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Transplanted Aquatic Mosses for Monitoring Trace Metal Mobilization in Acidified Streams of the Vosges Mountains, France

Jacques Mersch, François Guérold, Philippe Rousselle, and Jean-Claude Pihan

Laboratory of Ecology, University of Metz, B.P. 4116, 57040 Metz Cedex 01, France

As a result of acid depositions, trace metals are mobilized from the soils to the aquatic environment (Borg 1983; Bergkvist 1987). Especially in poorly mineralized waters, elevated metal concentrations may rapidly have adverse effects on aquatic organisms. In particular, it has been shown that aluminium, a key element in the acidification process, is a toxic cofactor for fish and other biota (Baker and Schofield 1982).

An accurate assessment of this specific form of water pollution may not be possible when only based on analyses of single water samples. On the one hand, water metal concentrations are often close to the detection limit of usual analytical techniques, and on the other hand, levels in acidified streams undergo strong temporal variations caused by acid pulses following meteorological events such as heavy rainfall and snowmelt. Compared to water analyses, indirect monitoring methods provide undeniable advantages for assessing water contamination. Aquatic bryophytes, in particular, have been regarded as interesting indicator organisms for trace metal pollution (Wehr et al. 1983; Mouvet 1984). However, their use has mainly been restricted to the lower course of streams for evaluating the impact of industrial discharges. The purpose of this study was to test the suitability of transplanted aquatic mosses for monitoring aluminium and four other trace metals (copper, iron, lead and zinc) in the particular context of acidified streams draining a forested headwater catchment.

MATERIALS AND METHODS

The study area is a 17-km^2 headwater catchment located in the Vosges Mountains (northeastern France). The vegetation of the basin is mainly a mixture of silver fir (*Abies alba*) and European beech (*Fagus sylvatica*). The geology is dominated by a poorly-weathered granitic bedrock overlain by a mosaic of upland soils consisting of stagnopodzols, acidic brown soils and ochre podzolic soils. All the investigated streams are located above any developed and agricultural area. Six monitoring stations were selected according to previously obtained pH and Al data. The altitude ranged from 625 m at the lowest sampling site (station 1) to 1,010 m at the highest (station 6).

Moss tufts of the species *Amblystegium riparium* were collected from a non-acidified stream (site 1). Samples of about 5 g spin-dried wet weight were placed into plastic bags (mesh size 10 mm) and transplanted to the different monitoring

Send reprint requests to J. Mersch at the above address.

sites (2 to 6). One bag was re-introduced in the native stream to provide a control sample after exposure. The experiment was carried out twice, in October and in November 1990. The samples were recovered each time after an exposure period of 28 days. The washing procedure of the mosses has been described by Wehr et al. (1983). For each sample, two replicates of 300 mg dry weight were digested in 20-mL polyethylene test tubes for 24 hours at 70 °C under pressure using HNO_3 (6 mL, 4*M*). The digests were made up to 19 mL with distilled water to obtain the final matrix. During each exposure period, pH was measured six times in situ using a specific glass electrode for low ionic solutions. Water samples for Al analysis were collected on three occasions. The concentrations of Al in the water and in the bryophytes were determined by atomic absorption spectrophotometry (AAS) using a graphite furnace; Cu, Fe, Pb and Zn in mosses were analyzed by flame AAS. Al in the water was detectable down to 5 μg L-1. The detection levels in the organisms were 0.5, 2, 4, 4 and 2 μg g-1 for Al, Cu, Fe, Pb and Zn, respectively. Quality control of metal analysis was performed using certified reference moss material supplied by the Community Bureau of Reference (Brussels, Belgium).

RESULTS AND DISCUSSION

Monthly measurements of pH and Al concentrations during 1990 provided information about the spatial differences in water acidification (Table 1). Three cases can be distinguished: site 1, the reference location, is neutral to slightly acid, site 2 is moderately acid and sites 3 to 6 are strongly acidified. The temporal variations of Al in the water were closely associated with proton concentrations as illustrated by the case of site 4 (Figure 1). Comparing both exposure periods of bryophytes, the lower pH values, concomitant with the greater Al concentrations, were recorded in the November experiment (Table 2). Increased Al concentration in the water accompanying pH depression has been mentioned by several workers as being a result of Al mobilization from the soil (Dewalle et al. 1988; McAvoy 1988).

