

# Heavy Isotope Analyses in Soil Sciences: Possibilities and Challenges

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## Abstract

In this study we summarize spectroscopic methods used in Pb isotopic analyses as well as show the role of the methods in modern soil science. The study is focused mainly on Pb isotopes due to their wide applications in soil sciences, especially in solving environmental problems. Pb and Sr isotopic composition-based methods are effective when distinguishing a two-source mixture, and comparing with the known signature of a potential pollution source. Advancing analytical methods and more data containing isotopic composition from many natural and anthropogenic sources gives them a much higher possibility of use. This text shows the wide use of spectroscopic methods and their impact on many aspects of environmental science.

**Keywords:** soil science, environmental science, spectroscopic methods, lead, strontium

## Introduction

Recent advances in analytical techniques and especially in mass spectrometry allow for high precision and accuracy of elemental and isotopic measurements. Isotope studies are gaining more importance in soil and environmental studies and they are used in a wide spectrum of problems. Sr isotopes in soils are used to track the provenance of grapes for wine production [1], apples for cider production [2], or to understand soil genesis and evolution [3]. Pb, Zn and Cu are used for tracing the weathering of anthropogenic slag wastes [4] and the historical impact of smelting in specific regions [5]. Pb isotopes in soils, water, and tree bark are used to delineate polluted areas at regional [6-8] or local scales [9]. Pb isotopes also can be applied to characterize different sources of Pb in soils (e.g. lithogenic and anthropogenic) [10, 11] or two different lithogenic sources [12]. Pb isotopes in peat bogs are used as “time-capsules” recording past pollution history [13, 14].

## Variations of Pb Isotope Ratios in Nature

Pb isotopes are an ideal tool to track different sources of Pb in the environment provided that there are measurable differences in Pb isotope ratios between sources that contributed to the Pb budget in the area. Four Pb isotopes occur in nature:  $^{206}\text{Pb}$ ,  $^{207}\text{Pb}$ ,  $^{208}\text{Pb}$ , and  $^{204}\text{Pb}$ . Isotopes  $^{206}\text{Pb}$ ,  $^{207}\text{Pb}$ , and  $^{208}\text{Pb}$  are products of radiogenic decay of  $^{238}\text{U}$ ,  $^{235}\text{U}$ , and  $^{232}\text{Th}$ , respectively; the  $^{204}\text{Pb}$  budget has not changed since its formation. Differences in  $^{206}\text{Pb}/^{207}\text{Pb}$  or  $^{207}\text{Pb}/^{204}\text{Pb}$ , commonly used Pb isotope ratios, form when material with different U/Pb evolves over time. Therefore, differences between various anthropogenic Pb sources, e.g. petrol and smelting, are due to using ores of different ages (Fig. 1). Fig. 2 shows that there is considerable variation in Pb isotopes between different lithogenic and anthropogenic sources in Europe and in Poland.

## Analytical Methods Used in Soil Science

Mass spectrometry is a versatile research technique widely used in many fields of science. The basis of this

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technique is to measure the ratio between mass and the electric charge for each nuclide. Mass spectrometry allows for measuring very low concentrations of isotopes.

### Lead Isotopes

Pb isotopes are routinely measured by Quadrupole ICP-MS and MC ICP-MS. The Quadrupole based-technique is used more often due to the more readily available equipment, and faster sample preparation and analysis. However, it doesn't yield as precise and accurate data as the multicollector ICP-MS (Table 1). Also, Quadrupole ICP-MS cannot measure ratios with  $^{204}\text{Pb}$  with acceptable precision, due to interference on mass 204 by  $^{204}\text{Hg}$ , when measured, these ratios have very large errors (Table 1).

Mass spectrometry is used successfully in geology, but applying the same methods in soil sciences is often problematic. This follows from the fact that the soil material, as the object of research, is diverse both chemically and physically. The major problem is the presence of many substances of various origins, including substances derived

from the weathering of parent rock, autogenic products of the soil formation processes, organic matter elements assimilated on it, and pollution of anthropogenic origin. Such a large pool of substances becomes an obstacle during sample preparation. The current sample digestion technique uses  $\text{HNO}_3$  [15, 16] or three-acid attack ( $\text{HCl}$ ,  $\text{HF}$ ,  $\text{HClO}_4$ ) [17] and extraction in ion exchange columns first introduced by [18]. However, the digestion of samples by these methods can sometimes be problematic. For example, the use of  $\text{HF}$  to dissolve soil samples containing calcium ion or easily soluble compounds containing the element, results in the formation of insoluble salts and prevents MC ICP-MS analysis [19]. Similarly, K excess in the sample prevents Rb ionization.

