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Assessing in-stream erosion and contaminant transport using the end-member mixing analysis (EMMA)

INGO HAAG, ULRICH KERN & BERNHARD WESTRICH

Department of Hydraulic Engineering, University of Stuttgart, Pfaffenwaldring 61,
D-70569 Stuttgart, Germany
e-mail: ingo.haag@iws.uni-stuttgart.de

Abstract A special mixing technique, called end-member mixing analysis (EMMA) is adopted to quantitatively assess the contributions of distinct in-stream sources to suspended sediments and particle-bound contaminants. Application to a flood event in the River Neckar, Germany, illustrates the usefulness of the technique. The results show that the erosion of relatively small quantities of highly contaminated bottom sediments from a lock-regulated reservoir near Lauffen did considerably increase the heavy metal load of the river.

INTRODUCTION

In many industrialized areas aquatic sediments are severely contaminated with persistent pollutants, such as heavy metals, dioxins, or PCBs. In river systems, significant quantities of contaminated sediments are stored in regions of low turbulence, including groin fields and backwater sections of river reservoirs (e.g. Allan *et al.* 1983; Salomons, 1987). During flood events these bottom sediments and the associated pollutants can be mobilized by in-stream erosion, which increases the contaminant load and may negatively affect the aquatic ecosystem (e.g. Kern, 1997; Hollert *et al.*, 2000).

In this paper, a mixing approach is used to quantify the contributions of distinct in-stream sources to the downstream load of suspended particulate matter (SPM) and the associated contaminants.

THE END-MEMBER MIXING ANALYSIS (EMMA)

Mixing analyses have been used for decades in many scientific fields, including mineralogy, air quality studies and hydrology (Akerjord & Christophersen, 1996). A special technique, called end-member mixing analysis (EMMA), was introduced in the context of hydrochemical studies by Christophersen *et al.* (1990).

EMMA is based on the assumption that the composition of a given sample can be explained as a conservative mixture of a limited set of end members (EM). In the case of SPM, this means that any sample results from a mixture of distinct sediment sources. Figure 1 illustrates the case in which SPM samples downstream of a river reach are made up of three EMs: SPM from upstream (EM_1) and two distinct

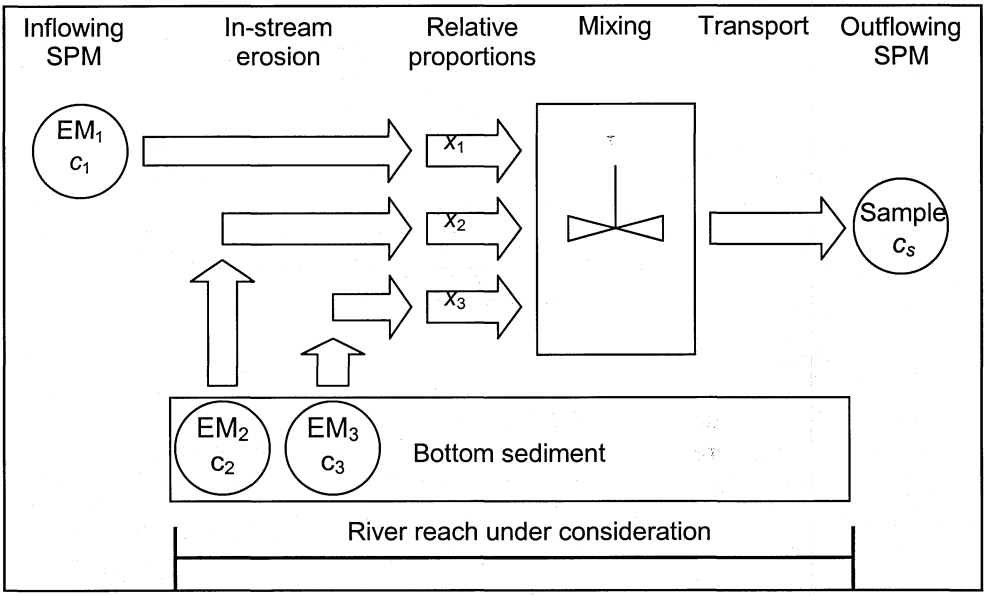

Fig. 1 Conceptual model of the mixing approach for the analysis of SPM samples.

