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# Buried Paleosols as Reference Objects for Assessing the Current Level of Soil Pollution with Lead in the Lower Volga Steppes

T. V. Pampura<sup>a, \*</sup>, M. Meili<sup>b</sup>, K. Holm<sup>b</sup>, F. Candaudap<sup>c</sup>, and A. Probst<sup>d</sup>

<sup>a</sup>*Institute of Physicochemical and Biological Problems of Soil Science, Russian Academy of Sciences, Pushchino, 142290 Russia* <sup>b</sup>*Department of Environmental Science and Analytical Chemistry, Stockholm University, SE-10691 Stockholm, Sweden*

<sup>c</sup>*Observatory Midi-Pyrénées, National Center for Scientific Research (CNRS), Toulouse, France*

<sup>d</sup>*EcoLab, Université de Toulouse, CNRS, Toulouse, France*

\**e-mail: pampura@mail.ru*

**Abstract**—The estimation of soil contamination with anthropogenic lead requires uncontaminated analogues of the recent soils for comparison. For this purpose, a paleosol buried under a 2-m high burial mound of the Bronze Age and protected by it from atmospheric deposition during 4500 years was studied. The content and isotopic composition of mobile and total lead in the buried and recent soils (roadside and remote from lead sources) were compared. Obvious signs of anthropogenic contamination were revealed in only the upper layer of the roadside soil within 10 m from a highway. These were an increase in the absolute content of all lead forms; a high relative content of mobile forms; high ratios of Pb relative to Ti, Zr, and Y; and the similarity between isotopic compositions of the soil lead and the lead from modern atmospheric aerosols and Russian gasoline. Interestingly, no significant difference was found in the total lead contents or in the isotopic compositions between the recent soil remote from roads and the buried soil. However, some signs of anthropogenic impact could be revealed by the analysis of mobile lead forms, which make up a small portion of the total content.

**Keywords:** lead of atmospheric deposition, soil lead, paleosol lead, soil lead forms, anthropogenic lead, stable lead isotopes, paleoenvironmental reconstruction

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## INTRODUCTION

Lead is a hazardous environmental pollutant well known for its negative effects on higher psychical functions and cardiovascular, immune, and other systems of the human organism [26]. It is assumed that the industrial development and the atmospheric long-range transport of pollutants resulted in a global contamination of the environment with this toxic metal. From some estimates [46, 47], the share of anthropogenic sources in the total lead emission was 94–99.7% in the late 20<sup>th</sup> century.

In some cases, lead sources can be identified from the analysis of lead isotopic composition. In many cases, the specific isotopic compositions of ore-lead from different deposits [60] make it possible to distinguish the natural lead of the local geological background from the extrinsic anthropogenic lead of ore origin and even trace its source [18, 22, 24, 25, 34, 37–39, 41, 42, 44]. The history of anthropogenic lead in atmospheric deposition can be reconstructed from the changes in the concentration and isotopic composi-

tion of lead in natural archives: bottom sediments [19, 21, 56, 57], ombrotrophic peat bogs [9, 35, 37, 39, 64, 65, 75], and glaciers [12, 29, 43, 58, 68, 74]. Numerous studies found that the lead deposition in Europe increased during the last 3000–4000 years. The isotopic composition of lead simultaneously changed from more radiogenic (i.e., enriched with isotopes <sup>206</sup>Pb, <sup>207</sup>Pb, and <sup>208</sup>Pb forming and accumulating from the radioactive decay of U and Th), which is close to the average composition of the upper Earth crust, to less radiogenic due to the increased input of anthropogenic ore-lead [10, 36, 75]. Anthropogenic lead was found not only in the close vicinity of local sources, but also far away from industrial centers: in Greenland and Antarctic glaciers and remote regions of Northern Europe. The change in the share of anthropogenic lead in fallout directly reflects the history of metal production on the global scale [62], with maxima during the periods of Roman Empire, Middle Ages, and Industrial Revolution. Fallout was maximal in the second half of the 20<sup>th</sup> century. According to Swedish research [10], atmospheric lead deposition in the

20th century increased hundreds or thousands of times compared to the pre-anthropogenic period 3500–4000 years ago. However, the situation with atmospheric fallout improved significantly during the past two decades due to the prohibition of leaded gasoline. According to the recent EMEP Status Report (Cooperative Program for the Monitoring and Evaluation of the Long-Range Transmission of Air Pollutants in Europe) [73], the emission of lead in Europe decreased by 90% from 1990 to 2010, which resulted in the reduction of atmospheric deposition by 75% on average. This value varied from 18 to 88% among the countries. The share of gasoline lead in atmospheric fallout also changed during 20 years, from 75% in 1990 to 11% in 2010. Metallurgy (29%) and stationary fuel combustion in industry (26%) begin to dominate in European countries as lead sources [73]. Nonetheless, even after the measures for lead emission control were undertaken, the level of recent atmospheric lead deposition in Europe is still tens of times higher than the natural background [10], so that the human and environmental health continue to face danger.

