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Temporal variations of environmental pollutants in channel sediments

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Abstract The general lack of data about temporal aspects of pollutants in channel sediments seems to indicate that the situation is either considered as more or less constant, or well understood from theoretical reasoning. In three sampling periods at five stations it could be shown that there is dynamic behaviour of sediment associated pollutants that relates to several groups of processes. The most important processes are the removal and mixing of channel sediment layers, input and mixing of different materials, contributions of different sources of particle and pollutants and the physio-chemical properties of the pollutants. Also, some biological controlled processes play an important role, but are not well understood.

INTRODUCTION AND OBJECTIVES OF THE STUDY

Previous investigations showed that even in armoured river beds channel sediments can be important sources of suspended particles (Symader & Strunk, 1992). They contribute significantly to the suspended load during the first stage of winter flood waves. Ongley (1982) pointed out that material from river bottoms differs from suspended matter. The same conclusion can be drawn from comparisons between sediment and soil material. Fundamental differences between material from river bottom sediments, soils and suspended particles provide good conditions for determining different particle sources by means of a fingerprint approach.

The temporal variations of sediment associated solids during the year, however, exceed the variations that can be found in suspended material during single flood waves. Channel sediment in mountainous or upland rivers turns out to be a highly dynamic system. Channel sediments display quite specific characteristics, and the processes that control the behaviour of sediment associated pollutants are not well understood. There is a common assumption by some that the river bottom is relatively constant. This assumption may explain the lack of data about the temporal aspects, whereas the spatial distribution of sediment associated environmental pollutants is well documented in a large number of studies.

There has been some consideration of temporal effects. Knox (1989) stated that sediments move significantly only during major events, separated by periods of high stability. Movements of channel sediments have been investigated in the field and laboratories and have been described with hydraulic models, but these approaches do not extend to sediment quality. Others claim that the concentrations of pollutants in channel sediments vary due to a random process (e.g. an anonymous revisor of the German Research Association). Very often it is suggested that sediment samples for environmental analyses should be taken after a long period of low flow at the end of the year, as pollutants tend to accumulate in the sediment. This suggestion implies the assumption of a strong annual cycle that is caused by adsorption, sedimentation of suspended particles and biological uptake.

This investigation aims to answer three basic questions:

(a) Should channel sediments be regarded as an independent subsystem with its own characteristics or merely as deposited suspended particles?

(b) Which processes are responsible for the dynamics of channel sediments and their associated solids?

(c) What are the implications of temporal variations of channel sediments to aspects of sediment and water quality?

In two small basins near Trier, basin area of 2.75 and 25 km^2, three sampling periods at five stations were started in order to obtain information on the variability of sediment associated pollutants. The initial results are presented here.

AREA UNDER INVESTIGATION, MATERIAL AND METHODS

The two basins are mountainous basins and are characterized by a wide variety in land use. Steep slopes are covered by forests or vineyards. The predominant permanent pasture is sometimes combined with ancient orchards and often has patches of arable fields or bushland. Waste waters coming from small villages and minor sites of industry have a considerable impact on water quality.

The small basin of the Kartelbornsbach lies in the southern Eifel mountains about 8 km northwest of Trier and drains an area of Triassic bedrock. Shallow soils cover a wide variety of clayey, silty or sandy marls or limestones with layers and pockets of gypsic material. The bedrock of the other basin (Olewiger Bach) consists mainly of schist, with localized areas of quartz or quartzite.

Two concrete squares, with an area of about 0.1 m^2 each, were placed into the rivers at five sampling sites. The surface of the concrete squares were formed in a way that mimics the surface of the armoured river bed. At the two sites of the Kartelbornsbach the channel sediment samples consisted of a large number of small quantities of channel sediment material that was taken weekly. This procedure limits the disturbance of the sediment and it can be assumed that microbiological processes will remain unchanged. Except for the first three weeks, when the material was still accumulating, all samples will reflect to some extent the results of biogeochemical ageing and biological activities. At the three sites of the Olewiger Bach, material was completely removed from the concrete squares. Any processes that occurred within the sediment on the concrete squares was terminated by the weekly sampling. This does not exclude remote effects of material adjacent to the squares, but it could be assumed that the temporal patterns of the Kartelbornsbach series are somewhat smoother than those of the Olewiger series.