sediment pools within the river reach (EM_2 and EM_3). The relative contributions to the mass of the downstream SPM sample are x_1, x_2, and x_3 for the three end members EM_1, EM_2, and EM_3, respectively. The mixing model implies two constraints: (a) the sum of all relative contributions x_i is 1 and (b) there must not be negative contributions from any EM ($x_i \geq 0$). If a sediment-associated chemical (tracer) mixes conservatively, its concentration in the SPM sample will be explained from the same mixture. The term “conservative” means that the concentration of the chemical is not altered by processes such as dissolution, precipitation, adsorption, or desorption. Hence, in the case of n end members the concentration of a conservative SPM-associated tracer in the sample (c_s) is given by:

$$c_s = \sum_{i=1}^{n} x_i \cdot c_i \tag{1}$$

Such simple mass balance equations can be formulated for any conservative SPM-associated chemical. The resulting set of equations can be written in vector form:

$$\mathbf{c} = \mathbf{C}\mathbf{x} \tag{2a}$$

or

$$\mathbf{x} = \mathbf{C}^{-1}\mathbf{c} \tag{2b}$$

Vector **x** contains the relative contributions of the end members x_i, vector **c** contains the concentrations of the tracers in the SPM sample, and matrix **C** contains the concentrations of the tracers in all end members. Constraint (a) is easily accounted for by substitution, which reduces the number of unknowns to (n – 1). Hence, to solve the mixing problem (n – 1) mass balance equations, and consequently (n – 1) tracers are needed. However, in natural systems the concentrations of the tracers in the EM are not exactly defined but rather show some spatial and temporal variations. Additional uncertainties arise from analytical inaccuracies and from the fact that most chemicals do not mix strictly conservatively. Therefore, the results obtained from equation (2b) depend on the set of tracers used for analysis.

To improve the reliability of a mixing analysis, as many conservative chemicals as possible should be used. Introducing $m > (n - 1)$ tracers and mass balances, results in an overdetermined set of equations, which does not have a unique solution. To obtain an optimal solution in the sense of least squares, the term $|\mathbf{C}\,\mathbf{x} - \mathbf{c}|$ has to be minimized. The solution for this minimization problem without considering constraint (b) is given by the Gaussian normal equations:

$$\mathbf{x} = \left(\mathbf{C}^T\mathbf{C}\right)^{-1}\mathbf{C}^T\mathbf{c} \tag{3}$$

If constraint (b) is violated, the optimal solution will be on the boundary. Hence, the contribution of the corresponding EM has to be set to zero and equation (3) has to be solved for the remaining EMs. A program based on equation (3), which additionally considers constraint (b) has been written in Microsoft QuickBASIC®.

Once the relative contributions (x_i) of each end member have been determined, the concentrations of the conservative chemicals in the SPM sample, as predicted by the mixing approach, can be calculated with equation (1). The quality of the mixing analysis can be assessed by comparing predicted with measured concentrations, which is a major advantage of EMMA over traditional mixing techniques.

STUDY SITE AND DATA ACQUISITION

The River Neckar is a major tributary of the River Rhine. It drains a densely populated and highly industrialized area in southwest Germany. Its downstream reach (200 km) is split up into 27 lock-regulated reservoirs. The Lauffen Reservoir is situated in the middle of this chain of reservoirs. At Lauffen, the mean discharge is 88 $m^3\ s^{-1}$; sediment yield varies between 58 000 and 560 000 t $year^{-1}$ (Kern & Westrich, 1997).

In 1991 and 1992, a total of 21 sediment cores were taken from the Lauffen Reservoir and sectioned into 199 subsamples. The fine-grained fraction smaller than 20 μm was obtained in a settling tube. Following HNO_3-HF digestion of the fine-grained fraction it was analysed for cadmium (Cd), copper (Cu), lead (Pb), and other heavy metals, using atomic absorption spectrometry (AAS). For details see Kern (1997). On the basis of this investigation, the fine-grained deposits in the backwater region of the reservoir were split into two sediment pools: highly contaminated old sediment (HCOS) and less contaminated younger sediment (LCYS) (Kern, 1997). The HCOSs were deposited before 1973, when a dye factory released large quantities of cadmium and other heavy metals into the River Enz (Fig. 2). After 1973 emission was reduced drastically. In subsequent years, HCOS was covered by LCYS and near-surface sediment quality has improved considerably. At present, HCOS is buried at depths ranging from a few centimetres up to more than one metre. However, during extreme flood events, when large amounts of sediment are eroded and transported downstream, erosion depth can reach down to almost 1 m (Kern,

