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Scale effects in particle-associated contaminants of river-bottom sediment

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Abstract Samples of river-bottom sediment were taken at daily and weekly intervals at five sampling stations in two small basins. They were analyzed for major ions, organic carbon and nitrogen, heavy metals, selected PAHs, PCBs, and DDT and its metabolites. Temporal variations of environmental contaminants in channel sediment are composed of a long-term trend, abrupt changes after catastrophic events, seasonal fluctuation due to farmland practices and bio- or geochemical processes, stochastic (mainly first-order) autoregressive process, pulses of waste material, and dilution processes due to mixing of material during winter floods. There was no general enrichment of contaminants during extended periods of low flow as often postulated in connection with the assessment of river quality by analyses of river-bottom sediment.

INTRODUCTION

There are two reasons why river-bottom sediment plays a key role in understanding the transport of contaminants. First, it is one of three transport agents that, although interrelated, show distinct individual characteristics. They are (a) river-bottom sediments and (b) suspended particulate matter, which are both responsible for the transport of particle associated solids, and (c) flowing water that transports both dissolved contaminants and suspended particulate matter, and furthermore causes the channel sediments to move. A second point of interest is that river-bottom sediment is a temporary sink for contaminants and suspended particles, which makes it a potential source for suspended particle-associated contaminants as well as for dissolved contaminants that are released from interstitial waters during remobilization. Furthermore, there are many sediment/water interactions that are not well understood.

What does this mean for the problem of scale effects? If river-bottom sediment is recognized as an individual agent of transport, it must be evaluated by the same criteria that are applied for flowing water and suspended particulate matter. We tend to view scale effects in a purely quantitative manner, but scale effect means systematic variation of the whole system due to change in time, space, and magnitude of external controlling factors. The paucity of information on the temporal variation of particle associated contaminants in river-bottom sediment, however, makes it difficult to understand all scale effects. That was the starting point for a research program in which temporal variation of these contaminants was studied.

MATERIAL AND METHODS

At five sampling points in two small river basins weekly samples were taken, wet-sieved, freeze-dried, and analyzed for calcium, magnesium, potassium, sodium, phosphate, organic nitrogen and carbon, zinc, manganese, iron, fifteen PAHs, four PCBs, and, at some stations, DDT and its metabolites. Additional information was gained by daily sampling over a limited period and by investigating suspended particulate material that was sampled during dry-weather flow conditions. The two drainage basins are characterized by mixed land use and vegetation ranging from woodland to shrubs, permanent pasture, arable land, and vineyards. Effluent from treatment plants and small local industries has additional impact on water quality. The Kartelbornsbach drains a basin of about 2.75 km^2 of the southern Eifel Mountains with shallow soils on Triassic bedrock of limestone, marls, and some gypsic pockets. The Olewiger Bach drains 30 km^2 of the northern Hunsrück Mountains. The dominating bedrock is schist.

RESULTS AND DISCUSSION

As information is stored in a brain, the characteristics of river-bottom sediment develop over a long period with different controlling processes at different time scales. This analogy may help in understanding the system.

The ultra short-term memory

At the Olewiger Bach, batches of daily samples of a week were compared with the corresponding weekly samples. Because of the small amounts of material that could be collected, chemical analyses were restricted to major ions and heavy metals. The differences between the 7-day arithmetic means and the weekly samples were small and statistically insignificant. A group of processes that can be labelled biogeochemical aging seems to play no important role within a time range of one week. During periods without increase in discharge, the chemographs are smooth and can be described by an autoregressive stochastic process. Minor change in discharge has two opposite effects. Precipitation events can tap fresh sources of contaminated material and bring this material into the river. In this case a resulting flood wave is only an indicator of a precipitation effect. The flood wave moves the bed material and causes a decrease of concentrations by mixing polluted and unpolluted material. Within the group of smaller events, controlling processes remain unknown.

The short-term memory

Figure 1 shows the results of weekly sampling from winter to early summer, 1992, at the Olewiger Bach. Each winter flood leads to a general decrease in contaminant concentration; a flood-induced increase observed in the daily samples has never occurred in winter. If new sources are tapped, the effect is cancelled by the dominating dilution process, when polluted and unpolluted sediment is mixed. Summer floods with even higher peak discharge, however, show no dilution effect. As its capacity of transport is exhausted by

