

## **Time series analysis of chemistry in bottom sediments of the Kartelbornsbach, Germany**

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**Abstract** The chemistry of river bottom sediments shows high temporal variability and is controlled by a complex set of different processes. A time series analysis of six years with a weekly sampling interval is used in order to find out the major controls affecting the variability in distribution of pollutants. The variability can be explained in terms of a continuous change between sedimentation and resuspension. The most important sources affecting sediment chemistry are bed rock (Ca and Mg), top soil (Fe, K, Cu and Zn) and waste water (Zn, Cu and P). On-site processes play an important role for Ca and Mg (bioprecipitation) and for organic C, N or P (rapid growth of periphyton).

### **INTRODUCTION**

Blachford & Ongley (1984) reported a pronounced decline in sediment-associated metals over a distance of 365 km below a major urban area in the Bow River in Canada, and explained this trend through sediment deposition and resuspension mechanisms. Chapman *et al.* (1982) investigated hydrophobic organic contaminants over a 900 km distance below a photochemical complex on the North Saskatchewan River and were unable to detect any continuity in the downstream direction at high or low river flows. They concluded that complex sedimentary, biological and chemical processes lead to chemical and biological transportation and to erosion, sedimentation and in-stream storage. Udelhoven (1998) and Udelhoven *et al.* (1997) showed that in small mountainous rivers, suspended particles transported during dry weather flow are primarily from river bottom sediments. The sediment itself acts both as a source and a sink for hydrophobic contaminants. Koll & Dittrich (1998) studied the behaviour of external sediment input and its interactions with the river bed. Their experiments in a laboratory channel showed that material of the armoured surface is mobilized, coarse grains rearrange and the feeding material is partly embedded. Symader *et al.* (1997) investigated temporal variations of PAHs and PCBs in bed sediments and concluded that during the summer, an equilibrium between sedimentation and remobilization is established which is temporarily interrupted by high floods. The most important question that has still to be answered is: Which process dominates over which time scale?

Therefore, the objective of this study is to analyse the data of a six-year time series of bed sediment-associated solids in order to establish a general framework of working hypotheses about the major controls that are to be investigated in detail in further studies.

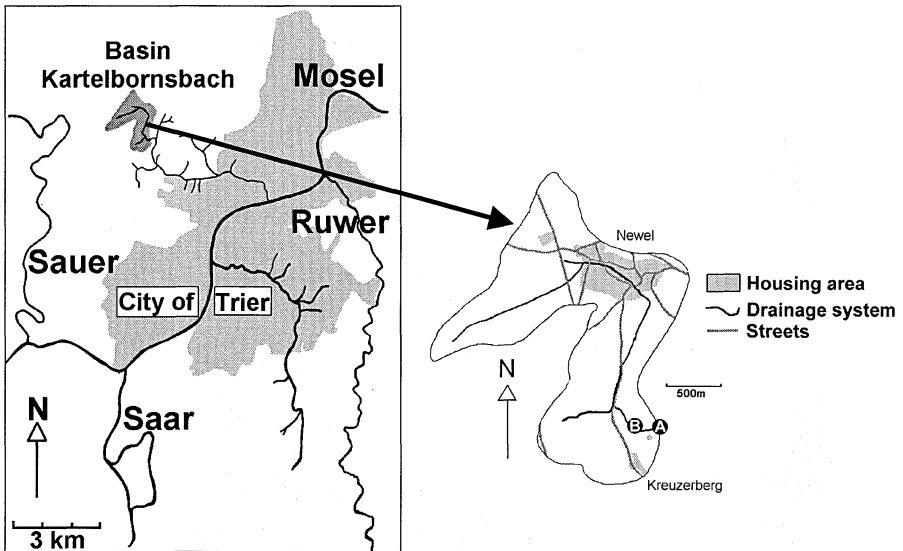


Fig. 1 Area under investigation.

