

Identifying major sources of organic micropollutants and heavy metals during flood events in a partly urbanized headwater catchment

ANDREAS KREIN & REINHARD BIERL

*University of Trier, Department of Hydrology, D-54286 Trier, Germany
e-mail: krein@uni-trier.de*

Abstract Since 1988 we have investigated flood events in a headwater catchment. Dissolved and particle-bound solids were analysed as well as particle characteristics. By surveying all the data, pollutant profiles and hydrograph patterns, different sources of pollutants can be identified and related to particular locations in the basin. The influence of main roads and sewer systems is obvious. Heavy metals are additionally mobilized from pore water during resuspension of sediments. There is also a clear tendency for a fast and distinct response of smaller polycyclic aromatic hydrocarbons (PAH) with higher solubility, which could be explained by a gradual enrichment of these partly mobile molecules at locations along the flow path. Patterns of PAH chemographs are further determined by chemical alteration and season. The maximum contents during flood events are controlled by pre-event climatic and hydrological conditions with storm intensity and duration controlling inputs of unpolluted material causing dilution. Experiments with artificial flood releases give some indications of in-channel source reactions.

PROBLEMS AND OBJECTIVES

It is the whole basin that responds to a precipitation event. Therefore the resulting flood waves show a complex pattern with many interrelated processes that take place within vegetation, soil, bedrock, human facilities, the channel and in different parts of the basin. Furthermore, they are influenced by scale effects. Normally, the transport of particle-associated contaminants is induced by flood events, but there are no indications that discharge, particle concentration, particle size or suspended organic carbon, play a decisive role in this process during natural events. The pattern of single flood events varies more markedly than can be explained by the properties of suspended sediments alone. It seems that there are some criteria of overriding importance masking the expected relationships (Umlauf & Bierl, 1987).

The transport of suspended sediments and their properties are supply controlled. The origins of ubiquitous micropollutants like polycyclic aromatic hydrocarbons (PAH) and polychlorinated biphenyls (PCB) are difficult to determine because they have both point and diffuse input sources. They are subjected to mixing processes, chemical transformations and selective erosion. Crucial to the understanding of catchment processes, and the ability to predict the fate of organic pollutants, is the identification of hydrological pathways within the basin, and the related transit times for particle bound solids. Analysing the response pattern is a challenging task and it is not always possible to prove the validity of the conclusions that have been drawn. A multi-tracer technique is a way to answer some of these questions (Strunk, 1992).

The main objective of this examination is the identification of parameters not only controlling intrawave variations but also the differences between flood events. For this purpose, locations and dimension of spatial sources have to be examined and parameters influencing their variations must be detected.

METHODS

The sampling and analysis programme covers aspects of the hydrological conditions (discharge, conductivity, temperature), dissolved (nutrients, heavy metals) and particle associated (major ions, heavy metals, organic pollutants) solids as well as particle characteristics (contents, grain size, organic carbon, nitrogen). Floodwater samples of 60 l were taken midstream when changes of water level, turbidity, smell or colour were observed. The suspended particles were separated by continuous throughflow centrifugation within 24 h of sampling. Suspended sediment concentrations were determined by filtering the sample through a 0.45 μm filter. Anions were determined by ion chromatography, cations and heavy metals by atomic absorption spectroscopy. Suspended matter was digested with HNO_3 before analysis. Total suspended carbon and nitrogen, as well as their inorganic and organic proportions, were measured using a C-N analyser. The particle size distribution was determined by a stream laser technique, using the GALAI CIS-1 system. The samples were spiked with internal standards, enhanced solvent extracted and purified by column chromatography. For identification and quantification, gas chromatography/mass-spectrometry was used.