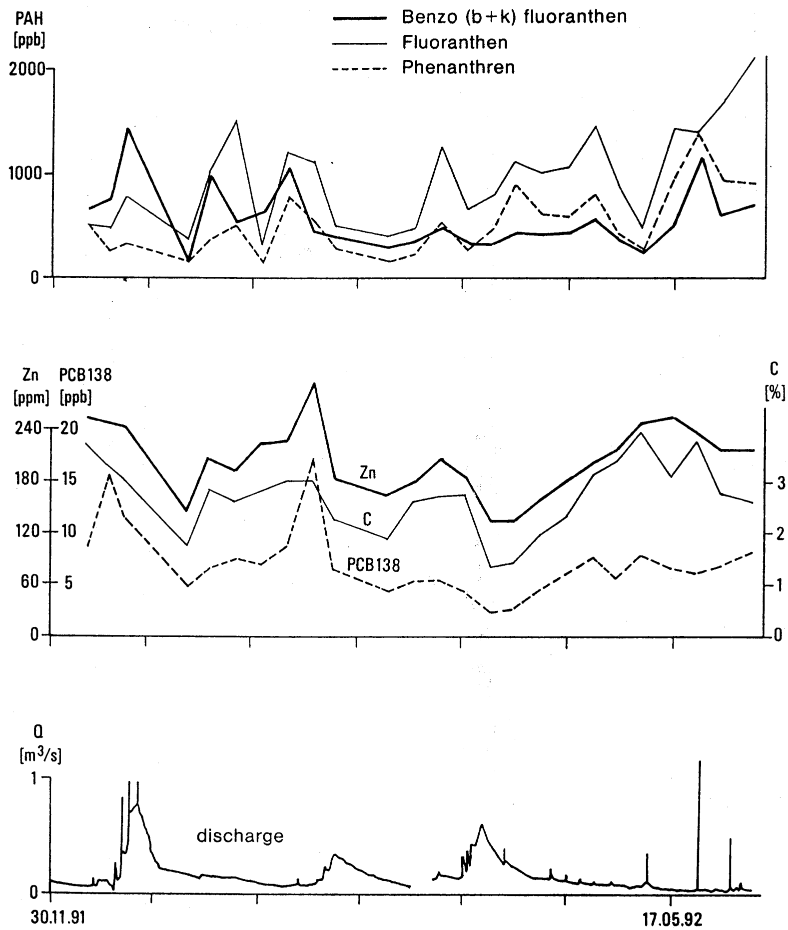

Fig. 1 Graphs showing temporal variation of environmental pollutants in channel sediment at Irsch.

high amounts of wash load, the channel sediment remains mostly undisturbed.

Occasional high concentrations of contaminants probably go back to the impact of waste material. This hypothesis is supported by the observation that always more than one contaminant, but hardly any major cation, is involved. Although peaks are randomly distributed, the time series is adequately described by a first-order autoregressive model. This finding shows that the randomly distributed peaks are not due to sampling or analytical errors, but are pulses that move downstream. There are considerable differences in the behavior of different groups of solids. Concerning PAHs, there is a tendency of decreasing autocorrelation with increasing molecule size or hydrophobicity. Zinc, iron, and organic carbon and nitrogen behave similarly as the three-ring molecules ($r > 0.6$). Potassium and PCBs show an intermediate position ($r > 0.3$), and the six-ring molecules are not autocorrelated. DDT and its metabolites behave more erratically. This correspondence between properties of the molecule and temporal behavior suggests that (a) short-term variations are controlled by processes, not by random fluctuations, and

(b) part of the memory is due to transitions from dissolved to particle-associated conditions and *vice versa*.

The long-term memory

Seasonal variations are more pronounced at the sampling stations of the Kartelbornsbach in the southern Eifel Mountains than at the Olewiger Bach, but they are not yet fully understood. In Fig. 2 the time series of zinc, manganese, and organic nitrogen over 13 months show three types of temporal patterns. Nitrogen, together with organic carbon and phosphorus, is controlled by liquid manure brought onto the fields in February and March. Increasing day length and sunny periods cause rapid growth of organisms on the surfaces of the river sediment, resulting in intensified accumulation of fine material. Increase of manganese during the summer corresponds to an increase of calcium, the controlling process of which is assumed to be bioprecipitation. In this case a distinct enrichment of phosphorus during the summer was expected but was not observed. It is possible that biological uptake is a counteracting process. If this hypothesis can be demonstrated, then the seasonality of zinc is explained by a change of material, because the precipitates are poor in zinc. Although many of these conclusions are speculative, two observations remain: (a) there is a distinct seasonality, and (b) there is no general enrichment of environmental pollutants during the summer/autumn low-flow periods, as is postulated in connection with sampling procedure for assessing river quality by river-bottom analyses.