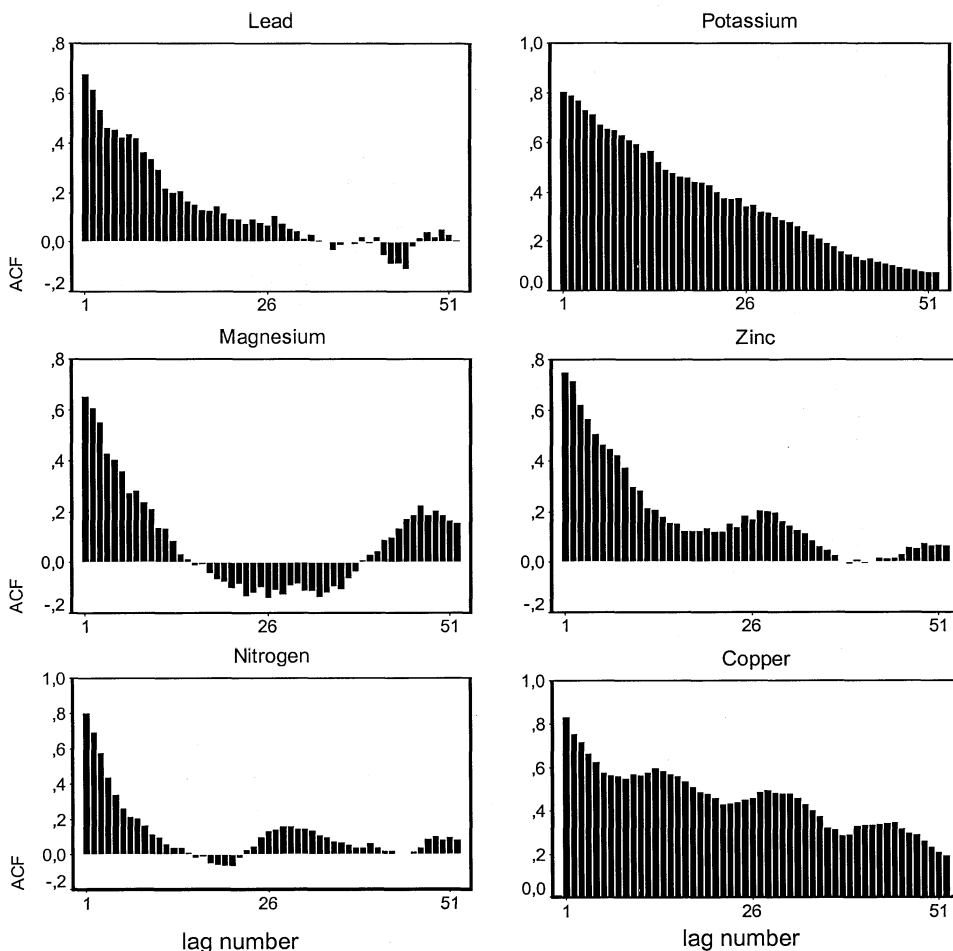
## STUDY AREA AND METHODS

The Kartelbornsbach is a headwater stream in the southern Eifel mountains, Germany, whose basin has been thoroughly transformed by human activities. The bedrock consists of limestone and marls with highly erodible soils. Pastures with old orchards dominate the patches of woods and the scattered fields, where mainly barley is cultivated. A small village and a cluster of houses called Kreuzerberg release sewage into the river. The surface runoff from the streets has an additional rather strong impact on the quality of this stream. Figure 1 shows the basin and the location of two sampling sites.

River bed sediment samples were collected weekly at two sampling stations in 1991 and 1992. The downstream station A is at the gauging site. Station B is situated about 200 m upstream and is not influenced by the waste water and street runoff from Kreuzerberg. Continuous sampling was resumed in February 1993 after a catastrophic high flood in January. At station B the sampling was terminated at the end of 1997. The samples of bed sediments were collected from concrete blocks embedded in the river bottom. The samples were wet sieved and the fraction less than  $63\ \mu\text{m}$  was analysed after decomposition under pressure with nitric acid ( $\text{HNO}_3$ , 65% p.a.) for metals (AAS, Varian SpectraAA 10). Organic nitrogen, total and organic carbon were determined using a Leco CHN element analyser at a temperature of  $1000^\circ\text{C}$ .

## RESULTS AND DISCUSSION

Figure 2 presents six types of autocorrelation functions (ACF) of sediment associated solids at station A (gauging station), which are characterized by different



**Fig. 2** Autocorrelation functions of six particle associated solids (station A: 1993–1998, data for Cu are from station B, 1993–1997).

combinations of deterministic and stochastic processes. The function of Pb represents a third order autoregressive process. No dominant source of Pb could be found, which may explain the complexity of the stochastic process. Potassium as well as Fe and Cu show a delayed decline of the ACF, indicating an additional process. After a catastrophic high flood in December 1993, the concentrations of K, Fe and Cu increased, reached a maximum in spring 1995 (Fe), summer 1995 (K), and summer 1996 (Cu), respectively, and decreased again. This behaviour is responsible for the delayed decline in the ACFs. As Fe, K and Cu come mainly from soil particles (Symader, 1999), it can be assumed that either new particle sources were tapped by the high flood or that material from top soil was trapped in the river system during the event and gradually removed afterwards. The ACF of Cu reveals an additional oscillating process with a period of thirteen weeks. This deterministic component is due to the quarterly cleaning procedures of the waste water treatment plant that is situated upstream of the sampling site. The ACF of Cu is from station B. This

pattern becomes less clear after the river receives waste water effluent from Kreuzerberg.

