Space-time patterns of organic contaminants in river bottom sediments

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Abstract For two and a half years highly mobile bottom sediments of small rivers in mountainous areas have been investigated, in order to find out the factors controlling the temporal variation of PAHs, PCBs and heavy metals. The dominating processes are discharge of waste waters from point and diffuse sources, mixing of material by high floods, and organic growth that enforces sedimentation by changing the surfaces on gravel and boulders. Biorecipitation plays an important role in the fluctuation of heavy metals in the limestone study basin. Changing hydrologic conditions from year to year and differing physical and chemical properties of the pollutants lead to a very complex temporal pattern. One of the major assumptions in assessing river quality by analysing river bottom material is that contaminants accumulate during extended periods of low flow. This assumption could not be supported, which throws into question the comparability of spatially distributed sediment data. Regional patterns of contaminant concentrations obtained from river bottom sediments are influenced by both considerable temporal variability and spatial scale effects. Recommendations for representative sampling cannot be given without a basic understanding of the dominant temporal patterns.

INTRODUCTION

The fingerprint approach identifies samples of unknown origin by comparing their characteristics with those of known reference material. In the case of suspended particle sources, this approach may not be very successful, although a large set of characteristics potentially is available. A more promising approach may be to focus on patterns of characteristics, and to compare these patterns with a hypothetical pattern derived from known processes, sources or situations (Symader & Strunk 1992). The characteristics that may be studied include particle properties, variations of dissolved solids, the timing of the sample in relation to the hydrograph, and the interactions of all these characteristics. Using this approach, it is possible to classify some samples as resuspended river bottom material. A direct comparison of suspended matter and material from the river bottom as reference material, however, showed striking differences. One of the reasons for this discrepancy was the high degree of spatial and temporal variation associated with the reference material, and several projects have been undertaken to understand the reasons for this variability. In the present study, four time series with a length of between four and five years are available for two basins. These records comprise a sufficiently large database for investigation of dominant processes, and also provide a valuable background against which the fluctuations of organic contaminants can be interpreted.

STUDY AREA, MATERIALS AND METHODS

Two basins near Trier, Germany, were chosen for study, and these have been the
subject of ongoing investigations since 1988. The smaller of these basins is drained by the Kartelbornsbach, is underlain by limestone, has a mixed land use, and includes a small village and a small cluster of houses. The two sampling sites in this basin are separated by about 200 m and have upstream drainage areas of 2.2 and 2.75 km². The larger basin is drained by the Olewiger Bach, and is predominantly underlain by schist. Sampling sites are located at Irsch and Kleingarten, which have upstream drainage areas of 17 and 40 km², respectively and are separated by c. 5.2 km. The study basins are described in more detail by Symader & Strunk (1992) and Symader et al. (1994).

Concrete squares, which were c. 0.1 m² in area and had a surface that mimics an armoured bed, were installed in a mid-river position at each sampling site, except for Kleingarten. At the latter site, the concrete blocks were situated near the inner radius of a long meander where conditions are particularly favourable for sedimentation. The channel sediments at Kleingarten remain undisturbed by minor flood waves, but are completely removed by large ones. The main difference compared with the other sites is the short time interval over which new river bottom sediments are built up by freshly deposited material.

The blocks were sampled on a weekly basis, and the collected sediment was freeze-dried and analysed for major cations, heavy metals, PAHs, PCBs, phosphate, organic carbon, and nitrogen.

RESULTS

Kartelbornsbach

Preliminary results concerning variation of major ions and heavy metals in river bottom sediments have been presented by Symader et al. (1994, 1995). Although not all of the important processes could be identified for the Kartelbornsbach, mixing of material during flood events, the growth of organisms on the surface of gravel and boulders, and bioprecipitation seem to be particularly influential. Additional factors affecting sediment chemistry included waste water effluents and the activation of particle sources from outside of the river system.

Very complex patterns of behaviour were observed because the controlling processes are dependent on both the time scale and the physical and chemical properties of the contaminants. Results for calcium, zinc and manganese illustrate this complexity. In February and March, liquid manure is applied to the pastures and some of it is washed into the river. When this coincides with sunny periods, a springburst effect with excessive growth of organisms can be observed in the water. Sediment samples taken at this time are characterized by high concentrations of organic carbon, organic nitrogen, and phosphorus, and by low concentrations of nearly all of the inorganic ions. Accordingly, the concentrations of calcium, zinc and manganese drop considerably. In the summer months, however, calcium concentrations show a reverse pattern to zinc and manganese, which can be explained by bioprecipitation and changes in the bicarbonate-carbon dioxide equilibrium. The coincidence of zinc and manganese fluctuations, however, is restricted to the summer months and not the whole year. The annual cycles of zinc and manganese were
inverse in 1993, they corresponded in 1994, but were independent in 1995. The effects of bioprecipitation are confined to relatively short periods; the springburst effect is an event of a couple of weeks, and the mixing of material by high floods can change the characteristics of the river bottom sediments for any period from a week to nearly a year, depending on the magnitude of the event. This complex pattern of characteristics is the background against which the variations of organic contaminants have to be evaluated.