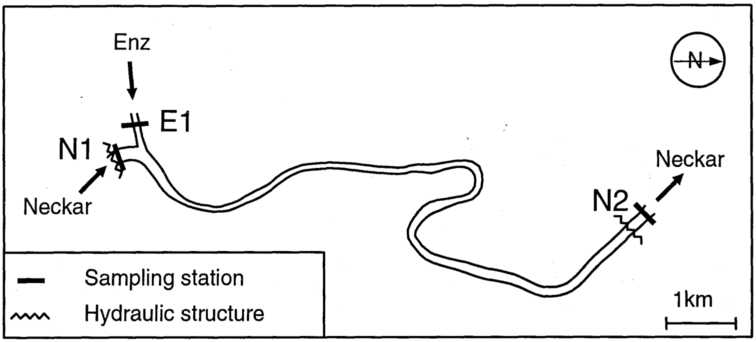

Fig. 2 The Lauffen Reservoir and locations of the SPM sampling stations E1, N1, N2.

1997). During such flood events, the bottom shear stress in the river clearly exceeds the critical shear stress of erosion even of old and very well consolidated HCOS (Haag *et al.*, in press). Hence, there is a substantial risk that severely contaminated bottom sediment is mobilized during floods.

During a flood event in April 1994, one litre water samples were collected from the rivers Neckar and Enz at stations N1, N2, and E1 (Fig. 2) with a mean sampling interval of 1.8 h. The samples were filtered through 0.45 µm cellulose acetate filters and SPM concentrations were determined gravimetrically. Both, SPM and the filtrate were analysed for heavy metals.

RESULTS AND DISCUSSION

Cadmium, Cu and Pb were selected as tracers. Based on the analysis of the filtrate, no significant (<2%) dissolution or desorption of the three metals was detected. Therefore, they could be regarded as conservative.

For the mixing analysis, inflowing SPM was considered as EM_1. Since the heavy metal concentrations in the inflowing SPM only changed by 5% during the flood event (data not shown), the concentrations of the tracers were taken as constant over time (Table 1). LCYS and HCOS were regarded as potential in-stream sources (EM_2 and EM_3). Echo sounding surveys conducted before and after the flood indicated that erosion depth reached down to 70 ± 5 cm in a narrow 300 m reach at the downstream end of the reservoir. In contrast, in all other regions of the reservoir, erosion depth was only a few centimetres (Kern, 1997). Since the highly contaminated old sediment is covered by younger material, HCOS was only mobilized from the

Table 1 End-member composition.

Tracers	Inflowing SPM weighed mean	LCYS: Median	Lower quartile	Upper quartile	HCOS: Median	Lower quartile	Upper quartile
Cd (mg kg^{-1})	0.75	2.41	1.6	6.7	27.0	23.5	34.7
Cu (mg kg^{-1})	41.3	98.5	61.7	118.7	383	361	457
Pb (mg kg^{-1})	38.5	86.5	60.7	111.2	246	222	280

Table 2 Total loads of SPM and particle-bound heavy metals during the 1994 flood event and relative and absolute contributions of the three end members.

	SPM		Cd		Cu		Pb	
	(%)	(1000 t)	(%)	(kg)	(%)	(kg)	(%)	(kg)
Inflowing SPM	88.2	200	45.7	150.6	67.6	8 299	71.5	7 704
LCYS	9.8	23	16.3	53.7	17.9	2 198	17.9	1 929
HCOS	2.0	5	38.0	125.2	14.5	1 780	10.6	1 142
$\sum$ calculated	100.0	228	100.0	329.5	100.0	12 277	100.0	10 775
$\sum$ measured	100.0	228	104.3	343.8	95.3	11 695	102.3	11 020

narrow downstream reach. Based on this information, the HCOS end member was assumed to be represented by the median concentrations of the HCOS samples in the 300 m downstream reach. Characteristic LCYS concentrations were calculated from all LCYS samples (Table 1).

