Isotopic trends and enrichment of atmospheric lead during the past two millennia in Lake Vrana on Cres Island (Croatia)

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Abstract: The present study was undertaken to evaluate the level of lead contamination during the Late Holocene in the Croatian karst regions. Multi-element analysis of samples allowed the evaluation of potential metal pollutants such as Pb, Zn and Cu, and lithophile elements such as Sc were used for the calculation of enrichment factors and the recognition of increases in atmospheric pollution. Isotope ratios $^{206}Pb/^{207}Pb$ were used to discriminate between lithogenic and differing anthropogenic inputs.

Key words: lake sediments, lead isotopes, pollution archive, land-use, climate change, Holocene

Introduction

Sediment records of lakes are often used to estimate long-term changes in anthropogenic metal emissions. Due to Pb pollution from mining and smelting the Pb/Sc ratios have increased (Shotyk et al., 1998; Shotyk, 2002) and $^{206}Pb/^{207}Pb$ ratios decreased since 3000 ^{14}C yr BP in Swiss peat bogs (Shotyk et al., 2000) and in Swedish lake sediments from 4000 ^{14}C yr BP (Renberg et al., 2002). The effect of Roman mining through atmospheric deposition has been detected in Greenland ice cores (Dunlap et al., 1999), peat bogs in the Swiss Alps and Spain (Shotyk, 2002) and lake sediments from Sweden (Renberg et al., 2002).

Sediment cores from the fresh water Lake Vrana (Vransko jezero) obtained on the island of Cres (northern Adriatic Sea) were found to be the most suitable to trace the history of anthropogenic, atmospheric lead pollution in the karst regions of Croatia as already determined in the topsoil of the karst hinterland (Miko et al., 2000). The shape of the lake reflects the geomorphic attributes of a karst polje (a closed basin with a flat bottom, karstic drainage, and steep slopes, and a swallow hole on its southwestern edge) from which it probably formed. It has no river inflow or outflow. Lake Vrana is an oligotrophic and monomictic lake and only negligible outflow occurs from the lake with most of the water derived from precipitation. A recent multi-proxy study (Schmidt et al., 2000) showed that considerable lake level changes have occurred during the last 16,000 years and that the lake has existed as a deep-water lake since 8000 ^{14}C yr BP. Today it has a surface of 5.75 km^2 and contains approximately 220 mil. m^3 of fresh water that has been used as a potable water supply for the islands Cres and Lošinj for the last 60 years.

Short scientific paper

RESULTS AND DISCUSSION

A total of 13 cores 85 to 90 cm long were obtained by scuba divers from the flat bottom (50 m +/- 2 m) of the lake. Two cores, selected for detailed chemical analyses, were sub-sampled at 2 cm intervals. All of the cores have a surface layer to a depth of 10 cm with 30 % $CaCO_3$, a dark layer depleted in $CaCO_3$ (<10 %) $CaCO_3$) with 3.5 % of organic C to a depth of 40 cm (+/- 5cm) and a gray laminated calcite sequence with more than 60 % $CaCO_3$ which extends to the base of the cores (85-90 cm). The ^{14}C dating of core (VS-8) gave sedimentation rates, which fall within a wide range of 0.1 mm/yr (pre-Roman age) to 0.8 mm/yr (Medieval Warm period). Modern anthropogenic pollution is registered in the top 10 cm of the sediment sequences with high Zn/Sc, Cd/Sc, Cu/Sc and Pb/Sc ratios. All Pb profiles are characterized by constant concentrations at depth. In the top 34 cm, Pb profiles follow the same trend and clearly show a dramatic increase in the flux of Pb to the sediment.

Chemical sequential analysis showed that less than 20 % of Pb can be attributed to labile mineral phases indicating a weak susceptibly to diagenetic remobilization in lake sediments, being strongly bound to refractory organic matter and residual mineral phases. The sharp rise in the Pb deposition rate above background levels occurred during the Roman period. This observation is consistent with what was reported for Pb in the sediments of undisturbed lakes and peat bogs from Sweden and the Swiss Alps. In order to evaluate the anthropogenic and lithogenic contribution of lead to the lake sediments the approach of SHOTYK ET AL. (2000) was used utilizing Sc as a reference element and the average Pb/Sc ratio of the three deepest samples as pre-anthropenic reference material. The Pb/Sc ratios of 2.4 in the core interval from 86 cm up to 70 cm lie within the crustal value range (1.8 - 2.4) and have high radiogenic values ($^{206}Pb/^{207}Pb$ ratio of 1.24) with a carbonate dominated sedimentation (>65 % $CaCO_3$) and 1.1 % organic C. These values are considered to be indicative of Pb concentrations of soil derived from rock weathering (SHOTYK ET AL., 2002) and correspond to pre-Holocene palaeosoil ($^{206}Pb/^{207}Pb$ ratio from 1.228 to 1.245). The Pb/Sc ratios increase to over 3.5 from 65 to 50 cm, with a peak value of 5.8 in the interval from 56 to 58 cm ($^{206}Pb/^{207}Pb$ ratio 1.210). The calculated anthropogenic lead contribution for this interval is 60 % and could correspond to the Roman Pb mining peak encountered in other parts of Europe. In the interval from 47 to 50 cm the lead concentrations are lower and the $^{206}Pb/^{207}Pb$ ratios slightly higher indicating the post Roman Pb mining decline (400-900 AD). During this period there was a dramatic change in land use, due to forest clearing by the Croats. The Pb/Sc ratios drop slightly (to 3.1) and in the interval from 40 up to 18 cm the ratios range from 4 to 6. Due to the unfavorable climatic conditions (strong winds) and a thin soil cover on carbonate bedrock, erosion was very intensive and the lake catchment lost most of its soil cover during the period from 1400 to 1650. This period was characterized by the absence of sunspots (Spörer Minimum) which caused a cold climate with a great frequency of sea storms in the Adratic (CAMUFFO ET AL., 2001). The concentration of lithogenic Pb in this core section varies slightly (30-35 mg/kg) and is similar to the concentrations in pre-Holocene

soils. The highest Pb/Sc ratios are found above 18 cm (^{14}C cal. date 1600 to 1650) and range from 7 to 8 while the amount of calculated anthropogenic Pb reached 70 % of the total Pb concentration. The ^{206}Pb/^{207}Pb ratios in this section range from 1.175 to 1.181, which is in the range of topsoil from the karst hinterland. A similar range of values was obtained in the top 5 cm of other cores from the lake.

Conclusions

Although dramatic changes in lake sediment composition due to deforestation occurred in the Lake Vrana sediments the cores nevertheless contain a continuous history of both background anthropogenic inputs as reflected by Pb/Sc and ^{206}Pb/^{207}Pb ratios, which correspond to hemispheric Pb contamination observed for the past three millennia. This also implies that the topsoils of the mountain karst regions of both Croatia and Slovenia which are polluted by atmospheric Pb have been receiving a considerable flux of Pb during the past two millennia and not just during the industrial era.

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