Heavy metals in water, suspended matter and sediment

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Abstract. Using principal component analysis, relationships are investigated between heavy metals in solution, suspended matter and sediment. It can be shown, that especially in former mining areas the heavy metal content in sediment does not reflect the properties of the water body except for Cu and Ni. Mn and Fe show no relationships at all. The heavy metal content of suspended matter is generally more influenced by sediment than by water. Nevertheless it may show quite a different behaviour if special waste waters are discharged, like those containing Cd and Zn.

Concerning temporal relationships between dissolved and suspended heavy metal contents, it is strongly suggested that the lack of significant correlations is due to comparison of different dimensions. At least in highly polluted rivers such interrelationships do exist.

Les metaux lourds dans l'eau, les matières en suspension et les sédiments

Résumé. L'auteur présente une recherche des relations entre les métaux lourds en solution, dans les matières en suspension et dans les sédiments, au moyen de la méthode des composantes principales. On peut montrer que, spécialement dans les anciennes régions minières, le contenu en métaux lourds des sédiments ne traduit pas les propriétés de l'eau, sauf pour Cu et Ni. Pour Mn et Fe, on ne trouve aucune relation. Le contenu en métaux lourds des matières en suspension est généralement plus influencé par celui des sédiments que par celui de l'eau. Néanmoins, on peut avoir un comportement tout à fait différent en présence de certaines eaux usées à caractère particulier, comme celles qui contiennent Cd et Zn.

En ce qui concerne les relations entre le contenu en métaux lourds dissous et en suspension, l'auteur penche fortement pour l'hypothèse que l'absence de corrélation spécifique est due à un problème de dimension. Néanmoins, dans les rivières fortement polluées, de telles interrelations existent.

River water is used to an increasing extent as drinking and irrigation water particularly in highly urbanized and industrialized areas. In addition to water pollution by nutrients or organic compounds, the heavy metal content in flowing waters has become one of the most important problems because of its toxic effect even in minor concentrations. In general, suspended matter and sediment work as a trap for dissolved heavy metals, but remobilization can sometimes be observed.

An investigation to supply information about the interactions of heavy metals in water, suspended matter and sediment, sponsored by DFG was started in 31 basins in the Northern Eifel Mountains and the adjacent loess zone (Fig.1).

For that purpose water samples were taken every fortnight and analysed for Ni, Cd, Pb, Cu, Zn, Mn, and Fe in solution, suspended matter and sediment by means of atomic absorption spectroscopy. The system is indicated together with the heavy metal by adding the indices sol, sus, sed. Analysis of sediment was confined to particles less than 1 mm.

The area of investigation which has previously been subjected to water quality research (Rump, 1976; Symader, 1976; Herrmann *et al.*, 1977) includes rural, industrial and urban regions and former mining areas.

To study the spatial variability of heavy metals a principal component analysis followed by a varimax rotation of the normally distributed means was calculated. This principal component analysis can be seen as a sorting mechanism of the information of

