



HEAVY METALS IN FRESHWATER ECOSYSTEMS INTRODUCED BY URBAN RAINWATER RUNOFF – MONITORING OF SUSPENDED SOLIDS, RIVER SEDIMENTS AND BIOFILMS

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ABSTRACT

Sediments, suspended solids and biofilm samples at different locations of the River Alb near Karlsruhe were analysed for their heavy metal content (Pb, Cu, Cd). The main task of this study was to validate the biofilm method by comparing the measured pollution with the results of long term monitoring programs based on sediments and suspended solid samples. All compartments of the surveyed systems showed increasing heavy metal concentrations towards highly urbanised areas. The translation of data into pollution classes detected similar pollution situations for sediments and biofilms. The presented biofilm method recommends itself as a practicable instrument for assessing the heavy metal pollution in freshwater ecosystems. The easy sampling-technique, the low variability in the detected values and the ecological relevance of biofilms are the obvious advantages of this biofilm monitoring. © 1997 IAWQ. Published by Elsevier Science Ltd

KEYWORDS

Biofilm; heavy metals; micropollutants; monitoring method; receiving water quality.

INTRODUCTION

The pollution of urban stormwater runoff has been intensively surveyed in a great number of research projects. It is no longer a matter of argument that according to the extent of human activities the concentrations of heavy metals, PAHs and other anthropogenic micropollutants increase. A comparison between selected data on heavy metal pollution in stormwater runoff of different compartments in urban drainage areas and water quality standards (EC directive for drinking water) resp. ecological relevant limits for aquatic life illustrates this. The listed concentrations represent mean values, whereas the registered maximum concentrations exceed these values by 2-3 orders of magnitude.

The data in Table 1 reflect the high pollution arising from the stormwater runoff which is suspected to cause acute and long term toxic effects in the receiving waters. In spite of research activities in this area including field and laboratory experiments the question of the ecological relevance of such pollutant loads introduced in freshwater ecosystems is still open to discussion.

Table 1. Comparison of stormwater runoff pollution in urbanised areas with water quality standards in limnic systems

Parameters	measured data				water quality standards/guidelines		
	1	2	3	4	5	6	7
Pb [$\mu\text{g/L}$]	156.4	42.9	311	25.6	4	1	50
Cu [$\mu\text{g/L}$]	14.08	76.2	108	70.5	5	2	20
Cd [$\mu\text{g/L}$]	0.59	1	6.4	0.33	0.5	0.05	1

1) roof runoff (Förster, 1990); 2) stormwater runoff from a traffic area (Pfeifer and Hahn, 1994); 3) road runoff from a residential area (Xanthopoulos, 1993); 4) combined sewer overflow (Fuchs, 1995); 5) Wachs (1986); 6) Behra *et al.* (1994); 7) European Community Limits for Drinking Water (1986)

Most of the investigations carried out recently focus on the loading of river sediments and suspended solids. Even if the enormous variability of chemical pollution data is neglected, the measured sublethal concentrations and their ecological importance can be hardly correlated. The aim of several field studies was to detect the degree of heavy metal uptake in benthic organisms (e.g. Bascombe *et al.*, 1990). Due to the dynamics of transport in freshwater systems and the mobility of the monitoring organisms the results of these investigations are not always clear. Often only a tendency of higher loading downstream of the discharges can be found. But to justify the enormous financial investments for an advanced treatment of stormwater runoff more detailed results about the importance of heavy metals in freshwater ecosystems are desired. For this reason the Institute of Aquatic Environmental Engineering of the University of Karlsruhe developed a measurement method based on aquatic biofilms/microcoenoses in order to prevent the difficulties described above. The main characteristic of biofilms in natural systems is their ability to accumulate material, thus they are destined for use as pollution indicators.

Biofilms can be found at almost any surface exposed to water. They represent a microbial community with various inhabitants such as sessile bacteria, protozoa, fungi and algae. The microbial cells as well as abiotic materials are embedded in an organic polymer matrix of microbial origin, the EPS (Extracellular Polymer Substances). According to their structure biofilms are able to adsorb various materials, to grow rapidly and to offer an easy sampling possibility, so that these aquatic microbial communities can be used as pollutant-indicator-systems. In order to prove the applicability of the indicator properties of biofilms some measurements in the river Alb near Karlsruhe were carried out. Biofilms, sediments and suspended solids at different locations were analysed with regard to their heavy metal pollution. For these measurements the metals lead, copper and cadmium were chosen as indicators of manmade pollution. For the collection of representative (and followingly comparable) microcoenoses a biofilm sampling device was designed consisting of 6 glass plates installed in an open PVC pipe of 30cm diameter.

