

INFLUENCE OF WATER SCARCITY ON THE FATE AND EFFECTS OF METALS IN FLUVIAL ECOSYSTEMS

Helena Guasch, Natàlia Corcoll, Berta Bonet and Alexandra Serra

Institute of Aquatic Ecology, Campus de Montilivi 17071, Universitat de Girona

Human activity is one of the major causes of elevated concentrations of metals in fluvial ecosystems causing a great concern about their potential toxicity and trophic transfer. Metal concentration is very variable in time and space depending on the source of pollution (diffuse or point-sources), the hydrological regime and the processes affecting their transfer from the water phase to the benthic compartment. Based on this framework, it is expected that a water scarcity situation, understood as the period when surface water flow is well below average flow conditions, will also cause remarkable changes on the fate and effects of heavy metals at ecosystem scale. Furthermore, the duration and frequency of water scarcity episodes is also important since metal bioaccumulation and toxicity are strongly influenced by the time of exposure. In comparison with stable high flow conditions, it is expected that low flow will be linked to higher metal concentration in the water phase (due to low dilution) and further retention in the benthos (if conditions are stable). This retention, however, is expected to be transient since a sudden water flow increase will easily remove the sediments and transport them downstream. On the other hand, high flow conditions are expected to be linked to low metal concentration (due to dilution) but may also lead to high metal bioaccumulation due to low but chronic exposure. Low flow conditions are also associated with higher nutrient concentration. If this is the case, it is also necessary to consider the interaction between nutrients and metals in order to predict real toxicity. Finally, it is expected that biotic metal retention in fluvial systems will also be affected by water flow.

In this paper we present a summary of results obtained from a set of experiments aiming to investigate metal transport, retention and toxicity in simplified fluvial systems (artificial streams with fluvial biofilms) and their implications for understanding the potential influence of water scarcity on the fate and effects of metals in fluvial systems. Specifically we address four aspects: the influence of the time of exposure; the kinetics of bioaccumulation; the interaction between nutrients and metal toxicity and the influence of discharge on metal retention.

The influence of the time of exposure on metal toxicity was experimentally investigated exposing fluvial biofilms to 320 $\mu\text{g/L}$ Zn. Acute exposure (up to 24h) caused a clear inhibition of the photosynthetic efficiency (physiological effect) and the enhancement of early anti-oxidative enzymes (ascorbate peroxidases), but no structural damage was observed. On the other hand, chronic exposure (up to 5weeks) caused a clear effect on the structure of the biofilm (marked algal biomass reduction, inhibition of the maximal photosynthetic capacity and high metal accumulation) but the photosynthetic efficiency was recovered and the anti-oxidative enzyme catalase was enhanced as a result of adaptation. In spite of the fact that this investigation was based in a real case-study (the Riou-Mort, France), the concentration of Zn found in most human impacted streams is on average much lower and such high metal concentration is only reached during short episodes. If this is the case, it is expected that the community may recover since no structural damage was observed during acute exposure.

The simultaneous study of both, Cu accumulation kinetics and toxicity was investigated using biofilms differing in their Cu-exposure history: one unexposed (No-Cu), the second receiving three pulses of 20 $\mu\text{g/L}$ Cu (Cu-Pulsed) and the third continuously exposed to 26 $\mu\text{g/L}$ of Cu

(Cu-Continuous). Biofilms that had been continuously exposed to Cu, differed from those unexposed and also from those exposed to short Cu-pulses in their species composition (due to the replacement of sensitive algal classes by tolerant ones) and also on their metal content, several orders of magnitude higher. When these three types of biofilms were acutely exposed to a higher and potentially toxic Cu concentration (100 $\mu\text{g Cu/L}$), Cu-pulsed biofilms showed a fast saturation of intracellular Cu concentration compared with control biofilms (No-Cu) which showed an exponential increase. This was explained by the fact that their metal binding sites were already occupied with Cu. These two last communities (No-Cu and Cu-Pulsed) were more sensitive to Cu than the chronically exposed community showing a decrease in the photosynthetic efficiency after the short exposure to 100 $\mu\text{g Cu/L}$. From these experimental studies, we can conclude that both long-term exposure to higher Zn or Cu concentration due to an anomalous situation (e.g. a long period of water scarcity), as well as acute exposure caused by a sudden flow increase after a dry period, may have negative repercussions for the fluvial ecosystem. Acute exposure may lead to photosynthesis inhibition if the community has not been previously adapted. On the other hand, chronic exposure leads to community adaptation, which is often related to changes in species composition. Metals will therefore be retained in fluvial biofilms and transferred to higher trophic levels in the fluvial food web.

The interaction between nutrients and Cu toxicity was investigated in field and laboratory experiments. In the first case, it was shown that the sensitivity of fluvial biofilms to Cu followed the gradient of eutrophy (basically driven by phosphate) found in the field. Communities from oligotrophic sites resulted more sensitive to Cu than communities developed under more eutrophic conditions. In addition, P supply increased the tolerance of the communities developed under low P conditions but did not enhance the tolerance of those developed under higher P conditions. Additional experiments performed with algal cultures showed that high P conditions during growth and the presence of P in the media during the toxicity tests led to an increase in copper tolerance of the algae of the same magnitude than the previously studied field communities. These results indicate that P is one of the main factors determining Cu toxicity on fluvial biofilms. It is expected that accidental or point-source metal pollution in fluvial systems will have greater negative impact in pristine rivers, especially under low flow situations, when a lower toxicant dilution is expected.

The dynamics of Cu was investigated by applying the concepts and methodologies developed for the study of nutrient dynamics in rivers based on the nutrient spiraling theory. Cu retention was studied at sub-toxic concentrations to avoid negative/lethal effects on biota and compared with phosphate dynamics. Results from this study showed higher retention efficiency for PO_4 than for Cu. The biofilm played a key role in retaining both solutes; however, its influence was more pronounced for PO_4 as a positive relationship between uptake rate and algal biomass was found only for PO_4 and no for Cu. Finally, retention efficiency for both solutes was influenced by the hydrology of the system, showing lower retention efficiencies under higher flow conditions. These results suggest that the fate and toxic effects of metals on stream biota may be strongly influenced by the prevailing environmental conditions especially water flow that modulate significantly the transport and retention of these toxicants.

Overall, the experimental results reported in this paper indicate that a water scarcity may increase metal exposure (due to low dilution), uptake (due to higher retention under low flow), toxicity and/or accumulation (depending on the dose and time of exposure). In addition, the influence that water scarcity might have on nutrient loads will also modulate the fate and effects of metals.