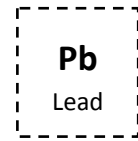


Stable Lead Isotopes



Lead in the Environment

Lead, in chemistry also denoted as "Pb" from the Latin "plumbum", is a commonly found heavy metal. It is not essential for human beings. In contrast, it has toxic effects on human health, once it is ingested via contaminated water or food, or inhaled as dust. The international agency for research on cancer, IARC, classified lead as being potentially/ probably carcinogenic. Especially children are affected by an exposure to lead: It can cause harm to their nervous systems. For adults, lead has harmful effects on the oxygen supply of the cells.

Lead is emitted by mining and smelting industries as well as by the combustion of coal. Although leaded gasoline (anti-knock agent) was banned, a main source of lead emissions in Germany is still road transport, because of the abrasion of tires and brakes. After a deposition on the soil, the lead is further distributed in the environment as it leaches out of the soils into rivers, lakes and into the groundwater. Furthermore, the use of lead e.g. in batteries or ammunition is a source of lead found in the environment.

Lead-Isotopes

The four most important lead isotopes occurring in the environment are ^{204}Pb , ^{206}Pb , ^{207}Pb and ^{208}Pb . They are stable, which means they are not radioactive and do not decay. ^{204}Pb is a so-called primordial nuclide. The term primordial denotes an isotope, which was already present when the earth was formed. The three isotopes ^{206}Pb , ^{207}Pb and ^{208}Pb are, in contrast, final products of the decay chains of the radioactive isotopes $^{238}\text{Uran}$, $^{235}\text{Uran}$ and $^{232}\text{Thorium}$.

The frequency of occurrence of the three Pb-isotopes, therefore, depends on the original concentrations of lead, uranium and thorium, as well as on the half-life of their parent nuclides.

Stable isotopes are measured as ratio of two isotopes of one element. The values of lead isotopes are, for example, given as the ratio $^{206}\text{Pb}/^{207}\text{Pb}$ or $^{208}\text{Pb}/^{206}\text{Pb}$. The Pb-isotope ratios vary for different lead deposits, because the half-lives of the parent isotopes are different. The specific Pb-isotope ratio of each deposit, hence, depends on the geological age, at which the parent isotopes became present in the deposits, and on the amount of parent isotopes before the decay started.

In contrast to other stable isotopes like ^{18}O or ^2H , Pb-isotope ratios do not show a significant fractionation. Isotope ratios, which differ from the natural ratios of the lead deposits are a result of mixed lead from several deposits.

Pb-isotope ratios are mainly measured using a mass spectrometry with thermal ionization (TIMS) or with inductively coupled plasma, e.g. with quadrupole (ICP-QMS).

Beside the stable lead isotopes, many other short-lived Pb-isotopes exist, like ^{210}Pb , which are determined using alpha-spectrometry or liquid scintillation counting (LSC).

Application of Stable Lead-isotopes

Measuring stable Pb-isotopes can be helpful to identify the source of lead, which was found in e.g. groundwater or soils. With the measurements, it can be clarified, whether the lead occurs naturally in this region or is of anthropogenic origin. It is not sufficient to measure the concentration in order to determine the origin of lead.

The determination of the origin of lead is possible, because each lead deposit has its specific Pb-isotope ratio value. Lead in processed materials deviates from this deposit specific isotope ratio, as

the processed lead was transported over long distances or was mixed with lead from other deposits. Lead, which has an anthropogenic influence, can therefore be distinguished from local, geogenic occurring lead. The differences are visible when the isotope ratios are shown in a diagram. This is applied for some examples in figure 1.

Samples for the analysis of Pb-isotope ratios are taken in groundwaters, or so called geo/- or climate archives, such as lake sediments, swamp, tree rings or undisturbed soil, whose layers can be dated back. In forensic science, lead isotope ratios are used as well. Lead accumulates in bones and teeth over the lifetime. Because of that, it can be determined where a person had lived at a certain time of his life.

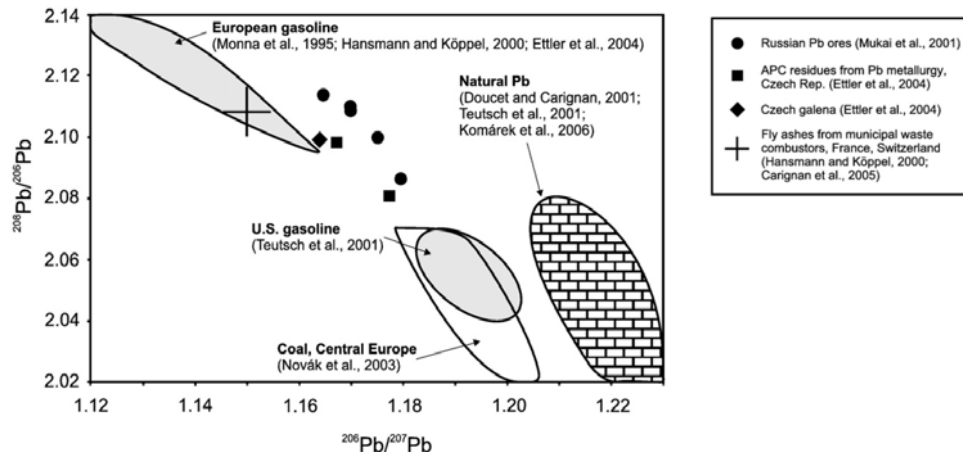


Figure 1: Isotope ratios of some sources of lead (Komarek et al., 2007).

