That Heavy Metal

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The urban environment is strongly exposed to pollution, mainly from industry and road traffic. Good pollution control can only be guaranteed when the exact sources and concentrations of toxic substances are known. When there are many polluters in a relatively small area, isotopes may help to "fingerprint" them

Some of the most dangerous toxic substances in the environment are heavy metals, and the most common heavy metal is lead. Lead emission levels in Poland have been falling in recent years, estimated at about 600 tons in 2002 - with about 65% coming from car exhaust fumes, and most of the rest split equally between the metallurgy sector and coal-burning power plants.

The harmful effects that are caused by lead in children include intellectual impairment, hyperactivity, hearing loss, and behavioral problems. The element disturbs biochemical processes in cells, reducing the activity of some enzymes; it can also stop the biosynthesis of hemoglobin. It is highly toxic for fetuses, as it makes its way into the womb, interfering with proper development. In adults, it can cause elevated blood pressure, kidney and liver damage, as well as infertility. Extensive doses can even cause death.

Lead accumulates in tissues and is dangerous even in small doses. Nevertheless, a large dose is required before

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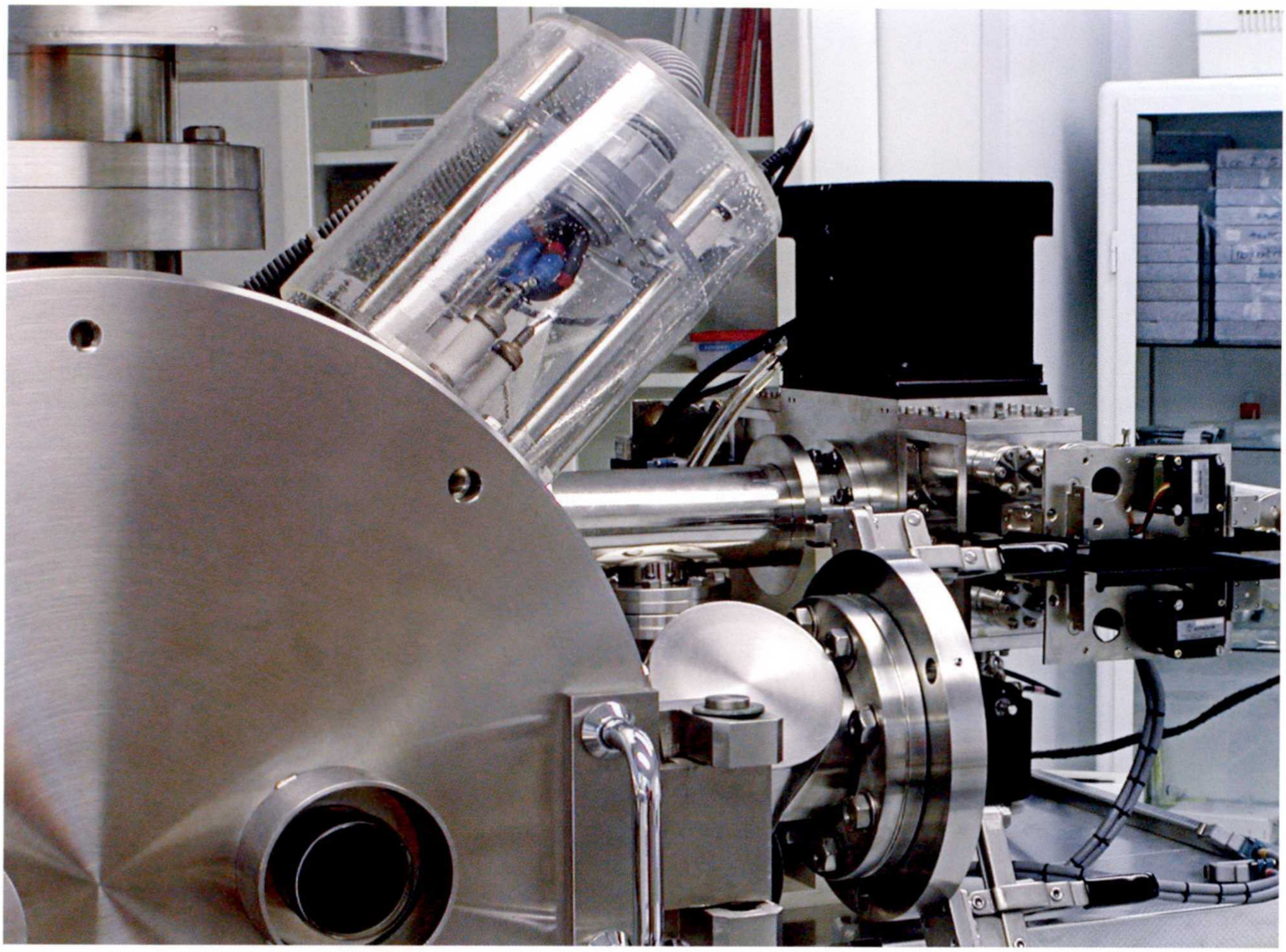
View of the Siekierki power plant in Warszawa from nearby bridge over Wisła river



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Thermal ionization mass spectrometer at the Institute of Geological Sciences in Warszawa used for measuring lead isotope ratios

any obvious symptoms of poisoning develop, and so it is crucial to try to keep tabs of even minute amounts present in soils, water, atmospheric dust, or plants.