AREA UNDER INVESTIGATION

The size of the basin located in the northern Hunsrück Mountains near the city of Trier is about 35 km² (Fig. 1). The bedrock consists of schist with quartzite layers. Mosel River terraces in the northern part are covered with Pleistocene gravel, sand and loess. The vegetation is in patchwork form with arable land on the plateau, forest on the north and east facing slopes of the valley and vineyards on the south facing slopes with the valley bottoms consisting of pastures. In the northern densely populated part, the river is polluted by wastewater from housing areas, minor industry and some major streets; human interference is focused on the terraces.

SOURCES OF POLLUTION DURING FLOOD EVENTS

In summer, multi-peaked flood waves which are traceable back to the chronological sequence of the horizontally connected transport streams, are characteristic of the catchment area. They are characteristic of a steep gradient and a relatively short outlet. The long lasting low intensity winter precipitations cause a single broad discharge maximum which is primarily composed of laterally flowing soil water and groundwater. Surface discharges, as well as particle transport from the plateaux, are minimal factors during this season; transport of eroding riverbanks and sediment materials dominate.

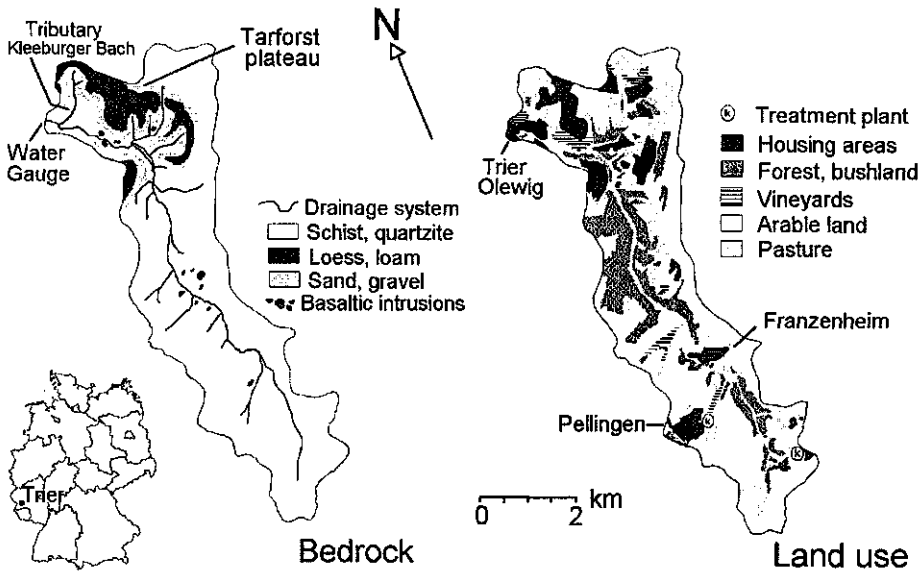


Fig. 1 Olewiger Bach drainage basin, bedrock and land use.

Reaction of the urban characterized part of the catchment

Due to short thunderstorms of high precipitation intensity the first hydrograph peak occurs 15–30 min following the onset of precipitation. The discharge increase is brought about by the influx of the Kleeburger Brook in the district of Olewig. This drains the surface water of a heavily frequented main street as well as neighbouring residential areas. It transports calcium-rich erosion materials (loess) from the Tarforst plateau as well as particles originating from the street surface. These are contaminated with heavy metals and PAHs (Fig. 2). In flood events of low precipitation intensity, transport of terrace materials is not observable and the dilution with uncontaminated material does not appear. Precipitation events of very small intensity and amount make themselves visible often as single peak waves which result predominantly from the sealed surface of this area. They are often registered only by a negative peak in the conductivity, but convey a highly contaminated cloud of suspended particles to the water. The catchment area shows a fast and distinct response of smaller PAHs with higher solubility, which could be explained by a gradual enrichment of these partly mobile molecules at locations along the flow path (Fig. 2(b)). Another possible explanation is that the street and surface material shows a relatively fresh PAH contamination. These are not yet enriched through selective erosion with larger PAHs. The extremely contaminated particles are primarily mobilized from the busy main street through surface flushing, and are carried into the Olewig Brook. The dominance of phenanthrene, fluoranthene and pyrene in the PAH profile in association with high concentrations of suspended zinc and lead, clearly points to automobile traffic as the prime source of contamination. The heavy contaminant influx is however only of short duration because an effective surface flushing of the main source pathway leads to a quick depletion. This first-flushing can also be strongly supported by the antecedent precipitation index. Figure 3 illustrates the dependency of the maximum particle lead