Samples were freeze dried and dry sieved. The fraction smaller than 63μ was used for analysis. Nutrients and heavy metals were analysed after digesting the sediment with nitric acid. For the analyses of particle associated organic pollutants the samples were spiked with internal standards, afterwards they were solvent extracted and purified by column chromatography. Identification and quantification was achieved by gas chromatography/mass spectrometry operating in the single-ion-monitoring mode.

RESULTS

Field observations

Since observations started in 1988 only three flood events have changed the river bed significantly. In February 1990, a succession of three low pressure cells, remnants of tropical cyclones, led to flood waves that destroyed a part of the equipment. Changes in other parts of the river bed were limited. In January 1993, 50 mm of rain fell within two days on a frozen soil and caused a flood wave with a recurrence interval of about 1 in 70 years. The river bed changed completely. Deposits of gravel and boulders formed a completely new pattern of riffles and pools that differed distinctly from the energy line of the flowing water. Because of these unstable conditions even minor floods modified the river bed during the following year. In December 1993, extended precipitation for about three weeks led to a high flood shortly before Christmas with a recurrence interval of about 1 in 100 years in the River Mosel and the middle section of the Rhine. This flood removed most of the riffles and barriers from the January event and re-established some of the former pattern. As far as river bed morphology and movement of boulders are concerned, the channel sediments looked stable during the time periods between these three events. These results from small basins support the statement of Knox (1989) that the mobility and storage of sediment in watersheds is an episodic process at nearly all time scales.

Channel sediments in small rivers exhibit a wide variety of chemical environments at the small scale. Reduced and oxidized sediments alternate and their position is controlled by the flow pattern. This is why sediment quality in a cross section can be highly variable. Temporal sampling includes a certain amount of spatial heterogeneity and therefore random patterns. A careful and well designed sampling procedure is needed to get a representative sample that contains as little random information as possible.

The third hypothesis examined was that environmental pollutants tend to enrich in channel sediments after an extended period of low flood. Enrichment takes place, but the general situation is very complex, because different processes are involved. This cannot be proved by field observation but requires chemical analyses to establish.

Case study: Kartelbornsbach gauging site

Samples of channel sediments were taken from March 1991 to May 1992 and since February 1993. Only the data for particle associated nutrients and heavy metals are available. Organic pollutants have still to be analysed.

The data in Fig. 1 show distinct temporal patterns, which support the hypothesis that the temporal variations of sediment associated solids are not predominantly caused by random fluctuations. However, the nature of these processes is less clear.

There is a distinct seasonal change in organic nitrogen and carbon as both accumulate during the summer. The C/N ratio remains more or less constant. In 1991 there was a dry and sunny summer. This may explain the exceptionally high values at the beginning of September. A more detailed explanation is hampered by the gaps in the data, when no samples were taken.

The most surprising finding is the surprising behaviour of calcium and magnesium on the one hand, and zinc, iron, manganese, phosphate and potassium on the other.