### Application of Isotope Studies in Soil/Environmental Sciences – Case Studies

#### Pb Isotopes as Pollution Tracers

Pb is a non-essential and health threatening element whose levels of emission into the environment should be strictly controlled. However, environmental monitoring projects using novel methods are still young, and large amounts of lead have already been released during past few centuries. Knowledge about Pb origin and behavior in the natural environment is essential in order to protect people from adverse effects. The studies can be done in both local and global scales. One of the studies constraining lead origin on a local scale was done by [20]. The experiment was made in order to identify Pb isotopic signature in wine and vineyard soils from different regions of Czech Republic. Soil and wine samples were taken from industrial regions (northernmost Bohemia) and agricultural areas (Roudnice, in central Bohemia). The research involved ICP-MS analysis of  $^{206}\text{Pb}/^{207}\text{Pb}$  and  $^{208}\text{Pb}/^{206}\text{Pb}$  of plants and soils, which were later compared to Pb isotope ratios of geological basement and anthropogenic pollution. The authors noticed that in both polluted and unpolluted areas Pb isotope composition of plants more resembles the composition of airborne particles rather than that of the basement rocks and soils. The implication was that the atmospheric Pb was a major source of plant contamination. It is important to note that the answer could be obtained only by means of Pb isotope analysis, since standard chemical/physical laboratory methods would not recognize two sources of Pb within soils [21].

The problem of the global extent of Pb anthropogenic contamination was approached by [10], who estimated anthropogenic-to-natural Pb proportions in tundra soils located far from pollution centers. They analyzed surface soil horizons of high-latitude ecosystems and tundra soils. Samples were taken from podzols, cryosols, and ombrothropic peat cores. The research was carried out on soils in which Pb reservoir and its location was affected by different factors, e.g. in-mixing due to plant translocation (bioturbation), cryoturbation, and heavy metal enrichment of organic-rich top levels by air contribution. They found that

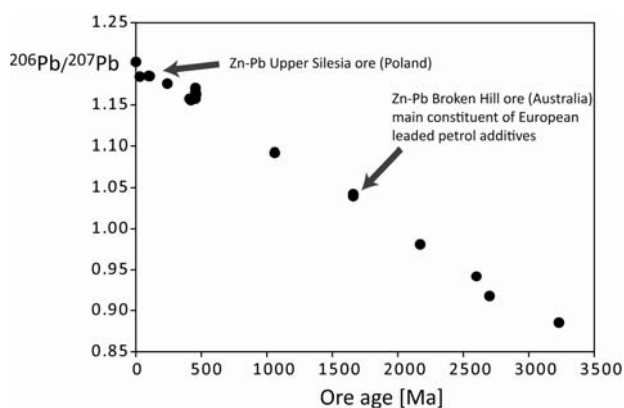


Fig. 1. Pb isotope composition of Pb ores with different ages; data taken from Stacey and Kramers [29] and Tyszka [11].

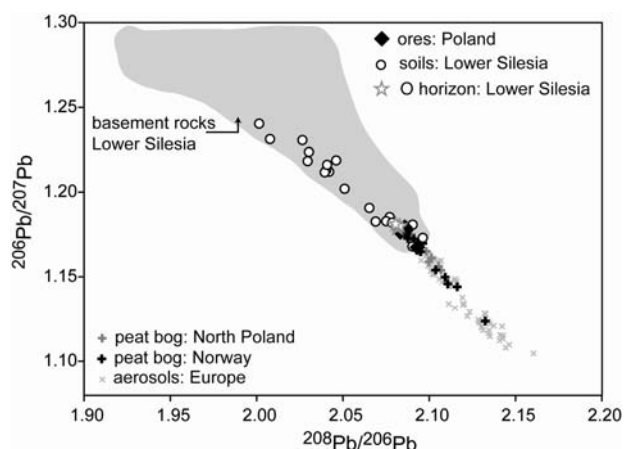


Fig. 2. Three-isotope plot comparing the Pb isotope composition of samples from Lower Silesia analyzed by Tyszka [11], with European aerosol samples analyzed by Bollhöfer and Rosman [30], and peat samples from northern Poland [26], and Norway [31].

