

## **A sampling strategy for an investigation on particle associated contaminants**

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**ABSTRACT** The design of sampling programmes depends on the objectives of the study that is planned, the information that is available beforehand, and the number and characteristics of the catchments. Contrary to many technical details of sampling, measuring and analysis, or details of the catchments, these three items are seldom discussed thoroughly enough in view of their importance to the design of sampling programmes. This deficiency is one of the reasons that makes it difficult to compare results from different studies. A case study of a scientific investigation about the transport of hydrophobic pollutants in catchments of heterogenous land use is used to illustrate the link between conceptual approach and sampling strategy. The sampling programme consists of several components, each component is based on the results of the previous steps.

### **INTRODUCTION**

Contradicting results of case studies may require further evidence from a wide variety of fluvial environments, as Lambert & Walling (1986) pointed out. In many cases, however, they are caused by differences in network design or sampling strategies, and what seems to be contradicting is a matter of comparison of findings that cannot be compared. Comparability of results is sometimes difficult to assess. Although in many studies all necessary details are given, the underlying conceptual approach is not always evident and it is seldom discussed, in how far the objectives of a study can be reached by the chosen sampling programme. Furthermore, limited funds, limited man power or insufficient laboratory capacities can require considerable modifications of the original approach.

In this present paper it is tried to summarize a line of thought that led to a complex sampling programme, we use to investigate particle associated contaminants in flowing waters.

### **GENERAL FRAMEWORK**

The design of a sampling programme is determined by mainly three conditions.

### The objectives

We try to understand the dynamics of the transport of hydrophobic pollutants and its controlling factors. Therefore the sampling programme is focussed more on temporal than on spatial aspects. In this context there are at least three different responses of a catchment to precipitation events. These are runoff generation or flood response, transport of suspended particles, and changes in the concentrations of dissolved and particle associated solids. Each response has to be studied and, because they are interrelated, their interrelationships have to be understood. As this whole system is complex, no simple sampling programme will work. The programme must consist of several components that fit to each other.

In the case study presented here, sampling is restricted to the river. It is highly recommended to substantiate the data from these sampling programmes by gaining additional information about the catchment, but due to limited resources this could not be done during the first stages of our study.

### The catchment(s)

We work in three different catchments with a catchment size of 2.75 km<sup>2</sup>, 35km<sup>2</sup> and 222 km<sup>2</sup> respectively. The most intensive sampling programme is needed for the smallest of the catchments, because due to superimposition of different influences and the increasing importance of tributaries, temporal patterns become less distinct with increasing catchment size.

The three catchments have only two things in common. They are mountainous catchments and they 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 interrupted by patches of arable fields or bushland. Waste waters coming from small villages and minor sites of industry have a considerable impact on water quality.

A comparison with the literature shows that most groups working in small catchments prefer homogenous catchments for their investigations, where it is easier to study individual processes. Indeed, working in heterogenous catchments complicates the analyses of data structures and processes because of the great number of possible influences, and some conclusions remain hypothetically until further evidence has been gained from additional investigations. The striking advantage of working in heterogenous catchments is that the obtained results, once they are established, can be easily transferred to many other catchments of the same region and therefore can be used for planning purposes. Moreover, phenomena like antagonism or synergism can only be studied, if different influences occur simultaneously.

Working in heterogenous catchments does not affect the number of samples or the sampling intervall, but it has consequences for the laboratory work. In order to distinguish between different processes or between influencing factors, the measuring programme has to cover as many aspects as possible.

### Available information

This is probably the most important point. A complex programme cannot be designed starting from scratch. Besides, a sampling programme that is focussed on temporal aspects can hardly deal with many fluvial environments. For results obtained only in one or a few catchments, it is difficult to decide, whether they can be generalized, are of local importance, or reflect only special conditions of the catchment under investigation.

For our investigations we could use the results of several studies which were carried out by R.Herrmann and his working group about fifteen years ago. In twenty to thirty catchments of the Northern Eifel mountains and the Lower Rhine area nutrients, heavy metals, pesticides and cyanides were investigated (Symader 1976, Symader 1984, Rump 1976, Krutz 1979). It was an interesting result from these studies that both the general degree of pollution and the average composition of dissolved minerals correlated with the properties of the catchments. But it was much more important that different temporal patterns of intercorrelations between dissolved major ions and heavy metals that can give a deep insight in the most important processes depended on catchment characteristics as well (Symader 1985). With these results and information that was gained from topographic maps, it was possible to estimate a rank order of importance for potential factors controlling the transport of solutes and suspended solids.

The smallest catchment of 2.5 km<sup>2</sup> with its shallow soil on triassic limestones shows the same characteristics as a group of catchments, where soil erosion dominates waste water influences (Symader 1976). So it can be expected that the concentrations of most of the nutrients, above all phosphorus, ammonium and potassium, perhaps even nitrate tend to increase during flood events. Waste waters will have a stronger influence on the sediments of the small river than on its water body. The high organic content of the sediment is due to material rich in organic carbon that has settled during low flow periods. The redox conditions in the sediment permit the remobilisation of zinc, iron and manganese from interstitial waters and it can be expected that during high floods, water rich in these metals, will be released from the sediment (Symader 1984).