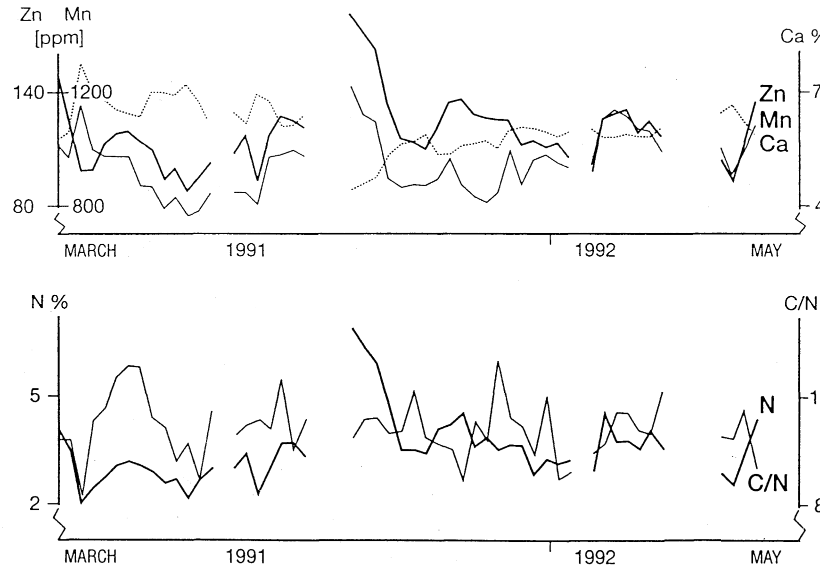

Fig. 1 Heavy metals in channel sediments, Kartelbornsbach gauging station.

Copper and lead establish a third group, where random fluctuations dominate the behaviour. The expected enrichment of heavy metals in channel sediments could not be observed. A first explanation is the mixing of two kinds of material as the dominating process. The subsoil is rich in calcium, the topsoil is rich in all the other nutrients. But the following studies showed that the situation appeared more complicated.

Case study: Kartelbornsbach bridge and gauging station

A second monitoring programme that is still in progress supports the hypothesis that several processes are involved in the temporal variations. The distance between bridge and gauging station is only about 150 m. Several tile drains and the waste water of a cluster of houses enter the river shortly downstream of the bridge. The results are shown in Fig. 2.

The increasing concentration of sediment-associated calcium during the year cannot be explained by mixing of channel material with subsoil material alone. Four weeks before sampling started, an extremely high flood terminated a three year period of stability. As the river left its bed, fresh material transported from outside the river may be responsible for the low calcium and high zinc concentration. The erosion process within the river bed does not explain this behaviour, because a second period of very high flood waves in December, which caused a considerable mixing and transport of channel sediments at the end of the year, did not show a similar effect. On the contrary, six percent of calcium may be a good first estimation of the background values of freshly mixed sediments.

If this hypothesis can be supported during the following year, then the high concentrations of zinc, exceeding 120 ppm, indicates polluted material which requires about three month to move to the gauging site. The maxima themselves, however, are due to waste water effects as they correspond with maximum lead concentrations.

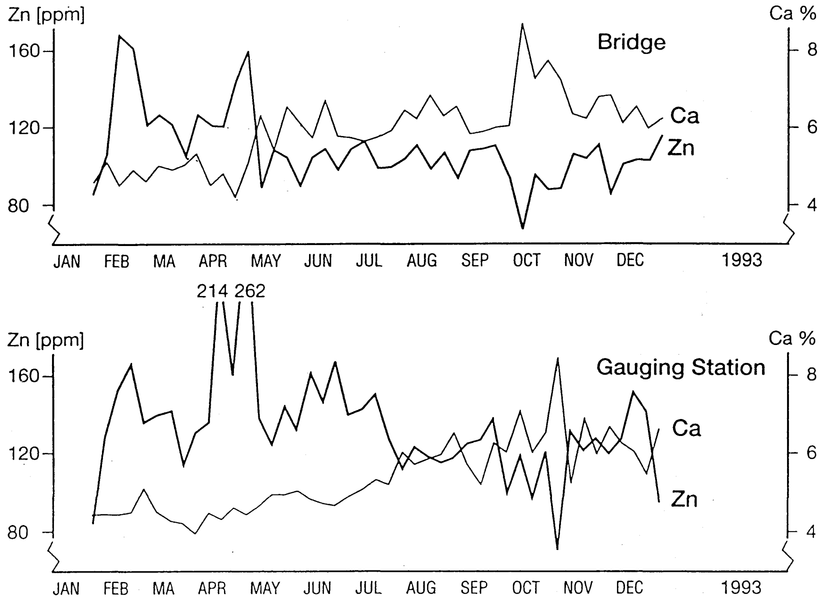

Fig. 2 Zn and Ca in channel sediments, Kartelbornsbach.

In addition to mixing processes, the increase of calcium can be explained by the deposition of suspended particles during low flow. These particles are mainly inorganic and are one of the main sources of the fine fraction of channel sediments. Their mean calcium concentrations is a little more than seven percent. Heavy metals show higher concentrations than in the sediment. A grain size effect is probable, but has to be quantified yet. A third possibility for the increase of calcium is biological processes such as bioturbation or biologically induced calcareous precipitations.