Surprisingly, there was no connection between the behaviour of organic and inorganic solids. The typical pattern for PAHs is one of low concentrations (fluoranthen c. 50 ng g\(^{-1}\), benzo(ghi)perylen about 30 ng g\(^{-1}\)) with short-lived peaks more than ten times higher than the normal level. The maximum value of fluoranthene was more than 3000 ng g\(^{-1}\).

Comparing the results at the different sampling sites revealed three different situations. Firstly, peak concentrations may decrease downstream and show a time lag of about one week over a 200 m reach of channel. Secondly, on some occasions, peaks could be observed that occurred simultaneously at both sampling sites. This indicated control by the same event, such as precipitation after a dry spell, but nevertheless in an independent manner. Thirdly, the occurrence of only one peak at one of the two sites, clearly indicates a local effect.

Using data on the Ca/Mn ratio after a catastrophic event, Symader et al. (1995) estimated a travelling speed for river bottom sediments of about 100 m in two months. Time lags of only one week or less for organic contaminants can only mean that this movement is restricted to a very mobile upper layer that moves within days.

An important finding is that most of the patterns are not random but may be explained in terms of processes. However, even more important is the fact that there is no general accumulation of contaminants in the river bottom sediments over the year or after long periods of dry weather flow. This holds true at least for this headwater catchment which has a limited number of sources of pollution. The lack of accumulation includes the heavy metals and could be observed in all years from 1991 to 1996.

**Olewiger Bach**

There are three main differences between the Kartelbornsbach and the Olewiger Bach. They are bedrock, basin size, and the number of point sources of waste water. Although the upstream drainage area at Irsch is only about half that at Kleingarten, the seasonal patterns, average pollution and variation within the year are rather similar at both sites (Fig. 1) High peaks of organic nitrogen and carbon were evident at the end of 1993. This resulted from a blocked sewer system, which caused all of the sewage to be spilled into the river. Since the sewage mainly comprised suspended matter, which consisted of flocs, concentrations of heavy metals or organic contaminants were hardly affected. It was expected that the concentrations at Kleingarten would be lower and lagging behind those at Irsch due to processes of transport and temporary storage. However, the absence of a lag in the case of organic material can be explained both by eutrophication that causes local growth of organic material and by a wide range of transport due to the low density of the suspended matter.
The "Christmas flood", a catastrophic event in December 1993, removed most of the fine material and was responsible for the minima at the turn of the year. However, there was a time lag of four weeks in the behaviour recorded at the two stations, which can be accounted for by a special situation at Kleingarten. The remnants of old material not removed in the flood were mixed with freshly deposited unpolluted material, which diluted contaminant concentrations. However, a second minor flood started the same cycle at Kleingarten but hardly affected the site at Irsch.

Peaks in the concentration of heavy metals generally occur simultaneously at the two stations because they are mostly caused by the activation of contaminant sources. Any time lags that do occur, range between a couple of days to a little more than a week. This indicates that the transport of contaminants in the Kartelborns bach and the Olewiger Bach is similar, although the travel distance is different in these rivers. The peaks are due to the deposition of suspended material. Creeping of river bottom

![Graph](image)

**Fig. 1** Chemographs of contaminants in channel sediments collected at two sites in the Olewiger Bach during 1994 and part of 1994.
space-time patterns of organic contaminants in river bottom sediments

sediments, which also can be observed, is a process that occurs over a different time scale involving months or years. The spatial influence of creeping depends on the number of minor or medium floods, because during low flow the particles are continuously resuspended and deposited. During very large floods, the river bottom material is removed which leads to a completely new situation.

In contrast to the Kartelbornsbach, bioprecipitation is not a key process in the Olewiger Bach, where mixing of bottom material controls the timing of concentration minima, and discharge of waste water effluents is responsible for most of the peaks in concentration. It has not been possible to determine whether the growth of organic material and uptake of contaminants has an influence on concentrations. However, the increasing roughness of the surface will intensify the sedimentation of fine material, which may explain the coincidence of high concentrations of organic material, heavy metals and organic pollutants in May and July. The large number of waste water sources in the Olewiger Bach to a certain extent causes contaminants to accumulate during the year. This effect could not be observed in the headwater catchment of the Kartelbornsbach.

The PCBs and PAHs represented by PCB138 in Fig. 1 show the same overall patterns as the organic material and heavy metals but differ in the detail of the variation. The magnitude of fluctuation in concentrations of organic contaminants in river bottom sediments is higher than for heavy metals, and the maxima at the two sampling sites do not match. This behaviour supports earlier findings that suggest PAHs come into the river from a number of small sources (Symader et al., 1994). Local processes control the elements iron, manganese and titanium, which exhibit completely different behaviour.