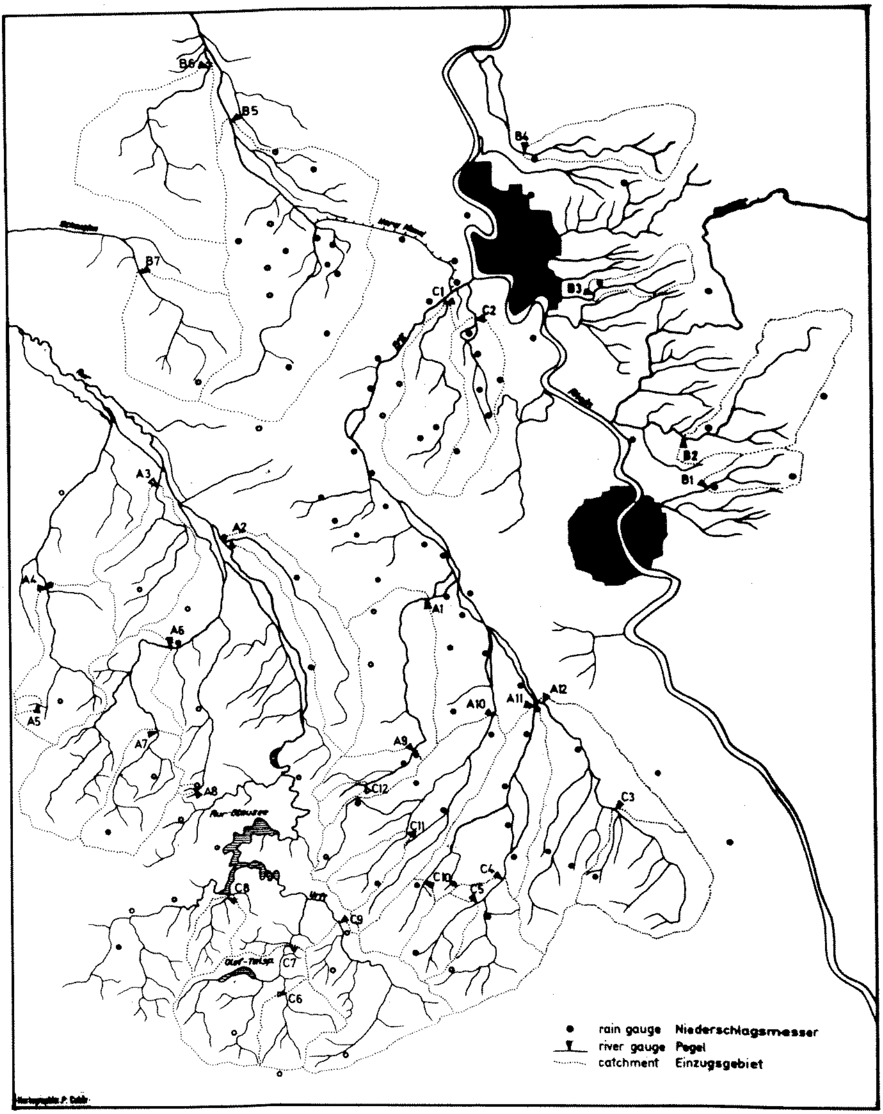

FIGURE 1. Location map.

a correlation matrix. To facilitate the interpretation of the results it is useful to distinguish three sources of heavy metal input:

(1) dissolved heavy metals from waste waters;
(2) heavy metals as particles from waste waters;
(3) heavy metals from soil erosion.

A study of the variability can only give information about a simultaneous occurrence of the different sources. To find causal relationships an analysis of temporal variance should be used. Both points of view are necessary to characterize the extent of pollution.

Ten principal components are sufficient to cover 90 per cent of variance from 21 variables (seven heavy metals in three systems). Principal components were arranged

TABLE 1. Principal component analysis of heavy metals in water, suspended matter and sediment. Varimax rotated matrix

	1	2	3	4	5	6	7	8	9	10
VAR %	14	11	11	10	10	9	8	7	5	5 SU = 90%
Ni							−0.6			
Cd					0.9					
Pb				−0.6		0.4				
Cu		−0.8								
Zn		−0.4	−0.4		0.5					
Mn										−0.8
Fe									0.8	
Ni							−0.9			
Cd					0.5	−0.6				
Pb	0.4			−0.9						
Cu		−0.8								
Zn						−0.9				
Mn	0.9									
Fe	0.9									
Ni							−0.4			
Cd			−0.6							
Pb				−0.8						
Cu		−0.4	−0.7							
Zn			−0.8							
Mn	0.7							−0.5		
Fe								−0.9		

The first set shows heavy metals in solution, the second in suspension, the third in sediment.

according to their shares of variance. Loadings less than 0.4 were omitted.

The first principal component shows high loadings in $Mn_{(sus)}$, $Fe_{(sus)}$ and $Mn_{(sed)}$. $Mn_{(sol)}$ and $Fe_{(sol)}$ are obviously of another origin, because they load components 9 and 10. Indeed $Mn_{(sol)}$ and $Fe_{(sol)}$ come from industrial waste waters, whereas $Mn_{(sus)}$ comes from erosion. The highest concentrations occur in catchments with Triasic sandstones which also hold Pb, which the middle loading of $Pb_{(sus)}$ suggests.

The eighth component indicates that in spite of a close relation between $Mn_{(sed)}$ and $Fe_{(sed)}$, $Fe_{(sed)}$ has an additional source possibly from corrosive material. The second principal component has Cu in all three systems which originates from waste water effluents. The third and fifth components must be considered together and show a specific feature of this area of investigation. The simultaneous occurrence of Cd and Zn is not confined to specific effluents, but can also be found in the subsoil. That means that Cd and Zn sediments of some catchments are influenced both by waste waters and the subsoil. The sixth component shows the same relationship which is due to a specific waste water with particles of Cd and Zn enrichment. The fourth component is dominated by Pb of lithologic origin. The medium loading of $Pb_{(sol)}$ is based on waste waters, whose injection points by coincidence are in the same catchments. The seventh component reflects pollution from Ni contaminated waste water with its influence on sediment and suspended matter.