Case study: Olewiger Bach

At three different sampling sites of the Olewiger Bach approximately six months of data have been analysed for organic pollutants. Irsch lies in the upper part of the basin. As in the other two case studies Fig. 3 shows clearly that the temporal variations of most of the sediment associated solids are not dominated by random processes. The first important results were obtained by calculating the autocorrelation functions for each pollutant. Although the data base for this calculation is not sufficient for statistical testing, and minor details of the function have probably no hydrological meaning, some basic patterns can be observed.

The temporal variations of most solids can be modelled by a first order autoregressive model. This is important, because it shows that even the short term variations carry more than random information. The sampling procedure was a total clearing of the concrete forms. Therefore the "memory" of the system was restricted to processes on the concrete blocks of not more than a week.

The analysed solids can be divided into four groups. Organic carbon, nitrogen, zinc, iron and the three ring PAHs show autocorrelation coefficients of lag one that exceed at least 0.4 with some coefficients between 0.6 and 0.7. Potassium, PCBs, PAHs with

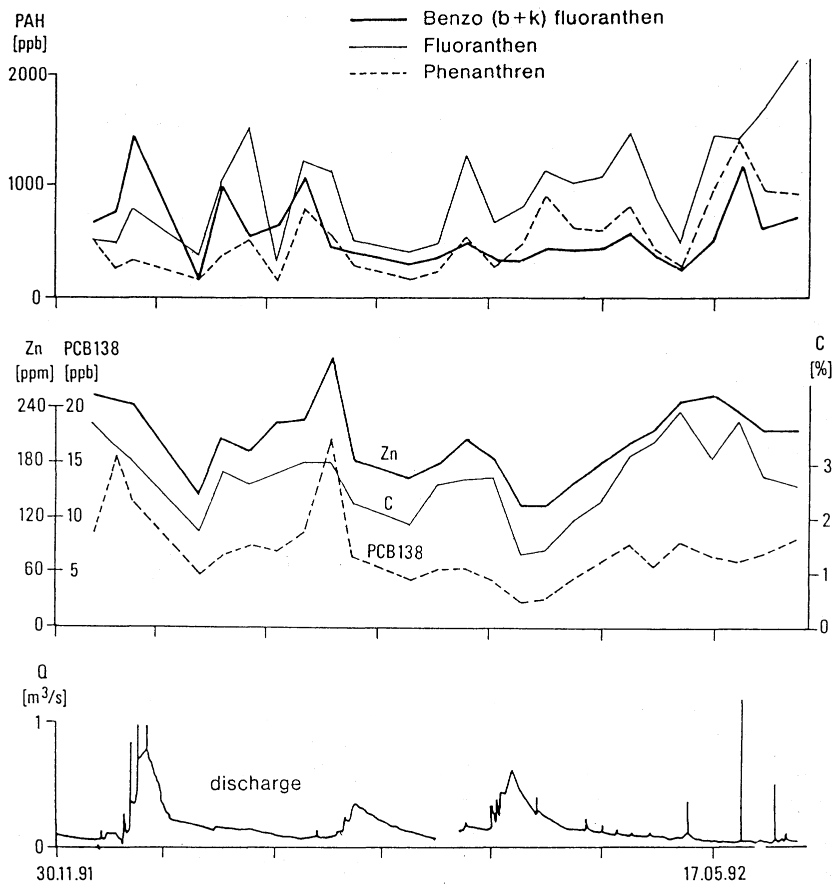

Fig. 3 Temporal variations of environmental pollutants in channel sediments at Irsch.

four rings, and the two five ring molecules exceed 0.3. The larger PAHs are not autocorrelated. DDT and its metabolites that can still be found in aquatic systems show a pattern of their own with highest autocorrelation at lag two or three. At present the number of data is not sufficient for a detailed hydrological interpretation of DDT behaviour. Comparisons between DDT concentrations and the metabolites indicate a degradation under aerobic conditions, as they are found in agricultural soils.