Table 1. External reproducibility of Pb isotope measurements obtained by different authors in environmental sciences. The reproducibility is calculated using duplicate or triplicate analyses of samples or standards treated as unknowns.

Isotopes analyzed	Standard	RSD	Reference	Analyzing Technique
$^{206}\text{Pb}/^{204}\text{Pb}$	NIST981	0.29%	[25]	ICP-MS
$^{207}\text{Pb}/^{206}\text{Pb}$	NIST981	0.15%	[25]	ICP-MS
$^{208}\text{Pb}/^{206}\text{Pb}$	NIST981	0.15%	[25]	ICP-MS
$^{207}\text{Pb}/^{206}\text{Pb}$	NIST981	0.25%	[8]	ICP- SFMS
$^{208}\text{Pb}/^{206}\text{Pb}$	NIST981	0.09%	[8]	ICP- SFMS
$^{208}\text{Pb}/^{204}\text{Pb}$	NIST981	0.004-0.013%	[26]	MC ICP-MS
$^{207}\text{Pb}/^{204}\text{Pb}$	NIST981	0.004-0.006%	[26]	MC ICP-MS
$^{206}\text{Pb}/^{204}\text{Pb}$	NIST981	0.003-0.008%	[26]	MC ICP-MS
$^{208}\text{Pb}/^{206}\text{Pb}$	NIST981	0.001-0.004%	[26]	MC ICP-MS
$^{207}\text{Pb}/^{206}\text{Pb}$	NIST981	0.001-0.002%	[26]	MC ICP-MS
$^{207}\text{Pb}/^{206}\text{Pb}$	NIST981	0.2-0.7%	[11]	Quadrupole ICP-MS
$^{208}\text{Pb}/^{206}\text{Pb}$	NIST981	0.4%	[11]	Quadrupole ICP-MS
$^{206}\text{Pb}/^{207}\text{Pb}$	NIST981	0.11%	[27]	Octupole ICP-MS
$^{208}\text{Pb}/^{206}\text{Pb}$	NIST981	0.14%	[27]	Octupole ICP-MS
$^{208}\text{Pb}/^{207}\text{Pb}$	NIST981	0.14%	[27]	Octupole ICP-MS
$^{208}\text{Pb}/^{207}\text{Pb}$	NIST2709	0.1-0.49%	[7]	ICP-MS
$^{206}\text{Pb}/^{207}\text{Pb}$	NIST2709	0.015-0.018%	[7]	ICP-MS
$^{206}\text{Pb}/^{207}\text{Pb}$	n/a	4.13%	[28]	Quadrupole ICP-MS
$^{206}\text{Pb}/^{204}\text{Pb}$	n/a	4.55%	[28]	Quadrupole ICP-MS
$^{207}\text{Pb}/^{204}\text{Pb}$	n/a	0.64%	[28]	Quadrupole ICP-MS
$^{208}\text{Pb}/^{204}\text{Pb}$	n/a	1.47%	[28]	Quadrupole ICP-MS

most of the Pb present in upper soil horizons is of anthropogenic origin and suggested that anthropogenic Pb may travel via the atmosphere even to areas located far from pollution centers. Again, their results were based on the fact that Pb isotope composition of geological basement was  $^{206}\text{Pb}/^{207}\text{Pb} = 1.2-1.30$ , whereas Pb isotope composition of the O-horizons in tundra soils was  $^{206}\text{Pb}/^{207}\text{Pb} = 1.17$ , and therefore similar to Pb composition of anthropogenic materials in Europe:  $^{206}\text{Pb}/^{207}\text{Pb} = 1.16$ .

#### Sr Isotopes as Origin Tracers

With the progress of globalization, increasing amounts of imported goods from all around the world, and new EU restrictions, the problem of food origin authenticity has become more and more noticeable. To protect local brands from being overwhelmed by mass production, a PDO (protected designation of origin) regulation has been created, meaning that a product characteristic for each region must be created from resources originating from the same region. Such a regulation was in need of an analytical method to verify its authenticity. And that's the moment when ICP

MS, alongside other technique combinations regarding soil samples, came in handy.

