Título: TRACE ELEMENT BIOGEOCHEMISTRY IN HIGH MOUNTAIN LAKE CATCHMENTS: IDENTIFYING ANTHROPOGENIC VERSUS NATURAL COMPONENTS FROM THE ATMOSPHERIC CONTAMINATION LEGACY IN REMOTE NATURAL AREAS

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Resumen: Human activities have been interfering with the natural biogeochemical cycles of trace elements since the ancient civilizations. Although they are inaccessible and remote, high mountain lake catchments are irrefutably trace-element contaminated by anthropogenic emissions, which can travel by long-range atmospheric transport before they are deposited. This has been revealed by several natural archives.

High mountain lake catchments are thus excellent sentinels of long-range contamination. Continuous accumulation can lead to a build up of potentially toxic trace elements in these remote, or relatively remote, ecosystems.

The thesis focuses on the biogeochemistry of a suite of trace elements of environmental concern (Ni, Cu, Zn, As, Se, Cd and Pb) in Pyrenean lake catchments, with special emphasis on discerning the natural components from the anthropogenic contributions. Five other metallic elements (Al, Fe, Ti, Mn and Zr) have also been studied to trace natural fluxes and biogeochemical processes within the lake catchment

systems.

Current atmospheric major and trace element fluxes over the Pyrenees were directly measured from monthly bulk deposition records. In this study, prevailing meteorological factors were related (quantitatively and qualitatively) to element deposition fluxes. In a different study, seasonal atmospheric major and trace element fluxes were estimated from the winter snowpack sampled along a gradient of altitude. On the basis of these two studies, we conclude that concentrations of airborne trace elements in the Central Pyrenees can be considered representative of the background contamination levels of remote areas in Europe. However, only the trace element composition collected above ~2100-2300 m a.s.l. in the Central Pyrenees can reliably be used as a signature of background long-range fluxes in SW Europe, as at a lower altitude the local effects are perceptible.

In addition, bulk atmospheric deposition measurements of major and trace elements were obtained from five other European high mountain sites for comparison. Remarkably, Al, Ti, Fe, Mn and As were found in higher concentrations in the Central Pyrenees. These elements were identified as part of the dust carried from the Iberian Peninsula and North Africa. During episodic events, this dust reaches the Pyrenean range in considerably higher amounts than in other more northern European high mountain sites. By contrast, Pb, Zn, Ni, Cu, As and Cd were found in higher concentrations in the Tatra Mountains, Ticino and Piemonte. Lower concentrations occurred in the Tyrol and intermediate concentrations appeared in the Pyrenees and the Grampian Mountains.

Long-term, historical trace element deposition over the Pyrenees was examined using soil records and lake sediment cores, which take into account post-depositional processes that occur in the terrestrial catchment and additional inputs from the catchment to the lake, respectively. Trace element concentrations in Pyrenean soils were consistent with those recorded in soils from other mountainous areas in Europe and were, in many cases, above the thresholds recommended for ecosystem protection. In conclusion, Pyrenean high mountain soils had a ~2- to 5-fold increase in Pb, Ni and Cu as a result of long-range contamination, whereas enrichment of As was most probably caused by localised As-bearing veins in the area.

Cumulative whole-catchment inventories of Pb, Zn, Cu, Ni and Cd were calculated for three Pyrenean lake catchments. In this study, Pb isotopes were successfully used to reliably estimate the natural and anthropogenic contributions of Pb both in catchment soils and lake sediments, and then calibrate the relative apportioning for the other trace metals. Lead and Zn anthropogenic inventories were in good agreement with those in other mountainous and rural areas in northern and eastern Europe, whereas Ni, Cu and Cd anthropogenic inventories were lower in the Pyrenees. Interestingly, the estimated trace metal inventories were three orders of magnitude higher than the current annual atmospheric deposition to the Central Pyrenees. This result highlights the potential of sediments and soils as sources of delayed, long-lasting contamination if possible environmental changes favour the remobilisation of anthropogenic trace metals accumulated over the course of time.

Finally, a simple transport model of atmospheric trace elements through the catchment/lake system during the snow and ice-free season was applied for the three Pyrenean catchments. Results showed a net export of Pb and As from the catchments whereas Zn was largely retained. We propose that Pb originates from the delayed

release of previously accumulated anthropogenic Pb contamination and the weathering of As-rich rocks is the most likely source of As. By contrast, possible saturation of Zn in the catchments can also make them a source of Zn contamination.

Ultimately, several aspects of concern in this thesis indicate that further long-term atmospheric deposition monitoring is required at a greater number of mountain sites. Likewise, we should also carry out integrated long-term monitoring of atmospheric deposition, stream and lake water transport, sediment fluxes and vegetation uptake in mountain catchments.