The time series for Ca and Mg are dominated by an annual cycle with a maximum in late summer or early autumn. During this time of the year rainfall is sparse and river discharge is low. Water temperature is at a maximum and the concentrations of dissolved ions are highest. As calcareous crusts and coatings can be found at several locations we hypothesize that bioprecipitation is the controlling process for Ca and Mg in this limestone basin. Chemical precipitation may be the reason for the annual cycle of Mn, for which high concentrations are found from July to December and low ones from February to June.

At station B, the ACFs of Zn and P are similar to the ACF of Cu, but the 13-week oscillation is less clear. From station B to station A, the pattern of Zn changes distinctly and a semi-annual cycle with minima in winter and summer are found. As the summer minimum can be found only at station A, its source is likely to be from the area of Kreuzerberg. A probable explanation is a decrease in waste water effluent due to the summer holidays. The time series of organic N and C are similar to those of Zn and P, but miss the trend component.

These results show that the variations of sediment chemistry in bed sediments are not white noise and that major discharge events cannot be the only reasons for changes in river bed chemistry as Knox (1989) reported. Instead they are controlled by several processes. That has far reaching consequences for understanding the role of river bottom sediments in the storage and fate of sediment-associated contaminants. There are three possible explanations for the chemical variations in bed sediments being process controlled: (a) the bed material changes its properties by shifting downstream, (b) the bed material does move slightly, but is changed by *in situ* processes, or (c) the bed material is the result of a continuous change between sedimentation and resuspension processes and reflects the changing contributing sources.

Bed material that moves slowly downstream would result in similar temporal patterns that are separated by a time lag, which are identical for chemical elements. As this is not the case, the first explanation can be excluded. The second and third explanations are both supported by the coherence and phase functions describing the relationship between stations A and B. The coincidence is high, but limited to periods of more than ten weeks. The short-term variations up to seven weeks show no coincidence and the phase varies randomly around zero. From this basic pattern there are some exceptions. The short-term patterns of Fe and K do not match for periods shorter than 15 and 30 weeks, respectively. Calcium and Mg behave independently up to 12 weeks and correspond with coherence only between 0.6 and 0.8 at the larger time scales. From the point of view of the explained variance, both the singular power spectra and the comparisons between stations A and B show the dominance of temporal trends or major cycles for all elements. Bed sediments seem to be highly sensitive to changes in the boundary conditions of a basin, whereas local processes play a secondary role.

Comparisons of the chemistry between bed suspended sediments during low flow and high flow conditions suggest that mean concentrations of Ca and Mg are characteristic of the bedrock of the basin, whereas top soil is the suspended source of Fe and K (Symader, 1999). The main sources of Zn and Cu during high floods are

most likely from the sewer system. The coherence spectra show several clusters with similar temporal behaviour. Calcium and Mg have a good coincidence for most of their periods. A second cluster consists of C, N and P. The coincidence between Fe, K and Cu is limited to the long-term effect of the catastrophic event of December 1993. Calcium and Mg show an inverse relationship to the other elements.

Looking at the short-term variation that is most important for the ecology of a river, no relationships between the elements can be found. However, this may be a result of the applied method. The shortcoming of cross-spectral analysis is the underlying assumption that the autocorrelation structure is time invariant. Consequently, time variant changes of the intercorrelation structure appear as white noise in the coherence spectrum. Therefore spectral analysis was accompanied by a moving correlation matrix that encompasses data blocks of 12 weeks and moves forward in steps of four weeks.

The intercorrelations between Mg or Ca, K or Fe, N or C, and Zn or Cu are shown in Fig. 3. Calcium and Mg show an inverse relationship to all other solids. In late summer and in autumn, when high water temperature and consumption of CO<sub>2</sub>

