

## Lead cycling in forested catchments: Trends in input-output mass balances over 12 years of easing industrial pollution

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In Central Europe, forested headwater catchments are an important source of drinking water. In the second half of the 20th century, extensive coal mining and burning, along with chemical industry, metal smelting and traffic contributed to high emissions of a number of environmentally relevant elements. Lead (Pb) entering ecosystems via wet and dry deposition originated from all these sources. The highest anthropogenic emissions of Pb occurred in the mid 1980s, and a considerable decrease in Pb emissions has been observed over the past 25 years. The fate of lead and its potential release to stream water has been studied in 11 small spruce-forested catchments in the Czech Republic. Here we compare Pb input-output mass balances for the hydrological years 1996 and 2008, i.e., for periods of time 12 years apart. Atmospheric input via spruce canopy throughfall was monitored monthly. In clearings, two rain/snow collectors were installed per site. Stream discharge was sampled once a month near a gauging station. The calculated catchment-level Pb inputs have been vegetation-type weighted. In 1996, catchments situated in the more industrialized north of the country showed high Pb deposition rates of 25 to 50 g Pb ha<sup>-1</sup> yr<sup>-1</sup>. Catchment situated in the less polluted south of the country showed lower Pb deposition rates of less than 17 g Pb ha<sup>-1</sup> yr<sup>-1</sup>. Lead export via stream discharge formed less than 20 % of the input at most sites across the country. Only two sites in the industrial north (Krkonoše and Orlické Mts.) exhibited a higher proportion of exported Pb, relative to contemporary input (32 to 60 %). Overall, most of the anthropogenic Pb entering the ecosystems remained immobilized within the biomass and soils. Twelve years later, in 2008, atmospheric Pb depositions into all catchments significantly decreased, averaging 11 g Pb ha<sup>-1</sup> yr<sup>-1</sup>. The amount of exported Pb, and the proportion of exported Pb, relative to contemporary atmospheric input, decreased in comparison with 1996. In 2008, the annual Pb export was less than 2 g ha<sup>-1</sup> yr<sup>-1</sup> at 8 out of 11 sites. Our data show that, with easing atmospheric pollution, less Pb is exported from the catchments, even though the total amount of Pb that had accumulated since the beginning of the Industrial Revolution (1860) was sizeable.

## Biom mineralization and seawater dynamics in foraminifera studied with the fluorescent dye Calcein

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The calcite shells of foraminifera which accumulate on the ocean floor are an important component of the global carbon cycle. These shells provide highly valuable paleoceanographic information based on their trace elements and stable isotopes. Understanding their biom mineralization is therefore an essential goal both for ocean acidification studies and for obtaining new and reliable paleoceanographic information. Recently we showed that perforate foraminifera precipitate their calcite directly from seawater vacuoles [1, 2]. Here we describe the uptake and release dynamics of seawater in the benthic foraminifera *Amphistegina lobifera* and *A. lessoni* using pulse-chase experiments with the membrane impermeable fluorescent dye Calcein. Three different reservoirs of seawater stored in vacuoles were found with residence times of ~ 20 min., ~ 6 hr and ~ 10 days. The internal volume of seawater is large and it is recycled fast enough to provide Ca<sup>2+</sup> and CO<sub>3</sub><sup>2-</sup> for the normal calcification process. At low salinities Calcein released during the chase is higher than in normal salinity by a factor of 2. This may be part of the osmotic regulation mechanism in these giant cells. Calcein is incorporated into the shells in direct proportion to calcification measured by weight increase or by alkalinity depletion. The distribution coefficient of Calcein in the shells is very low in the order of 10<sup>-4</sup>. It increases significantly with salinity and with calcification rate and using Rayleigh type fractionation model we calculate that higher fraction of the calcification reservoir is utilized at optimal conditions. These observations provide the foundations for a realistic model to describe the behavior of stable isotopes and trace elements in the modified seawater calcification reservoir in foraminifera. Furthermore, it explains the sensitivity of foraminifera to ocean acidification.

[1] Erez, J., (2003), *Reviews in Mineralogy and Geochemistry* **54**:115-149. [2] Bentov S., Erez, J and Brownlee, C. (2009), *PNAS* **106**(51) 21500-21504