, application of such ideas is commonly hampered by lack of data and models that quantify local or regional natural backgrounds. Our study shows that local lithogenic concentrations can be estimated by using an Aluminium-proxy following the baseline-(modelling) approach. Our results further show that when baseline data are lacking, measurements of the cold acid extractable fractions may, to a limited extent, serve as proxy for the enrichments of Cu and Zn. None of the extractable fractions considered in this study could reflect the Pb enrichment accurately, due to high variability found for this metal. The rough estimation by using a simple cold HNO_3 extraction method for Cu and Zn may lead into a simple regulatory way of refining an assessment of site pollution, after having seen that a site is contaminated beyond the quality criterion (based on total concentrations). This paper shows that a distinction between metal origins can be made when a refined, site-specific risk assessment of soils and sediments is needed.

In using such data, it might be so – but it is not proven – that the distinction of metal sources relates to differences in exposure (and thus effect levels) of species in such ecosystems. But for retrospective assessments and site-specific risk management problems, the information gained may help taking meaningful risk management decisions.

4.2. Solid–solution measurements and modelling

Results obtained with both models showed variances in predicted soluble metal concentrations between sites.

The empirical functions (model 1) predicted soluble metal concentrations in the same order of magnitude as the measurements, and only Cu concentrations were underestimated (Fig. 6). When the degree of accuracy or bias is known and acceptable in the context of an assessment (see discussion below), the empirical functions can be used to predict the situation in the field, provided that the training set to derive the empirical models has relevance to the site under investigation.

Results obtained with the mechanistic model Biochem-Orchestra (model 2) showed good agreement between predicted and measured concentrations of Cd (example graph: Fig. 2) and Pb. For Cu, the predicted dissolved concentrations were under predicted by one order of magnitude as compared to the field measurements. Most likely, this is explained by a suboptimal characterisation of both the distribution and the actual composition of the various fulvic and humic compounds in solution. The lack of data on reactivity of local Fe-phases most probably caused the slight over prediction of Zn concentrations.

None of the models was perfect. In general, the partitioning predictions were in close agreement with the measurements, or are at least within an order of magnitude. A good performance can be obtained by a model that is "trained" on a set of data similar to a site under investigation. But over- and under-prediction may occur. This phenomenon underscores that the choice of applying a model for site-specific risk assessments is not solely dependent on its prediction accuracy and performance. Depending on the purpose of the user, different models may be selected in view of their typical characteristics and proposed range of application. When a risk assessment is made in the context of generic environmental protection (that is: applicable to derive national guidelines, and thus a prospective use), it can be considered acceptable when a model

would consistently over-predict exposure of biota. The model results may then be (known) biased, but the model may be simple enough for broad use, and in case it is used in the context of protection there is little chance of false negatives (effects observed when they are unexpected). When the (retrospective) assessment of a site would, however, lead to costly remediation in case the compounds that are present are considered to pose a serious thread to local biota, then a more precise model or measurement technique will be preferred. Mechanistic-based models are a priori excellent tools for scenario analyses, and can therefore aid in decision support, e.g. by allowing for comparisons between different basin management scenarios. In relative homogeneous areas, the empirical models perform mostly sufficiently accurate for practical management problems. However, extrapolations to other soils or areas may limit their applicability. For specific answers on risk evaluations, when site-specific remediation decisions need be taken, e.g. under changing or fluctuation conditions, the more complex prospective models based on mechanistic understanding are needed.

Acknowledgement

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