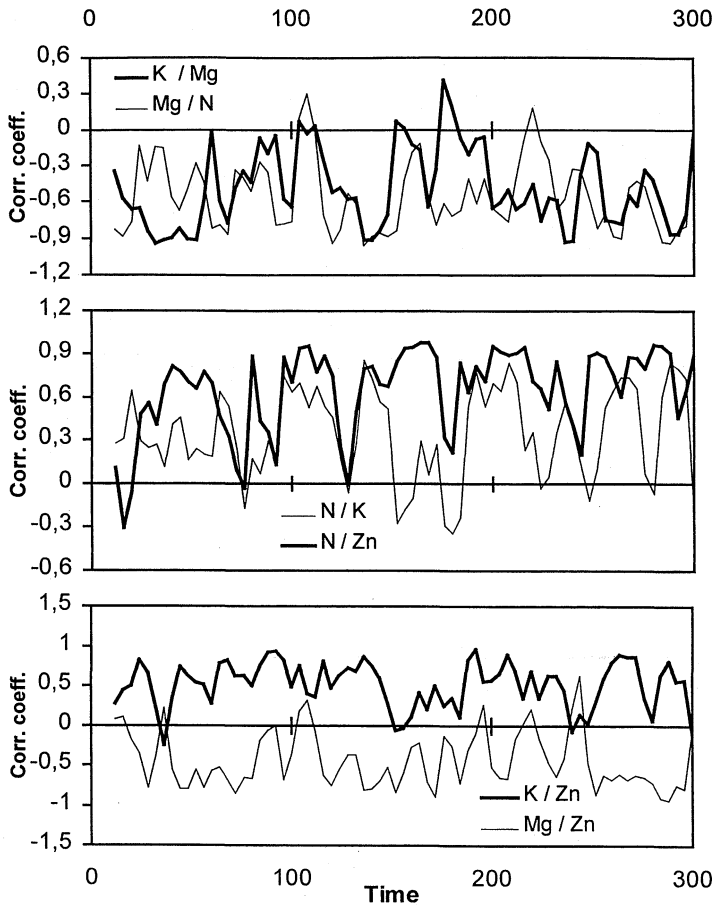


Fig. 3 Changes in the intercorrelation structure over time at station A.

by algae and macrophytes lead to oversaturation of Ca and Mg and precipitation processes, the concentrations of K and organic N decrease. In spring, increased amounts of organic material due to accelerated growth of periphyton and submersed macrophytes lead to a decrease in Ca and Mg. The data illustrate a classical pattern of changes in contributing sources. In the Kartelbornsbach these sources are bioprecipitation of Ca and Mg, growth of periphyton/macrophytes and the input of top soil material.

Zinc, Cu and phosphate come mainly from waste water. However, as waste water particles adhere to macrophytes and periphyton, there is a high intercorrelation between Zn, Cu, phosphate, organic N and C for most of the year. A detailed analysis of the data shows that the concentrations of organic C and N increase very rapidly in March, whereas the corresponding increase in Zn and Cu is less dramatic and lagging behind. In autumn, however, organic N, and C, Zn and phosphate decrease simultaneously. The responsible processes can be observed in the field. After a short spell of sunny days in early spring, gravel and boulders are quickly covered by a thick layer of black and brown periphyton. In summer and autumn, water moss and macrophytes become dominant until the first winter flood moves the bed sediments. The favourable conditions for an enrichment of fine particles last from the end of February to early December. The limiting growth factors are solar radiation and day length in spring and high floods and turbidity in winter. During March, magnesium concentrations are low, which fits into the pattern of changing sources. In summer and autumn, when Ca and Mg are assumed to precipitate, Zn is generally diluted, but single Ca peaks can coincide with minor peaks of Zn. As this is a short-term effect, coprecipitation of Ca and Zn is a possible explanation. So the result is a combination of dilution and a secondary enrichment. Beside these mechanisms, Zn shows secondary peaks of its own which sometimes go together with K and Fe. This means that variation in Zn is controlled by at least four different processes. First Zn will vary depending on the behaviour of its main sources, e.g. waste water and top soil. Second its proportion is reduced, when additional material which is poor in Zn, such as organic detritus or calcareous precipitates, is deposited. Third, if environmental conditions are suitable, Zn may coprecipitate with Ca and Mg, and fourth it is controlled by the growth of periphyton and macrophytes that accumulate fine particles.

From these analyses it can be concluded that the chemistry of river bottom sediments in small mountainous rivers continuously changes due to sedimentation and resuspension processes, modified by on-site chemical and biological processes.

## CONCLUSIONS

Temporal variations of particle-associated solids in river bottom sediments are not white noise, but controlled by processes that differ on different time scales. This has consequences both for the understanding and the assessment of river bed sediments.

Bed sediments seem to be highly sensitive to changes in the boundary conditions of a basin and are therefore an excellent indicator for manmade changes of the environment.

The dominant influence in the sediment characteristics is competition of contributing particle sources modified by on-site processes. The dominant sources are bedrock and, probably, bioprecipitation for calcium and magnesium, top soil for iron and potassium, and waste water for copper, zinc and phosphate. There are indications that soil material and decaying litter may be additional sources for zinc and copper. Carbon and nitrogen come mainly from local growth of periphyton and submersed macrophytes within the river. This material is a second source for phosphate. It can be assumed that the biota enrich dissolved phosphate. The influence of soil erosion could not be confirmed. The temporal patterns of lead and manganese are not well understood yet.

Slow shifting of bed material as a controlling process can be excluded in future in this stream.

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