This pattern is a good guideline for designing the sampling programme, and it is not necessary that the response of the catchment corresponds with it in every detail.

### COMPONENTS OF THE SAMPLING PROGRAMME

When erosion is the dominant process for the transport of suspended particles and many dissolved solids, the central component must be a sampling programme that is based on events.

Bulk samples between 20 and 50 liters are taken about 30 minutes after the beginning of heavy rains. The criteria for taking a sample are the rise of the water level, changes in turbidity, or most important, changes in colour. It is the last criterium that makes automatic sampling impossible. That is why we have no data about flood waves that start after midnight, and not every flood wave could be sampled for its entire length.

According to the objectives of our investigations and the three interrelated responses of the catchment, this sampling programme contains three sets of variables



or measurements. The flood response is measured by continuous recording of precipitation and discharge at the gauging station, as it is common practice. Major dissolved ions such as sodium, potassium, calcium, magnesium, carbonate, sulfate, phosphate, chloride, nitrate, silicate are analyzed in order to get an idea about the processes of runoff generation. Remobilisation of fluvial sediments and the influence of the local waste water plant are described by the temporal behaviour of dissolved zinc, iron, manganese, copper and lead. As a result from our study it was found out that dissolved iron and manganese were also appropriate to study runoff generation processes. But that was not an established fact from the beginning.

Suspended sediment concentrations were determined after filtering. Turbidity at different wavelengths, and the density of the dried material were measured to get some information about particle size. Encouraging results from former investigation induced us to determine loss on ignition as a characteristic for suspended organic carbon. But what worked for suspended material consisting of varying proportions of waste water particles, was not an adequate method for a material with only a small range of organic carbon content. Therefore organic carbon and nitrogen had to be analyzed using a C-N analyzer.

We used chlorophyll, heavy metals and nutrients to describe the chemical composition of the suspended particles. PAHs and PCBs were determined only occasionally, or for selected individual waves

With these variables it was possible to understand the intra storm variations of the waves. It could be shown that the suspended matter was supply controlled, and up to five different types of sources of material could be distinguished (Symader et al. 1991; Symader & Strunk 1991).

Two important questions, however, could not be answered by this sampling programme alone. Although some ideas about the runoff generation process were gained from analyzing individual flood waves, the understanding was not good enough to develop a sound concept for a physically based runoff model. Concerning the transport of dissolved solids and suspended particle characteristics the inter storm variation was not clear. Therefore a second sampling programme with daily samples at the main gauge and for matters of comparison in an additional small catchment, where no influence of roads and domestic waste waters existed, was started. At first only the major ions were analyzed, later when we had more capacity in the laboratory, heavy metals were included. The heterogeneity of the lithologic subsoil with limestones, marls and some pockets of gypsum enabled us to reveal the predominant contributing area. These results were substantiated by weekly samples at important macropores and some outlets of the artificial drainage system that drains part of the slopes.

A third sampling programme deals with the characteristics of suspended particles. Daily samples are filtered, and the turbidity at different wavelengths is determined in the filtered and unfiltered sample. This programme was carried out, when we found out that most of the fluvial sediment is build up by particles that settle during the low flow periods. They come from the waste water plant and from the river banks where the vegetation is destroyed by cattle.

## FURTHER OUTLOOK

There are still important questions to answer. For the time being we understand most



of the runoff generation process and know the most important types of sources that deliver suspended material. This process changes during the course of the year, and even that is partly understood. But we do not understand the connection between the transport of suspended sediments and the particle associated contaminants. As most of the sampling was restricted to the river, important information about the catchment is missing. The knowledge about the type of sources alone is not sufficient. Above all we have to find out where the sources of particles and contaminants are situated, which means the location of sources. From the results of our studies, however, we know where to look. A fourth and fifth sampling programme have been started, where the temporal variations of fluvial sediment characteristics are investigated on a weekly base, and where the spatial patterns of PAHs in the catchment are studied.

## CONCLUSIONS

Many questions about the structure of a complex sampling programme are settled by the objectives, the chosen catchment and the amount of information that exists, before the sampling programmes are started. If nearly no information exists, it may be necessary to start with a limited study of one year. In most cases biweekly sampling will be sufficient to determine the sampling frequency for the following programmes.

Complex problems require complex programmes. In the case of extended measurements or a great number of analyses, a stepwise procedure can be recommended. The most important problem is that different components of a complex sampling programme fit to each other. Each subsequent component is designed in order to answer questions that remain open or have come up during previous components. This procedure requires at least a preliminary analysis of the data, while the programme is still in progress.

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