Table 1. pH values and Al concentrations in water samples collected monthly during 1990 (n = 12).

site	pH		Al (μg L-1)	
	mean ± SD	range	mean ± SD	range
1	6.96 ± 0.37	6.41 - 7.50	64 ± 24	32 - 114
2	5.74 ± 0.43	5.06 - 6.35	185 ± 64	94 - 296
3	5.25 ± 0.40	4.75 - 5.85	247 ± 54	156 - 325
4	5.12 ± 0.36	4.51 - 5.75	279 ± 86	150 - 424
5	4.90 ± 0.32	4.45 - 5.56	299 ± 59	224 - 432
6	4.64 ± 0.19	4.21 - 4.90	351 ± 82	230 - 481

The aquatic bryophytes accumulated Al, Pb and Fe at all the monitoring sites during both exposure periods (Figure 2). Al contents in the mosses exposed in acid streams ranged between 10,390 μg g-1 and 12,700 μg g-1 dry weight, whereas they remained below 7,750 μg g-1 in the control samples (site 1). The accumulation of Pb was also strongly influenced by acidity. Compared to the reference value of 26 μg g-1, observed at site 1, an extremely high concentration, 199 μg g-1, was recorded in the most acid stream (site 6). These elevated levels were surprising, since Pb, as opposed to Al, is not of geological but of anthropogenic origin. Accumulation of Fe in mosses depended only weakly on acidity. For all three metals, the higher accumulation levels were observed during the second experiment.

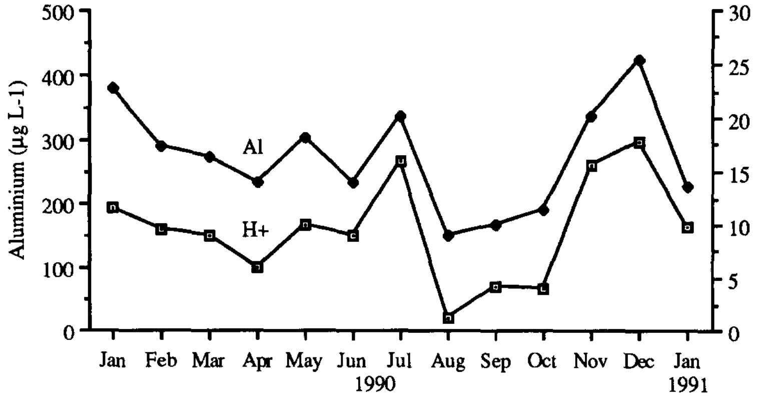

Figure 1. Temporal variations of acidity and Al concentrations in an acidified stream (site 4) based on monthly measurements.

This evolution may be attributed to the pH depression recorded in November. Lehtonen (1989) found that Al and Fe concentrations were higher in native mosses collected in an acidified Finnish lake than in those from a lake with a fairly good buffer capacity. Similarly, Sprenger and McIntosh (1989) noted that various macrophyte species, growing in the most acid lakes from a New Jersey area, exhibited the highest Al and Pb concentrations. These results, however, contrast markedly with the work of Caines et al. (1985) who observed a decrease in Al concentrations with increasing acidity in aquatic bryophytes from Scottish streams. Differences in Al accumulation may involve metal speciation which strongly conditions the availability to aquatic organisms. Besides cationic species, Al occurs as amorph forms and as anionic species (Petersen et al. 1987; Huang 1988; Lewis et al. 1988). The non-cationic species may not be available for mosses, since the accumulation process is based on cation exchange on the surface of the moss cell wall (Schwarzmeier and Brehm 1975; Breuer and Melzer 1990).

Table 2. pH values (n = 6) and Al concentrations (n = 3) in water samples collected during the exposure periods of aquatic mosses.

site	pH		Al (μg L-1)	
	mean ± SD	range	mean ± SD	range
October				
1	7.15 ± 0.35	6.58 - 7.44	55 ± 13	40 - 64
2	5.92 ± 0.45	5.05 - 6.19	128 ± 10	118 - 138
3	5.36 ± 0.43	4.64 - 5.72	205 ± 23	180 - 226
4	5.24 ± 0.36	4.57 - 5.55	207 ± 51	166 - 264
5	4.90 ± 0.32	4.39 - 5.22	270 ± 28	238 - 290
6	4.55 ± 0.20	4.27 - 4.76	302 ± 17	282 - 314
November				
1	6.74 ± 0.35	6.25 - 7.09	66 ± 23	40 - 80
2	5.33 ± 0.24	5.02 - 5.69	177 ± 43	138 - 223
3	4.83 ± 0.15	4.69 - 5.10	245 ± 57	180 - 289
4	4.78 ± 0.17	4.59 - 5.08	284 ± 82	190 - 335
5	4.57 ± 0.11	4.46 - 4.74	267 ± 63	224 - 339
6	4.55 ± 0.06	4.47 - 4.63	303 ± 68	230 - 364