The main source of the problem became a well known European beverage created from fermented apples: cider. This popular drink is produced in the UK, Ireland, France, Spain, and Switzerland, but only a few are PDO products such as "Sidra the Asturias." To ensure PDO regulation, a team of researchers [2] conducted a series of Sr isotope analysis on food products such as ciders, cheese, wine, and butter with the assumption that the Sr isotope composition of the goods should be similar to the soil composition in the area where their major ingredient grew or where animals were fed. The method included MC ICP-MS and multi-elemental alongside analysis of variance (ANOVA), which together became a tool for verifying PDO from commercial products. Using a multivariate statistical method involving Na, Mg, Al, K, Ca, Ti, V, Mn, Zn, As, Rb, Sr, Mo, Ba, and  $^{87}\text{Sr}/^{86}\text{Sr}$  isotopic composition the authors were able to determine 100% of the origin of ciders coming from different regions. The combination of a wide range of elements and Sr isotopes provided a good differentiation for regional distinction.

### Pb Isotopes as a Tracer of Soil-Forming Processes

Pb is the most commonly studied metal that is being introduced to the environment, mainly because of its toxicity and wide use through past years in, e.g., gasoline from the 1920s to 1980s. Its anthropogenic pool enriches the soil, but the main Pb reservoir in the soil vertical profile is the parent rock. The mixing of these two sources gives actual values of Pb isotope ratios in soil and this value is usually characteristic for certain regions. In order to present the correlation between different types of bedrock and anthropogenic influence a large-scale experiment must be conducted. Such an experiment has been undertaken by [8]. A transect of soil excavations has been established from east to west through the U.S.A. Soil samples have been taken from A and C horizons and Pb isotope composition was analyzed. The results showed significant differences in Pb isotope compositions between the coasts and the center of the continent. In many cases higher Pb concentrations in the top soil horizons is explained as the result of anthropogenic contamination [10, 22, 23]. In contrast to the majority of studies of Pb, isotopes in soils [8] present a different point of view. They propose that the different Pb isotopes in upper soil horizons are due to a natural enrichment process resulting from the interaction between soil and the biosphere. This critical approach shows that knowledge about heavy isotopes and their environmental behavior is constantly changing and the development of analytical procedures and large-scale experiments are crucial in order to verify a constantly changing state of knowledge.

### Sr Isotopes as a Tracer of Soil Forming Processes

Sr isotopes are better suited to study soil formation processes because they are not strongly enriched by anthropogenic sources. For example, [12] shows that Sr isotope composition of soils in Andalusia (Spain) is controlled by the mixing of two sources: weathered granite basement and Sahara dust. They show that the fine-grained Fe-oxide and Al-silicate fraction (<2  $\mu\text{m}$ ) of the soil contained 16-69% of material derived from Sahara dust, the proportion was higher in a separated Al-silicate fraction 33-69%.

### Sr Isotopes as Tracers of Anthropogenic Influence in the Environment: Waters Sources

Strontium, similar to lead, has two main origins, first of which is the natural geological source and the second is anthropogenic. The natural weathering of parent rocks enriches the pool not only of soils, but also waters, creating the opportunity to determine different watersheds. Due to different parent rocks the tracing of anthropogenic influence in waters in large areas is complicated because of many sources of Sr. However, at this point ICP-MS comes in handy with precise  $^{87}\text{Sr}/^{86}\text{Sr}$  measurements. Research performed in Austin, Texas [24], shows that, using Sr isotopes,

we can determine the anthropogenic influence in the base flow, stream waters, and municipal waters in the area. Strontium composition of  $^{87}\text{Sr}/^{86}\text{Sr}$  reaching from 0.70778 to 0.70918 is the effect of initial Sr from local limestone and the anthropogenic deployment from aerial deposition. Distinction of these different ratios shows the impact of anthropogenic influence in the environment.

### Conclusion

Pb and Sr isotope analyses are routinely analyzed to solve different environmental scientific and social problems, and progress is being made to use them in soil sciences. Pb isotopes are especially useful in distinguishing contaminated versus uncontaminated soils, especially around the contamination centers. The use of isotopic composition shows that information obtained by analyzing long distance atmospheric deposition and many components of the environment gives a more complete answer about human interference in the natural environment. Many questions still remain unanswered along the way to understanding these problems. The challenges remain to improve the analytical approach, e.g. by choosing a better sample digestion method, and better analytical equipment that provides more reliable and accurate data.

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