FIELD MEASUREMENTS – MONITORING OF HEAVY METALS IN SEDIMENTS, SUSPENDED SOLIDS AND BIOFILMS

The measurements relating to the heavy metal burdening of the biofilms were carried out at three sites in the river Alb (Figure 1). The river Alb rises from the northern Black Forest at a height of 750m and flows 55km up to its discharge into the river Rhine. The mean flow velocity ranges from $> 0.5\text{m/s}$ in the upper water course to 0.3m/s in the urbanised area. The middle discharge volume (MQ) accounts $3.4\text{ m}^3/\text{s}$ (LFU, 1970). The sampling sites were chosen to be in different river reaches, which are characterised by various human activities. The upper reaches of river Alb (Marxzell, site 1) are only influenced by extensive agricultural activities. The first minor effects of urbanisation are evident downstream of the city of Ettlingen (38000 inhabitants) although up to the boundary of Karlsruhe (shaded area, site 2) the river maintains its seminatural characteristics. Significant changes in morphology and pollution are the results of increasing human activities in the catchment of Karlsruhe (ca. 300000 inhabitants). At site 3 the river is highly degraded.

At all sites artificial substrates for the biofilm sampling were exposed. The locations of the sampling sites are marked in Figure 1.

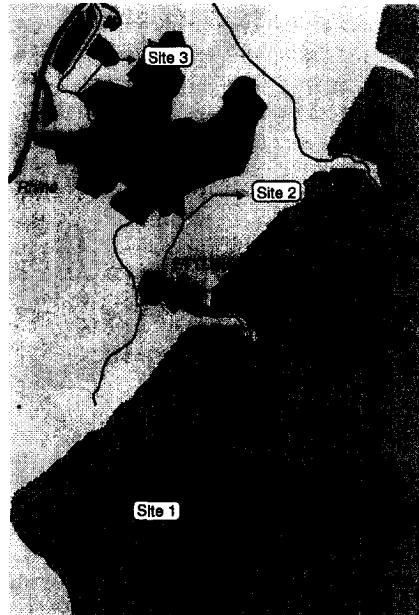


Figure 1. Map of the river Alb with the sampling sites.

The artificial substratum samplers contain several plates of glass with a total surface of 0.48m^2 . The plates were coated with a thin layer of stearic acid to enhance the microbial growth at the beginning of the exposure. The biofilm was allowed to grow for 14 days. After this period the samplers were collected and stored in water prior to the analysis in the laboratory. In addition the concentrations of heavy metals in sediments and suspended solids were determined at site 2 and 3. The sediments (upper layers 2-3cm) in lenithic zones were collected using a small shovel and were preserved in water. In the laboratory the sediments were fractionated by sieving into 4 grain classes ($>250\mu\text{m}$, $125\mu\text{m}$, $63\mu\text{m}$ and $< 63\mu\text{m}$). The suspended solids were collected under both dry and wet weather conditions - 2-5L of river water were filtered through glass fibre filters. In the laboratory the biofilm was scraped from the plates and characterised by organic content, water content, proteins and carbohydrates.

Finally the sediments ($< 63\mu\text{m}$), suspended solids and biofilms were freeze dried and analysed for their heavy metal content. All samples were digested with HNO_3/HCl (1:3) for 2h at 180°C , filtered and measured for cadmium, lead and copper with the AAS graphite furnace method. In this way 16 biofilm samples were treated in the period from January to December 1995. The sediments and the suspended solids were collected over a longer period beginning in November 1993.

RESULTS AND DISCUSSION

The main task of this study was to validate the biofilm method by comparing the measured pollution with the results of long term monitoring programs based on sediments and suspended solid (SS) samples. Figure 2 shows a comparison of the average heavy metal pollution in the selected river reaches as detected in different measurement campaigns. Starting from the upstream sampling site we found increasing heavy metal concentrations towards the highly urbanised area. This well known phenomenon was registered in all compartments of the surveyed system. Thus the biofilms distinguish themselves as an equivalent tool for the monitoring of river pollution.

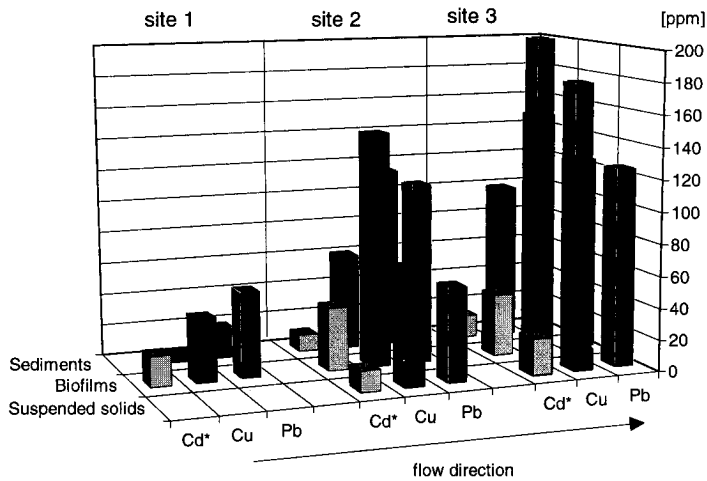


Figure 2. Average heavy metal concentrations in sediments, suspended solids and biofilms of different sites in river Alb (Cd*: [ppm x 10])