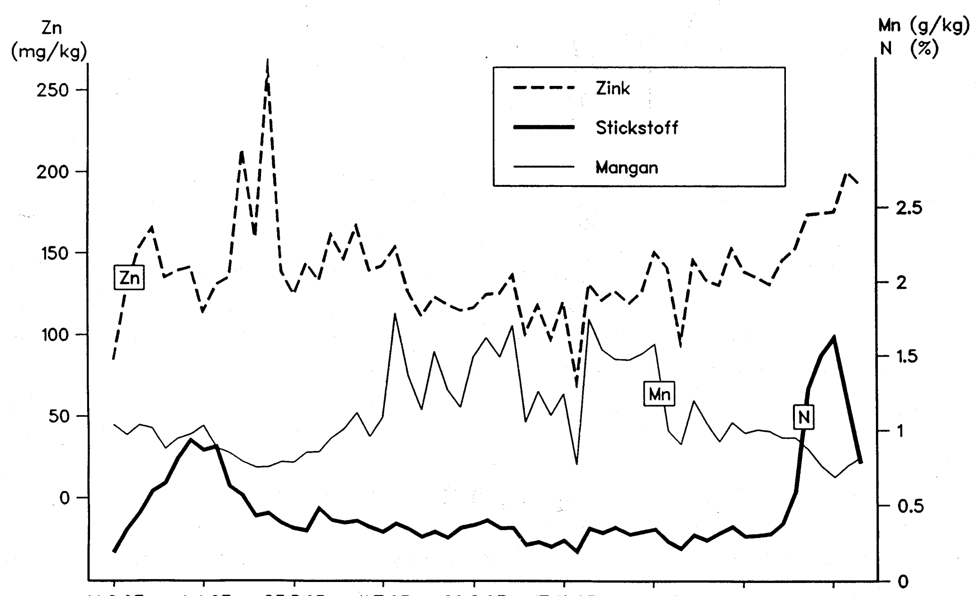

Fig. 2 Graph showing temporal variation of zinc, manganese, and organic nitrogen at Kartelbornsbach.

The phylogenetic memory

One step ahead on the time scale leads to the consequences of catastrophic episodic events. A catastrophic event completely destroys the equilibrium of river-bottom sediment and leads to development of new channel sediment. In the Kartelbornsbach, there has been an unusual succession of three catastrophic events. The first was a high flood on frozen ground in January 1993, that brought fresh material of unknown origin into the river and scoured the bed deeply. The event significantly changed the profile of the river bed. As a result of the disturbed equilibrium between the energy slope and the gradient of the channel bottom, even small summer floods moved bed material after this event. Chemical changes were less drastic, but the concentration of calcium fell below the level of suspended particulate matter that was sampled during dry-weather flow and the Ca:Mn ratio dropped nearly 50%. As expected, establishment of the former condition is a downstream process, requiring about 3 months for a distance of 150 m.

A 100-year event just before Christmas, 1993, re-established most of the former river bed pattern and terminated the period of manganese and calcium enrichment (Fig. 2). Other major ions and heavy metals only slightly were affected. As lateral erosion of the Kartelbornsbach endangered parts of the rural pathways, the river bed was moved about one meter. As a result, fresh soil from the valley bottom was mobilized during following flood events. Fine particles were deposited after several decameters and became part of the river-bottom sediment.

Long-term variations could not be investigated for these small rivers, but biweekly samples from freshly deposited material at the Elbe River, 1987-1992, show that change at this time scale is controlled by major changes in the basin. The Chernobyl accident and the reunion of West and East Germany, with their consequences in the industrial infrastructure, are reflected in the sediment.

CONCLUSIONS

River-bottom sediment is an individual agent of transport for environmental contaminants. Temporal variation of contaminant concentrations in river-bottom sediment sampled at daily intervals can be described by an autoregressive process and explained as a continuous release of small amounts of material stored at different locations in the basin. Slight changes in discharge may increase or decrease concentrations due to the tapping of fresh sources or the mixing of polluted and unpolluted material.

Temporal variation for weekly sampling may be described by a first-order autoregressive model as well; winter floods and occasional impacts of waste material are responsible for most of the variance. Temporary storage within river-bottom sediment is responsible for the autoregressive component. Seasonal variation is due to farmland practices, biological processes, and biogeochemical reactions. Episodic events result in disturbing the dynamic equilibrium of the river-bottom sediment, and their effect depends on the magnitude of the event and prior conditions. Long-term trends are due to severe changes within the basin. No enrichment during extended low-flow periods were observed.