To summarize the information given above sorted according to the single elements, the following conclusions can be drawn:

(1) Cu and Ni can be found simultaneously in all three systems. Their origins are waste waters.

(2) Pb in suspended matter and sediment comes from soil erosion in catchments with plumboferous subsoil.

(3) Cd occurs associated with Zn, both dissolved and incorporated.

(4) Three forms of Fe and Mn sources can be distinguished, specific waste waters, corrosive and lithologic material.

(5) Zn comes from the subsoil, nevertheless it shows significant correlations with nearly all the other dissolved elements. Therefore it may be used as a predictor for heavy metal pollution.

The relevance of these results is twofold:

(1) Regarding the spatial distribution of dissolved heavy metals near independence of variables can be observed. This is only possible, if effluents with waste waters of significantly different composition are distributed over different catchments. In an area showing this pattern water quality can be improved by controlling only a few injection points.

(2) Collection of water samples involves much effort and cost. Therefore it is of interest to find which system is best for judging heavy metal pollution.

Förstner and Müller (1974) suggest investigation and monitoring of sediments, because even injections of short durations can be discovered. Moreover concentration levels are much higher than in solution and therefore easier to measure. In former mining areas data derived from sediments are insufficient to estimate the respective share of lithological influences and waste water pollution. Therefore in this area of investigation this method is only satisfactory for Cu and Ni, but fails for Mn and Fe. Data on Cd, Pb, and Zn in sediments are difficult to interpret and may lead one astray.

Considering that ore deposits were often a factor influencing urbanization and industrialization it is evident that in many cases collecting water samples cannot be avoided.

Contrary to the analysis of spatial variance which gives information about the simultaneous occurrence, analysis of temporal variance can answer questions about interrelationships between dissolved and suspended heavy metals. As research is still in progress only preliminary results can be discussed.

The trace metal content is usually measured as mg/l. in solution and in suspended matter as mg/l. or mg/kg (=ppm) with runoff or suspended matter respectively as a reference. Schleichert (1975) suggests using only ppm for heavy metal content in suspended matter for two reasons. On the one hand he wants to eliminate the influence of the suspended load, on the other hand he postulates an equilibrium between heavy metal concentration in solution and suspended matter, depending on the concentration level at the single particle.

In this investigation no significant correlation between dissolved and suspended solids could be found, even though a highly polluted river was selected. This indicates that the postulated equilibrium does not exist or that it covers only a small percentage of variance. A further explanation of the lack of significance can be found by checking the method of comparison.

Both dimensions are quotients (mg/l. and mg/kg). Quotients are used to eliminate the influence of a certain variable. This is successful only if the interrelationship is a linear one. Therefore both the quotients imply a linear relationship, the 'eliminated' variables are different and show moreover dependencies among each other (concentration of suspended matter varies with discharge).

To avoid these difficulties a correlation matrix of 28 variables was calculated, including dissolved trace metals, trace metals in suspended matter not only in ppm but also in mg/l., additional variables describing suspended matter itself, for example by turbidity, loss on ignition etc. On account of an insufficient sample size a principal component analysis was not undertaken.

Discussion of results:

(1) No significant correlation between dissolved [mg/l.] and suspended heavy

metals [ppm] could be found.

(2) A comparison between dissolved and suspended heavy metals [mg/l.] showed a correlation of 1 per cent significance for Zn and Cu and of 0.1 per cent for Fe.

(3) Due to remobilization effects Ni, Cd, Zn, and Fe in solution correlated significantly with suspended matter and turbidity.

(4) Interrelationships between suspended matter and suspended heavy metals [mg/l.] are significant only for Pb and Fe. As Fe in ppm correlates with suspended matter too, it is obvious that it cannot be a linear relation. Except for Pb and Fe the quotient ppm is of little use, for Fe a nonlinear approach would give better results.

(5) Ni seems to be transported by hydrous Mn and Fe oxides.

These results indicate that interrelationships between dissolved and suspended heavy metals exist at least in highly polluted rivers. Lack of significant correlations is probably due to the comparison of non-comparable variables. The influence of disturbing variables cannot be eliminated by simple division but may be estimated by multiple correlation analysis.

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