The phasing out of lead from the environment was one of the major actions of Agenda 21, endorsed in 1992 at the United Nations Conference on Environment and Development (UNCED) in Rio de Janeiro. In 1998, the Aarhus Treaty was signed to shift Europe completely to unleaded fuel by 2005. This deadline, however, will almost surely not be met in the whole of Eastern Europe.

To curb the risk, lead levels should be monitored constantly. But once pollution is detected, tracking it down to its source may prove tricky. Let's say that pollution is observed in arable soil, in a place that is close to a coal mine, a motorway, a power station and a coking plant, and also neighbors on an illegal waste dump. Such situations do exist, especially in areas of intensive mining and industrial operations, like Upper Silesia in Poland. Soil analyses point to increased lead content in many places, but the pollution's exact sources are unknown. And without hard evidence, environmentalists are not sure who is to blame. However, it might be possible to identify the principal source through the use of isotopes, by means of which lead from different sources can be differentiated.

Decay in the crust

The lead present in the environment is a mixture of four natural isotopes: ^{204}Pb, ^{206}Pb, ^{207}Pb, and ^{208}Pb. The last three are the products of the slow radioactive decay of uranium (^{238}U, ^{235}U) or thorium (^{232}Th) isotopes, so their amounts are constantly increasing. On the other hand, the ^{204}Pb isotope is not produced in any known nuclear process, so its amount is believed to have been constant since the beginning of the Solar System. And so, the composition of the resulting lead cocktail may vary greatly, depending on the amount of decay products it absorbed during its lifetime. This picture is further complicated by geology.

In geochemical systems, lead does not generally team up well with its predecessors, uranium and thorium. And these two predecessors also usually take different paths. As magma containing all three elements crystallizes, lead becomes accumulated in the igneous rocks of the last stages of magmatic differentiation. Lead prefers to bond with sulfur (e.g. forming galena, PbS), thorium with phosphate, and uranium with oxygen and organic compounds. As a result, the three elements (and the lead isotopes that result from the predecessors' breakdown) all end up in different parts of the Earth's crust. The re-mixing of lead from these three different sources in the natural environment takes place when their respective minerals break down due to weathering, melting in a new magma, or metasomatism.

Because of these processes, each commercial source of lead has a unique isotopic composition, or "fingerprint." While the differences in composition are significant, it should be possible to identify the main source of pollution at a given location, and even to evaluate the input of various sources to the mixture. There is also the question of how sensitive this analytical method might be. It should be easy to identify different polluters in strongly polluted areas like Upper Silesia, but doing so will pose a challenge in areas that seem to be "clean," where there are no strong emitters but where an increased lead content has nonetheless been detected. The first obvious source to check is the weathering subsoil, but industrial or agricultural pollution also should be considered.

Where ashes wind up

To assess the robustness and sensitivity of the method, we chose the neighborhood of the Siekierki power station in Warszawa as the area of research. The Siekierki power plant burns coal from the Halemba coal mine in Zabrze (Upper Silesia), and produces a lot of slag and ash which are stored in open piles near the power station. We tried to answer the question of whether this operational power plant manifests itself in the lead found in its vicinity. It should be noted that the quantities of lead observed were small and far from alarming - in fact, there are many small private garden plots around the power station.

We measured the isotopic composition of lead with thermal ionization mass spectrometry (TIMS) at our laboratory. First we analyzed the coal from the Halemba and

Percentage of ^{204}Pb in lead from various sources. Differences are minute, but can be identified with proper research methods

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Although leaded fuel has not been sold in Poland for several years, substantial amounts of lead from petrol are still present in soils

the slag and ash from Siekierki. Then soil samples were taken from a depth of 20 cm in various areas within a few kilometers of the power plant. The measurements showed that samples from locations nearest to the power station and from a site 2.5 km to the north had lead isotopic composition identical to the ash, slag and coal. But 4 km east of the plant the composition was already quite different and virtually indistinguishable from natural (mineral) lead composition, implying no influence of the plant in this area. Generally, the spatial distribution of lead from Siekierki can be attributed to the influence of southerly and south-westerly winds - an interesting find, knowing that the prevailing winds in Warszawa area are westerly. This is possibly due to the fact that warmer winds from the south mobilize the ash to a greater degree.

Our work is still in progress. We plan to analyze more samples of soils and some types of plants to investigate the possibilities for discerning various coexisting sources of lead. Research has shown that the lead isotopic "fingerprint" is quite different for different emitters: coal, traffic and coking plants. Although leaded petrol has now not been sold for several years, high concentrations of petrol lead are still present in soils. Identifying this source should be straightforward, as there are only two producers of tetraethyl lead (the antiknock additive to petrol). ■

Further reading:

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