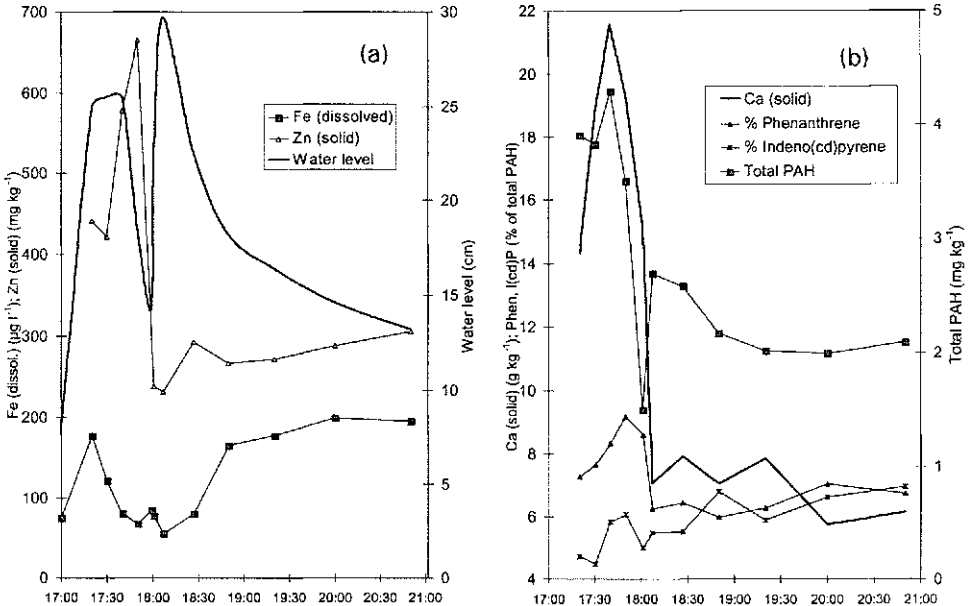


Fig. 2 Flood event 7 November 1997; water level and selected parameters.

content in individual waves on the respective antecedent ten day pre-rain period. Our investigations in several drainage basins show that the exponential decrease of contaminants only occurs if the source is spatially small and easily erodible. In addition, there must be a pool located well beyond the background level of the catchment area under consideration. The deviations from this curve are also of interest. The waves in Fig. 3(a) are characterized by especially high precipitation amounts and intensities. The percentage of uncontaminated material from other sources is responsible for a dilution. With the few waves noted in Fig. 3(b), the localized precipitation of the heavily human-influenced northern part of the basin yields elevated lead concentrations. Therefore, localized precipitation represents a further determining factor which controls the variance in particle bound contaminants during flood waves. The PAH structure in winter shifts to larger PAHs. The levels are however low, due to the dominating transport of uncontaminated river bank and sediment materials.

Reaction of the rural characterized part of the catchment

Sixty to ninety minutes after precipitation begins, diverse tributary streams which flow into the Olewig brook 2.5 km above the stream gauge, determine the maximum discharge. They transport eroded ground material and result in an increased river bed erosion. Observable in the descending slope of the main wave is the influx of deeper lateral soil water from the pasture lands above the Olewig district, which is illustrated by a small peak in dissolved iron levels (Fig. 2(a), 17:45 h). The transported solid material now indicates sharply reduced contents of heavy metals and PAHs. Aquatic sediments show a relative accumulation in larger molecule PAH (benzo(b+k)fluoranthene, benzo(ghi)perylene, indeno(cd)pyrene). After longer lasting heavy precipitation events, a third