Considering some ecological and toxicological criteria which were formulated by Wachs (1989) the measured concentrations can be translated into pollution classes. Wachs defined a detailed classification system depending on the heavy metal concentrations in different river compartments, like sediments <math><63\mu\text{m}</math>, SS, zoobenthon and phytobenthon. According to this system, river sites can be assigned to 7 classes, reaching from unpolluted (class 1) to excessive polluted (class 7). The resulting classification shows similar pollution situations for both, the sediments and the biofilms, it ranges from a low polluted (class 2) at site 1 to a heavy polluted situation (class 5) at site 3. Based on the SS samples a critical pollution at site 2 and a heavy pollution at site 3 was detected.

Beyond the proven applicability of biofilms as an indicator method the main advantages of this instrument should be pinpointed. The required properties can be summarised as follows:

1. The method should not require complex technical equipment and be applicable under the different specific conditions of river systems.
2. The results of monitoring should be reproducible for an appropriate number of samples.
3. The measured concentrations should be ecologically relevant.

All these expectations are fulfilled by the biofilm method while the sampling and quantification of sediments and SS are characterised by specific disadvantages.

As was mentioned in the chapter Field Measurements the biofilm monitoring can be performed with low technical efforts. On the contrary the analysis of sediment and SS samples requires an extensive pretreatment in order to get representative results (classification/sieving). Table 2 may illustrate this using the mean and extreme values of heavy metal concentrations for lead, copper and cadmium at the different sampling sites.

The most significant variations (min-max) are registered for the SS which were analysed without any pretreatment. This effect is generated by the transport capacity and the dynamics of running water systems that lead to rapid changes in chemical and physical characteristics. Especially brooks and rivers in mountainous regions show increased material movement during rain events.

Table 2. Pollution data characteristics at the sampling sites

[ppm]		suspended solids		sediment (<63µm)			biofilm		
		Site 2	Site 3	Site 1	Site 2	Site 3	Site 1	Site 2	Site 3
Pb	mean	113.92	174.6	18	118.4	220.5	54.7	59.5	132.6
	min	31.3	7.3		66.8	124.8	37.9	28.5	89.9
	max	801	440		184	550	95.2	87.5	208
Cu	mean	152.5	152.1	25	68	106.5	57.1	73.3	125.9
	min	1.8	31.6		35.9	52.8	32.4	33.6	39.4
	max	1431	854		97.4	227	99.6	135	180
Cd	mean	3.9	4.2		1.2	1.6	1.9	1.3	2.3
	min	0.5	0.7		0.5	0.7	0.9	0.5	1.1
	max	18.2	21.2		2.5	3.2	4.5	3.3	7.5

With regard to the classification of sediment samples and exclusive consideration of the fraction <63µm, the variation in the concentrations can be reduced significantly. In many investigations (e.g. Müller *et al.*, 1993) the clay fraction <2µm is declared to be the best monitor for expressing the heavy metal pollution of river sediments. This method is a practicable procedure, which allows a comparison of spatial and temporal development in the pollution state, but it also includes two disadvantages. The demand for a large amount of material in order to carry out the sieving process, as well as the time-consuming procedure and the needed equipment. Furthermore the assessment of the total pollution and its ecological relevance requires additional information about the specific situation in the river (hydraulic conditions; substrate composition, etc.).

Due to their integrated property the biofilm samples are characterised by a low variation which enables an evaluation of the average pollution situation on the basis of few samples. Considering the basics of food processing in freshwater ecosystems the ecological relevance of the heavy metals introduced in biofilms is obvious. For a major group of aquatic invertebrates (primary consumers) the community of microorganisms is an essential food resource and pollutants are likely to enter in the food chains by this way.

CONCLUSIONS AND PREVIEW

The results show clearly the increasing heavy metal pollution depended to the level of urbanisation of the basin of the river Alb. Summarising the above mentioned advantages of the biofilm method we can conclude that it is a feasible instrument for assessing the pollution of river ecosystems: a) it shows low variability in the detected values and b) the ecological relevance is given through the entry into the aquatic food net. For this reason this monitoring system (biofilm) is planned to be applied in other rivers in order to validate the presented results and to prove its wider applicability.

At the present state of research the biofilm was regarded as a black box consisting of inorganic matter, EPS, bacteria and other organisms. Further investigations will focus on a separation of the biofilm constituents to identify the binding sites for the heavy metals. The purpose of these experiments will be to get additional information concerning the bioavailability of the pollutants and the sublethal effects on microorganism communities.

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