

Mobility and bioavailability of some potentially harmful elements around an industrial contaminated environment (Estarreja, Portugal)

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Located in north central Portugal the industrial Chemical Complex of Estarreja (CQE) is composed of several chemical industries that could cause environment pollution. The most important inputs into the environment are chiefly related to past industrial activities, with the production of sulphuric acid from arsenopyrite roasting (e.g. As, Cu, Ni, Pb and Zn) and from a chloralkali plant (e.g. Hg).

The main purpose of this study was to evaluate the levels of some heavy metals and arsenic in soils and forage plants from Estarreja and from a reference site (Ouça, with no significant industry but a similar geology, pedology). These soils are sandy soils, often used as pasture and agricultural land. In Estarreja 90 topsoils and 27 forage plants were collected; in Ouça 20% of these numbers were sampled. Both soils and plants (separated into roots and green shoots) were analyzed in the same way, extraction with aqua regia and analysis by ICP/ES & MS, for 32 chemical elements. Three single extractants (water; ammonium acetate; EDTA) were used to assess the mobile and plant available fraction of some potentially harmful elements.

The first results show high levels of As and Hg in Estarreja compared to those given in the international guidelines. The maximum concentrations found in the soils are above 10.000 mgkg⁻¹ for As and above 100 mgkg⁻¹ for Hg. In green shoots, the maximum concentrations found are 255 mgkg⁻¹ for As and 5 mgkg⁻¹ for Hg. The spatial distribution of these elements shows a typical anthropogenic pattern, with the highest values near the factories and sewage outlets. It was possible to identify an area around the factories and sewage outlets where the median concentrations for As and Hg are more than 10 times higher than the median concentrations found in the reference area, which are close to the national backgrounds [1]. The EDTA was the most effective extractant for all the elements, except Zn, which was higher in the ammonium acetate extracts. However, the amounts extracted with these three extractants are low (less than 5%) for As, Hg, Pb, Cu and Zn, thus attenuating the impact of high metal contents in soils of green areas often used as pasture land and agriculture.

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Sequestering of phosphorus during freshening of a silled marine basin; Role of manganese

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We have documented sediment sequestering of phosphorus in the Bothnian Bay, northern Baltic Sea, during the last 7000 years, using a paleomagnetic dating method. High resolution sampling and multi-element analyses coupled with "absolute dating" of the sediment provides a powerful environmental record that can be used to foresee biogeochemical changes caused by climate-induced freshening of the Baltic and other silled marginal marine basins. Late Holocene freshening is pronounced in the Bothnian Bay, with a decline of surface salinity from 10-11‰ down to present day values between 1‰-3‰, consistent with the absence of a permanent halocline, and phosphorous limitation of primary production.

The P/Fe ratio in a 6-m-long piston core show distinct peaks above the time level 2500 years BP, closely related to temporal peak values for manganese, the Mn/Fe ratio and a major changes in magnetic susceptibility. We suggest that the changes in phosphorus sequestering in the core can be explained by the position of the suboxic zone at the time of deposition. A suboxic redox potential can be maintained in these layers if there is an excess of manganese that can oxidise formed sulphide in the sediment during burial. Particulate manganese maintains the suboxic redox level preventing dissolution of Fe-oxyhydroxides with associated phosphorus, at depth in the sediment. Today, the barrier between the sulfide zone and the sulfate zone is situated 0.5 m below the sediment surface. Trace metal data suggest that this zone has been located within the sediment during the whole lifetime of the core. Hence, a layer with high concentrations of Mn and Fe-oxyhydroxides, formed above the sulfide boundary, may pass through the sulfide barrier, leaving Fe-Mn oxyhydroxides in relative equilibrium below the active sulfide boundary.