# Investigation of climate change and history of lead deposition using soil archives

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**ABSTRACT**

Our study focused on the investigation of climate change and the fate of lead in soils from the Low Volga region of Russia over 3500 years. We used a comparative analysis of the modern soils and palaeosols preserved under burial mounds, which date back to the Middle Ages and the Early Iron and Bronze Ages. A climate reconstruction showed periodic changes, with the most humid climate conditions occurring during Golden Horde period. However, we could not find any consistent changes in Pb concentration and profile distribution following the climate change. We observed a clear difference in Pb isotopic ratios between the lower and upper horizons both for the modern and buried profiles, reflecting the influence of atmospheric lead depositions. However, there is no statistically significant difference in Pb isotopic ratios between the upper horizons of buried and modern soils (except modern soils collected in the vicinity of a motorway). This means that either anthropogenic input due to long range air transport was insignificant, or that airborne anthropogenic lead and natural airborne lead have similar isotopic composition.

## Introduction

Environmental contamination and climate change are the factors potentially influencing metal cycles, behaviour and accumulation in soils. Different environmental or archaeological archives can be used for historical reconstruction of climate change and the atmospheric deposition of metals and their accumulation in soils and sediments.

The investigation of environmental archives as varved (annually-laminated) lake sediments in Sweden (Renberg *et al.*, 2002; Klaminder *et al.*, 2005) and Northern Germany (Gäbler and Suckow, 2003), ombrotrophic peat bogs in Spain, United Kingdom, the Netherlands, Sweden (Weiss *et al.*, 1999; Bindler *et al.*, 1999; Klaminder *et al.*, 2005) and in the Jura Mountains of Switzerland (Shotyk *et al.*, 2001), ice cores in Greenland (Hong *et al.*, 1996) gave an opportunity to reconstruct the history of several thousand years of atmospheric-Pb deposition. Other archives such as corals, trees, herbarium collection (Weiss *et al.*, 1999) and more layers of forest soils (Klaminder *et al.*, 2005; Bindler *et al.*, 1999) are useful for more recent deposition reconstructions (since the industrial revolution).

Archaeological archives, such as soils preserved below burial mounds or ancient fortifications, are widely used for palaeoclimatic reconstructions. During the past 10–15 yeas this approach was successfully used for burial mounds, ancient settlements, rampartments belonging to different historical epochs (Neolithic, Bronze, Early Iron and Medieval ages) and located within the territory of desert-steppe and steppe zone of the Low Volga, Caspian, and also in the southern Urals regions in Russia (Demkin *et al.*, 2004).

The archaeological approach has promising potential in the historical reconstruction of

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metals deposition in the regions where other geochemical archives (as peat and ice cores, or varved lake sediments) are not available, and where soil characteristics and climate conditions result in low mobility Pb in soils and prevent its leaching out of the soil profile.

Sources of pollution and metal pathways can be traced using Pb isotope ratios. Isotope ratios were used to evaluate the relative impact of natural geogenic sources, local industrial and urban sources and long range atmospheric transport (Weiss *et al*., 1999; Haack *et al.*, 2003, 2004; Mukai *et al*., 2001). Analysis of Pb isotope ratios in lake sediments, soils and peat deposits from Sweden presented the opportunity to reconstruct the history of anthropogenic lead depositions during four millennia (Renberg *et al*., 2000; Bindler *et al*., 1999).

Our aim was to study the lead accumulation and fate in Chestnut soil influenced by climate change and industrial input over the last 3500 years using a comparative analysis of soil characteristics, Pb isotopic ratios and profile distribution in modern and buried soils.

## Methods

Samples of Chestnut soil were collected from all genetic horizons of palaeosols preserved under burial mounds of different ages, and from the modern reference soil (Salomatino, Volgograd region, Russia). The burial mounds belong to the following chronological sequence: Golden Horde period (XIII–XIV century AD), Late Sarmat (II–III century AD), Srubnaya Culture (XVI–XV century BC). Dating was based on archaeological methods.

Additionally, samples from the upper ($A_g$) horizon of the modern soil were collected at distances 2 m and 10 m from the Moscow–Volgograd motorway. The main soil characteristics such as organic matter, soluble salts, carbonate content, pH, mechanical composition and CEC were determined using standard methods. The complete dissolution of soil samples was performed using a mixture of HF/$HNO_3$/$H_2O_2$ on hot plates at atmospheric pressure in super-clean conditions. The major cations (analysed using inductively coupled plasma optical emission spectroscopy (ICP-OES)), metal concentrations and Pb isotopic ratios (analysed using a multi-collection high resolution inductively coupled plasma mass spectrometer (ICP-MS)) Neptune ThermoFinnigan) were determined.

## Results and discussion

The climate reconstruction was based on the comparison of organic-layer thickness, profile morphology and carbonate and soluble-salts distributions. Dry periods occurred in XVI–XV century BC and II–III century AD. The Golden Horde period was much more humid, with annual precipitation of ~370–420 mm; 70–80 mm greater than present amounts. However, we could not find any consistent differences in Pb concentrations and profile distributions relative to the climate trends.

We found a slight increase in total Pb concentration in the upper horizons and in the ratios between Pb concentrations in the A and D horizons of the soil chronological sequence over 3500 years, probably due to increasing input from industrial sources. However, the only statistically significant difference in isotopic ratios (upper horizons) was found between the ancient and modern soils collected along the motorway.

We did observe a clear difference in Pb isotopic ratios between the lower and upper horizons, both for the modern and buried profiles, reflecting the influence of atmospheric-Pb depositions, which has a different isotopic composition in comparison with the geological background.

The total Pb isotopic composition in the upper horizons fits to the European Standard Pollution Line and the Gasoline Line (Haack *et al*., 2003). Surprisingly, this observation is valid not only for the modern soil, but also for the buried ones. If the difference in isotopic ratios between the background and atmospheric Pb is attributed entirely to the anthropogenic factor (as follows from Renberg *et al*., 2000), then we have to conclude that the anthropogenic impact at present and 3500 yeas ago were the same in this region, which contradicts the historical deposition trends reconstructed by many researchers using sediment and ice and peat cores in other regions (Sweden, Switzerland, Greenland). Another possible explanation is that airborne anthropogenic lead and airborne natural lead have a similar isotopic composition.

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