Study case: Where does the lead come from?

A group of scientists from northern Europe performed a Pb-isotope analysis on samples from western Greenland (Bindler et al., 2001). They found, that inspite western Greenland has a shorter distance to North America than to Eurasia, the Pb-isotope ratio shows the signature of Eurasian lead. Russian emissions seem to be responsible for most of the emissions in the northern part, whereas for the southern part of Greenland, Europe is the major emitter of the lead found.

At Lake Constance, Pb-isotope analysis was conducted as well (Kober et al., 1999). It was possible to distinguish natural, geogenic from anthropogenic lead using $^{208}\text{Pb}/^{206}\text{Pb}$ and $^{207}\text{Pb}/^{206}\text{Pb}$ isotope ratios. Because of the differences of anthropogenic and natural lead in the isotope ratios, the anthropogenic input could be investigated. The results of the scientist from Heidelberg and Konstanz are shown in figure 2.

The increasing values of the $^{208}\text{Pb}/^{206}\text{Pb}$ ratio from the mid-19th century show, according to Kober et al. (1999), the rising input of anthropogenic lead in the course of the industrialization.

Main sources of the in Lake Constance deposited atmospheric lead, were the combustion of coal, iron ore processing and the use of leaded gasoline. The highest depositions were measured for the 1970s and 1980s.

After the $^{208}\text{Pb}/^{206}\text{Pb}$ peak at about 1980, the ratio is decreasing again, with an extreme event in 1987. This decrease of anthropogenic input, can be explained by the ban of leaded gasoline and environmental precautions. The very low $^{208}\text{Pb}/^{206}\text{Pb}$ ratio in the year 1987 was attributed to a flood event in this year. Because of the flood, mobilized geogenic lead mixed with the anthropogenic lead and, hence, weakened the signal of the anthropogenic lead.

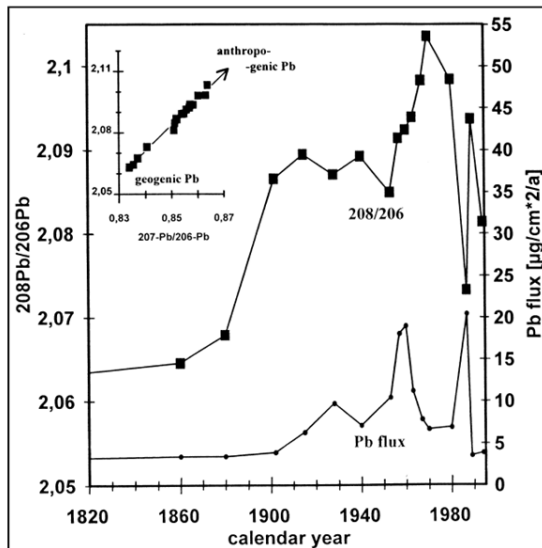


Figure 2: Time course of the $^{208}\text{Pb}/^{206}\text{Pb}$ isotope ratio measured at sediment cores of Lake Constance (Kober et al., 1999).

Application in Hydrogeology

In case elevated lead concentrations are measured in groundwater, analysis of lead isotope ratios can be necessary. Like described above, the analysis can reveal whether the lead has an anthropogenic source or occurs naturally. A typical source of anthropogenic lead in groundwater is, for example, ammunition or leaded gasoline.

Literatur

Bindler, R., Renberg, I., Anderson, N. J., Appleby, P. G., Emteryd, O., & Boyle, J. (2001). Pb isotope ratios of lake sediments in West Greenland: inferences on pollution sources. *Atmospheric Environment*, 35(27), 4675-4685.

Komárek, M., Ettler, V., Chrástný, V., & Mihaljevič, M. (2008). Lead isotopes in environmental sciences: a review. *Environment international*, 34(4), 562-577.

Kober, B., Wessels, M., Bollhöfer, A., & Mangini, A. (1999). Pb isotopes in sediments of Lake Constance, Central Europe constrain the heavy metal pathways and the pollution history of the catchment, the lake and the regional atmosphere. *Geochimica et Cosmochimica Acta*, 63(9), 1293-1303.