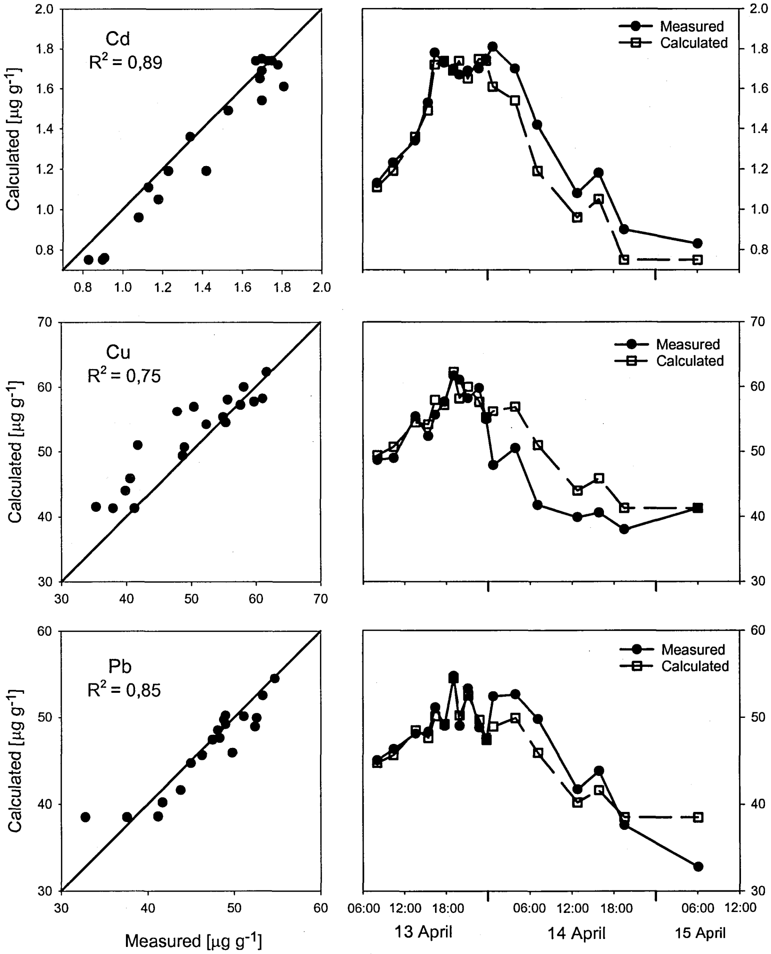

Fig. 3 Calculated *vs* measured concentrations of the three tracers.

First, the total load of the flood event, as determined by Kern (1997), was analysed using EMMA. Downstream SPM and heavy metal loads were assumed to result from a mixture of all three end members (medians of LCYS/HCOS). The results are given in Table 2. The measured particulate heavy metal loads are explained quite well with the three end-member mixing approach. Although EMMA allows sedimentation of inflowing SPM, the calculated erosion (LCYS + HCOS = 28 000 t) matches with the results of Kern & Westrich (1997), who determined a net erosion of 28 000 ± 5 000 t from a simple SPM mass balance. This indicates that sedimentation was of minor importance, i.e. all inflowing SPM was transported through the reservoir. It should be noted, that erosion of HCOS only made up 2% (5000 t) of the outflowing SPM load but 38% (125 kg) of the particle-bound Cd load.

Second, all downstream SPM samples were analysed separately. The percentage of variance explained (R^2) by EMMA varies between 75 and 89% (Fig. 3). The heavy metal concentrations during the rising limb and the maximum are reproduced very well. However, a lack of fit occurs during the falling limb, when EMMA predicts that downstream SPM consists almost completely of material conveyed from upstream (Fig. 4). The lack of fit can therefore, mainly be attributed to the simplified assumption of constant heavy metal concentrations in EM_1. Figure 4 also illustrates that the contribution of eroded bottom sediment to SPM concentrations is most important during the rising limb of the hydrograph. The erosion of HCOS starts later than that of LCYS. In terms of SPM concentrations, HCOS is of minor importance throughout the whole flood event. However, looking at the heavy metal flux the importance of HCOS becomes striking (Fig. 5). This is particularly true for Cd. During the time of maximum contaminant load, erosion of HCOS is responsible for almost 50% of the Cd flux.

The results illustrate that the in-stream erosion of highly contaminated bottom sediments in the Lauffen Reservoir do considerably increase the Cd, Cu, and Pb concentrations and loads in the River Neckar. This also explains the increase of SPM toxicity during floods in the River Neckar, which was reported by Hollert *et al.* (2000).