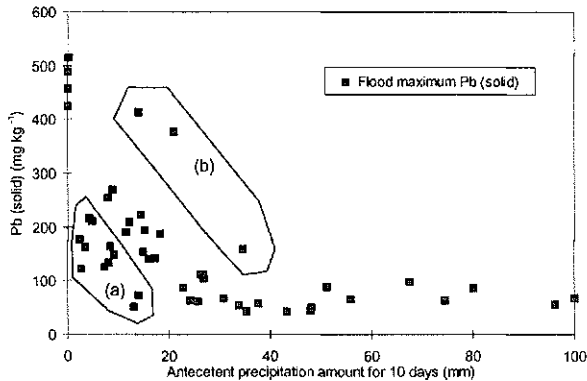


Fig. 3 Importance of the antecedent precipitation amount for the maximum lead contents.

discharge peak occurs 3–4 hours later but often is formed only as an attached secondary maximum. The water of this partial wave originates 10 km above the sampling point, from the residential areas Franzenheim and Pellingen (Fig. 1), as well as from an influx of lateral soil water from the large pasture lands below Franzenheim. While a yield of iron-rich fine particles and dissolved iron results from the surface discharge component, human contamination is especially noticeable in the drainage of the flood waves and is clearly recognisable in the increasing heavy metal and PAH concentrations. This is traceable to the residential areas and the outlet drainage of the Pellingen sewage plant.

ARTIFICIAL FLOOD RELEASES

A further source of dissolved heavy metals is the resuspension of sediment material with the release of pore water. This is documented by a controlled two peak artificial flood wave in the same catchment area (Fig. 4). Drinking water introduced from the local water works swirls the sediment up and releases dissolved heavy metals into the body of water. The interstices are cleaned by the first wave so that in the second rise in water no mobilization follows. The type and amount of dissolved heavy metals depends on the redox potential and therefore on the preceding hydrological and climatic conditions. The yield follows in the order manganese, zinc, iron and copper. It reflects a vertical succession in the sediment body, in which the redox potential sinks according to the depth of the sediment body. Iron and copper appear only after longer phases of sediment consolidation. The increase in concentrations prior to the wave is traceable to the opening of a small mill race weir (Fig. 4, 09:30 h). Accumulated sediments are resuspended. Also here, zinc reacts before manganese as in the following wave.

CONCLUSIONS

The differing sources of contaminants are catchment-area specific. Their yield results predominantly from streets, roof tops, combined sewage as well as from sewage

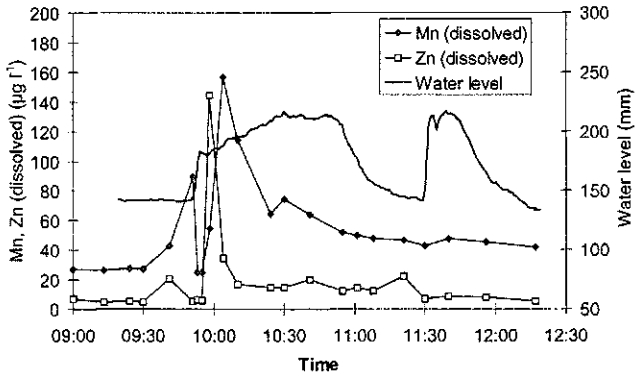


Fig. 4 Resuspension of dissolved manganese and iron during an artificial flood release.

plants. Pore water also represents a source of dissolved heavy metals. The sources of environmental contaminants are themselves variable according to diverse antecedent conditions, seasonal particularities and large scale climatological conditions covering longer time spans. They are differentially activated according to precipitation structure and distribution. The intensity and amount of rain determine dilution processes with uncontaminated material. With PAHs, it is shown that their mobility depends heavily on the physico-chemical properties. Different sources present changing profiles, the succession of which are illustrated in the chemograph.

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