In order to generalize these results, they should be supported by data obtained in a year with different hydrologic conditions. Both 1994 and 1995 started with a catastrophic flood event which inundated the valley bottoms and diluted all solids by removing the old channel sediments and replacing them with new material. Short periods between floods are sufficient to build up new material. The springburst effect was very late in these years and started by the end of the floods. Although the early parts of 1994 and 1995 were similar, the summer of 1994 was short but dry, whereas the summer of 1995 was marked by a thunderstorm in July, which resulted in a very high flood, and by a dry autumn. In 1994, significant rainfall commenced in September and the first winter floods occurred in November. This may be the reason that all graphs for 1994 show a clear seasonal maximum in concentrations for July and August.

Figure 2 shows that, unlike the situation in 1994 and in contrast to the Kartelbornsbach, concentrations of organic carbon, organic nitrogen and phosphorus in the Olewiger Bach during 1995 remained high until December and were only decreased by the thunderstorm in July and a period of heavy rain in September and October. Concentrations of calcium, copper and lead exhibited a continuous increase from May until July with a distinct peak in the second half of July. Calcium is derived either from ancient fluvial terraces or from the weathering of concrete, and the flow paths for calcium therefore are similar to those of the heavy metals. Surprisingly there was no accumulation of heavy metals after the peak of July, although the low flow period extended until September and a second period of low flows occurred during November. It is possible that in these highly mobile
sediments, accumulation tends towards an equilibrium, which is controlled by continuous resuspension and sedimentation. In this situation, concentrations will only remain at a constant level with constant input of contaminants, otherwise the concentrations in the channel sediments will decrease.

The temporal patterns of all PAHs were alike during 1995. Enrichment occurred during a period between two high floods in April and concentrations increased gradually from 300 to 500 ng g\(^{-1}\). The two high flood events in July and October had very little effect on the concentrations of PAHs. Most striking is a number of peaks, which were probably due to waste water effluents, together with a tendency for increasing concentrations during the winter period. However, the PCBs, which are represented by PCB138 in Fig. 2, follow the graph of organic material during the first half of the year. They show the same distinct maximum as the heavy metals, are sensitive to flood waves, but remain low in autumn. This pattern cannot be explained.

![Graph](image)

**Fig. 2** Chemographs of contaminants in channel sediments collected at Kleingarten in the Olewiger Bach during 1995.
by a general accumulation or by an affinity to organic material. A possible explanation is the differing physiological activity of organisms during spring and autumn. However, no detailed investigations have been carried out, so that it is not possible to say where the PCBs are stored. An alternative explanation is based on the idea of the equilibrium between deposition and resuspension. If this idea is correct, an exhaustion of sources or a cessation of waste water injections would be sufficient to explain this effect.

These results suggest that the difference between PAHs and PCBs, which occurred in the autumn of 1995, could not be detected in 1994 because of the dominating influence of the autumnal flood waves. The occurrence of large floods, waste water injections, and the dynamics of the biocoenosis are currently considered to be the main controlling factors, to which each group of contaminants responds individually.

CONCLUSIONS

Transport of contaminants associated with river bottom sediments in small rivers of mountainous regions is highly dynamic and exhibits fluctuations in concentrations that are of the same magnitude as those encountered for transport associated with suspended particles or in dissolved form. Therefore, there is no reason to focus only on spatial variations in the contaminants associated with river bottom sediments, as has often been the case in previous studies. The factors controlling temporal variation of organic contaminants in river bottom sediments are waste water effluents from point and non point sources, the mixing of river bottom material after flood events, the accumulation of fines on the surface of gravel and boulders and possibly the uptake by organisms. Although this is a limited number of factors, the influence of individual controls may change drastically due to variations in hydrological conditions which, in combination with the physical and chemical properties of the contaminants, lead to very complex patterns of behaviour.

Waste waters have a dominating influence at all sites. In small headwater catchments with low average contaminant concentrations, flood waves have no effect on organic pollutants and only a limited effect on heavy metals. Bioprecipitation is limited to the limestone catchment, and biological growth seems to be more effective through changing surface characteristics than by physiological effects.

These findings have important implications for the assessment of river quality through analysis of river bottom sediments. At least for small and medium rivers in mountainous areas, no reliable recommendations for a representative sampling can be given without knowing something about the temporal patterns of variation. Furthermore, variations from year to year due to different hydrological conditions make generalization difficult. Spatial comparisons of rivers in mountainous areas that result in a classification beyond a two class system of polluted versus unpolluted are not reliable. The accuracy of river quality assessment using just one river bottom sediment sample per year is very limited and is equivalent to using just one water sample a year to define water quality. The underlying assumption of continuous accumulation of pollutants in river bottom sediments during periods of low flow conditions has to be abandoned. Furthermore, it is possible that a spatial scale effect exists which complicates the interpretation of regional pollution patterns.
REFERENCES