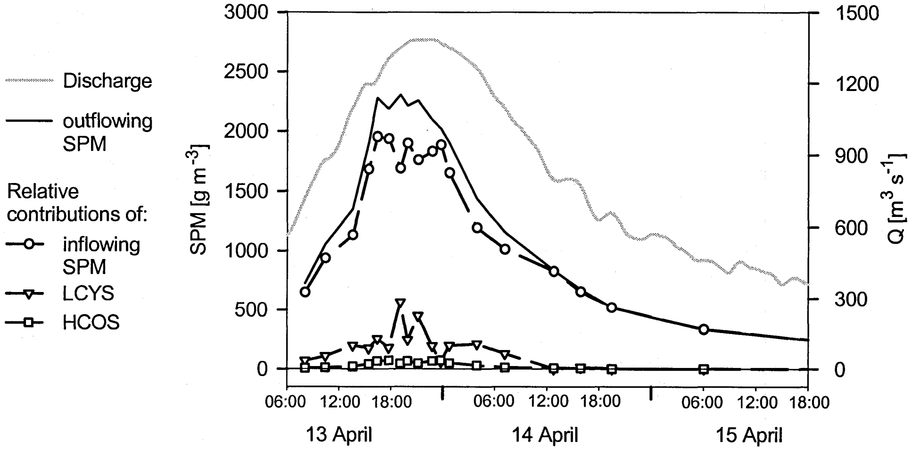

Fig. 4 Measured discharge and SPM concentrations at N2 and relative contributions of the three end members.

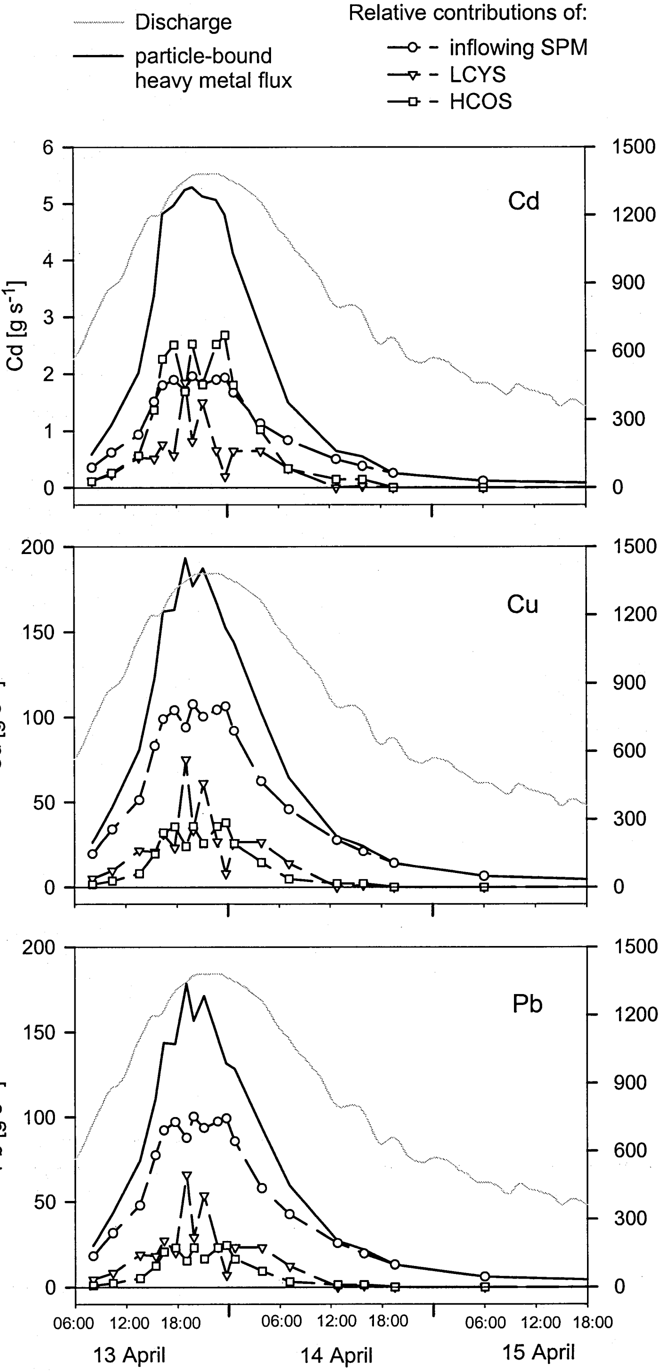

Fig. 5 Fluxes of particle-bound heavy metals and relative contributions of the three end members.

CONCLUSIONS

The end-member mixing analysis (EMMA) is a powerful tool to quantitatively assess the contributions of distinct sediment sources to the SPM and contaminant load. However, particular care must be taken in the choice of adequate tracers and representative end members.

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