Figure 3 reveals some mechanisms that control the variations of sediment-associated solids. Flood events of the summer type which usually occur between May and October show no effects. Winter floods, however, decrease the concentrations of most solids, because the sediments are thoroughly mixed. A grain size effect with a shift to coarser particles after flood events or on the enrichment of heavy metals could be excluded by grain size analysis. After a flood the concentrations of most solids increase again. It cannot be determined yet, whether the process of enrichment goes back to the deposition of suspended particles or the adsorption of dissolved solids. High concentrations of organic carbon and nitrogen during May 1992 are an on-site effect and can be explained by growth processes in spring. This effect could be observed at all five sampling sites, but varies between rivers and years due to weather and site specific conditions such as radiation balance or flow velocity.

As to PCB concentrations, two processes seem to be relevant. Waste water effluent cause single maxima or outliers. In these samples high concentrations of all PCBs that were measured were found as well as some heavy metals. Such a situation occurred in February 1992. In Fig. 3 zinc and PCB 138 were chosen to demonstrate the coincidence.

The behaviour of calcium, which has its main source in remnants of ancient fluvial terraces, may give a clue to a second process. Different amounts of precipitation tap different sources of suspended particles. During low intensity precipitation events material from the river banks and the valley bottom dominate. With increasing amounts of rainfall, material from the terraces is transported into the river. These two sources can be distinguished by the ratio between calcium and manganese. The increase of the PCBs after the last winter flood in April resembles the behaviour of calcium but not of manganese. Therefore it may be possible that the second process controlling the variations of PCBs is the availability of material from different sources.

Similar conclusions can be drawn for DDT and its metabolites. Its application has been prohibited for more than twenty years, but it can still be found in soils and channel sediments. The controlling factor is the proportion of material from its main sources, farmland and vineyards.

Linked to the question of the sources are the properties of the pollutants. The relationship between hydrophobicity and molecule size led to the effect that PAHs with three ring molecules associated to suspended particles respond immediately to flood events, whereas with six ring molecules there is little change in concentration (Symader *et al.*, 1992, 1994). Surprisingly, in channel sediments the group of four ring molecules (fluoranthene is a representative of this group) shows a behaviour that differs significantly from the three, five and six ring molecules. It is not known whether this is a result of chemical or delivery processes.

Biogeochemical ageing is a label of all kinds of processes that take place within the sediment, and change the chemical composition. Although it can be assumed that these processes play an important role, they could not be detected in the data. One reason may be the heterogeneity of this group of processes, another the interference of changing sources and hydrological situations.

CONCLUSIONS

Some general hypotheses have been formulated, which can serve as a base for subsequent and more detailed investigations.

(a) The behaviour of most of the sediment associated solids can be described by a first order autoregressive model of a lag one. This supports the idea that, beside a strong random element, controlling processes are involved that can be investigated.

(b) Through the autoregression coefficient, different groups of pollutants can be distinguished where there is a correspondence to the physio-chemical properties of the pollutants.

(c) Considering the temporal pattern, different pollutants show both an individual behaviour (e.g. heavy metals) as well as a group behaviour (e.g. PAHs with four rings).

(d) A general enrichment of sediment associated pollutants during the year was not be observed. Enrichment was restricted to short time periods, e.g. after winter floods, or to single pollutants.

(e) An important process is the removal and mixing of channel sediment layers by winter flood waves. Summer floods are not effective.
(f) The input of new material into the river includes material from outside of the river system during extreme events, and the continuous input of bank material and small amounts of wash load after precipitation events.
(g) Different sources which deliver both sediment material and sediment associated pollutants could be distinguished and identified.
(h) Waste waters are responsible for occasional maximum concentrations of pollutants.
(i) The occurrence of biogeochemical ageing as a heterogeneous group of processes was not found, however, biological growth processes, indicated by changes in the organic nitrogen and carbon concentrations were. Its influence on the pollutants remained ambiguous. But, as channel sediments show a wide variety of different chemical environments and as these environments are the result of chemical processes in the sediments, it must be assumed that biogeochemical ageing was masked by the processes described above. This requires a special sampling programme if it is to be investigated.

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