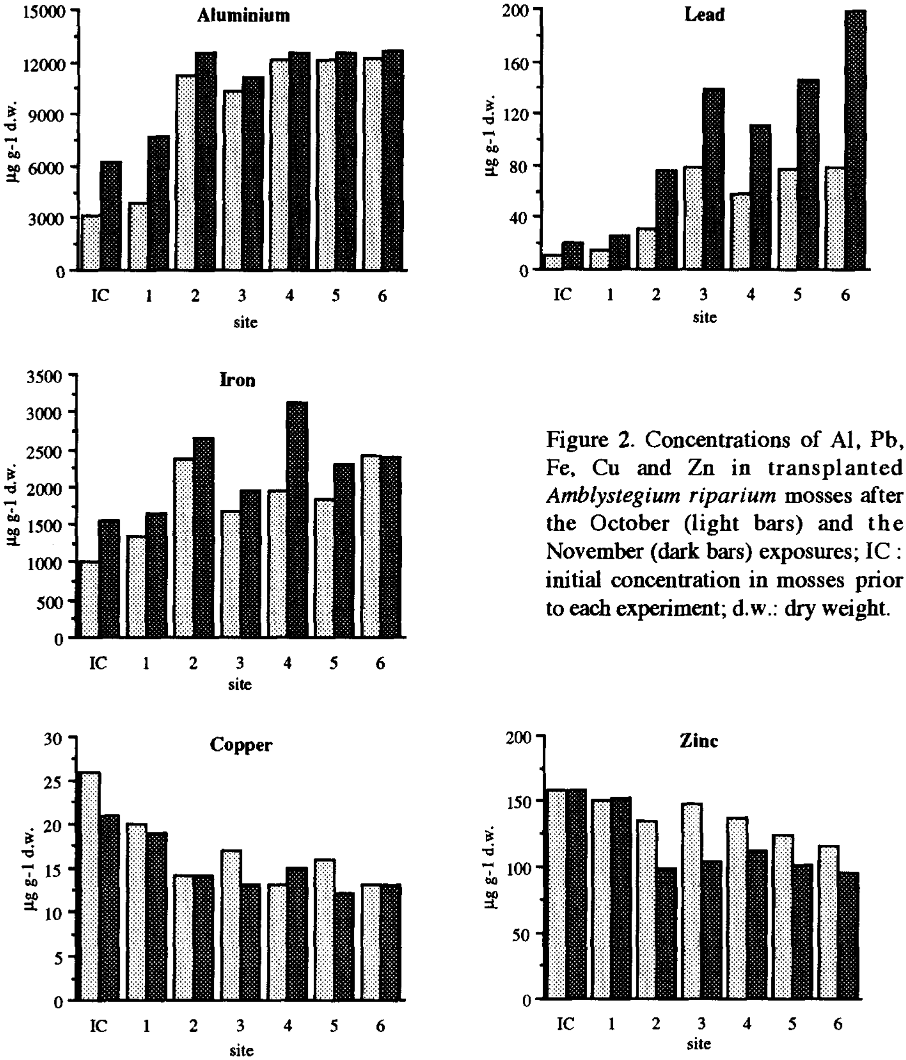

Figure 2. Concentrations of Al, Pb, Fe, Cu and Zn in transplanted *Amblystegium riparium* mosses after the October (light bars) and the November (dark bars) exposures; IC : initial concentration in mosses prior to each experiment; d.w.: dry weight.

Whichever site and sampling period considered, the levels of Cu and Zn in the transplanted bryophytes were lower than the initial concentrations (IC) measured in the control samples before introduction (Figure 2). The loss of these two metals was strongly influenced by acidity. During the second exposure time, characterized by the lower pH values, maximum loss amounted up to 40 % for Cu and for Zn at site 6; at the control site, metal release did not exceed 10 and 5 % for Cu and Zn, respectively. Similar results have been reported for Zn (Caines et al. 1985; Sprenger and McIntosh 1989; Lethtonen 1989). The observed decrease suggests a release of these metals from the mosses into the water. The correlation between metal desorption and pH depression might be interpretated as a competition between protons and Cu and Zn ions for binding ligands on the cell walls. The existence of a sequence in binding preferences of cations has been demonstrated in several studies with *Sphagnaceae* (Schwartzmeier and Brehm 1975; Breuer and Melzer 1990). This explains why some metals were accumulated while others were released.

The transplanted aquatic bryophytes provided useful indications about trace metal mobilization from the soil. Metal accumulation (Al, Pb, Fe) and loss (Cu, Zn) reflected the acidity level of each investigated site. This method could be particularly interesting for monitoring the environmental conditions during acid stresses which are the most critical periods for aquatic life. Future experiments should include analyses of trace metals in water samples from a wider range of streams draining catchments of different geological bedrocks in order to improve the understanding about the influence of acidity on metal accumulation in aquatic mosses. The mobilization of other, particularly toxic metals such as Hg, As and Cd should be investigated.

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