The conclusion about the high anthropogenic load of atmospheric fallout in Europe and North America is well documented in numerous studies; however, its implications for soil cover are still insufficiently understood, and the results of studies are contradictory and provoke intense discussion in the scientific literature [51, 52, 63]. A significant, sometimes thousand-fold, contamination of the upper horizons of forest soils with anthropogenic lead because of long-range transport was recorded in many remote regions [8, 9, 11, 20, 27, 28, 34, 45, 55, 61, 67, 69]. However, the results of mapping of the agricultural and grazing soils of Europe within the framework of the GEMAS project [53] show that the spatial distribution of lead and its isotopic composition in these soils are controlled by geological (rock age and chemical composition, presence of ore anomalies) and climatic (weathering processes, the last glaciation boundaries) factors rather than by anthropogenic ones. However, local anthropogenic anomalies (cities, industrial centers, highways) are also undoubtedly present.

The degree of soil contamination against the natural background depends not only on the level of atmospheric deposition, but also on the initial content of metal in the soil. The content of organic matter in the upper horizons of forest soils can reach 70–90%, and the content of mineral components is low. Since the anthropogenic lead is dominant in the current atmospheric deposition, its relative addition to the small amount of natural lithogenic lead in these horizons can be significant. In mineral soils (horizons), where the content of organic matter is low and the concentration of lithogenic lead inherited from the parent rock is significant, the addition of anthropogenic lead can be imperceptible against natural background. The level of contamination also depends on the migration rate of anthropogenic metal in the soil profile. Anthropogenic

lead, entering the soil profile, forms strong bindings with organic matter, carbonates, iron and manganese hydroxides and can remain in the soil profile for centuries [9, 33]. The soil acts as a barrier for the lead input into groundwater; the self-purification of soils is a very slow process. The lead-contaminated soil becomes a secondary source of anthropogenic metal due to its dispersion by wind.

The natural and anthropogenic components of the total metal pool in the soil should be distinguished to understand and predict the behavior of anthropogenic lead. The contamination level of the recent soils is frequently estimated from the difference in the content and isotopic composition of lead between the upper and lower horizons. The assumption is that the increased lead content in the upper soil layer compared to the lower layer is mainly due to anthropogenic input. From the significant difference in the concentration and especially isotopic composition of lead in the upper organic and lower mineral horizons, a conclusion about a 100- to 1000-fold contamination of forest soils in Scandinavia was made [9, 34, 68]. According to other authors [53, 54], the difference in the concentration and isotopic composition of lead in different genetic horizons of soil can also be due to natural reasons, e.g., the differentiation of material during the formation of soil profile. The comparison of contaminated soil profiles with soil profiles free from anthropogenic impact would account for this factor. Absolutely clean soils are difficult to find because of the global character of atmospheric transport of lead and the dominance of anthropogenic lead in current atmospheric deposition. A possible solution can be the use of buried paleosols protected from atmospheric fallout since the moment of burial and, at sufficient thickness of the burial mound, from the penetration of anthropogenic lead into the buried soil profile [49]. The comparison of the concentration, isotopic composition, and forms of lead in buried and recent soils can thus contribute to the assessment of the present-day contamination of soils and the determination of the pollution sources. We recently used this approach for assessing the contamination level of recent chestnut soils compared to paleosols buried under burial mounds of the Iron (1700 and 2000 years ago) and Bronze (3500 years ago) Ages [4]. In this work, we study the soil buried under a higher (about 2 m high) and older (about 4500 year old) burial mound. This allows us to consider the buried soil as an uncontaminated analogue of recent soils with a higher degree of confidence. The aim of this work was to assess the effect of anthropogenic lead deposition on soils remote from roads and industrial centers.

## OBJECTS AND METHODS

Field work was carried out within the framework of a joint expedition by the Laboratory of Archeological Soil Science (Institute of Physicochemical and Bio-



Fig. 1. Excavations of the solitary mound Perekopka 5.

logical Problems of Soil Science, Russian Academy of Sciences) and the Volgograd University in 2007. Buried and reference soils are located on the area of the Perekopka-2 burial mounds (2 km to southwest of the village of Perekopka, Kletsky district, Volgograd oblast) within the Don River bend on the territory of Don Ridge. The absolute height is about 80 m above sea level. The mean annual precipitation is about 400 mm. This is the area of chestnut soils (Kastanozems). The paleosol is buried under a solitary burial mound, which archeologists from the Volgograd University dated to the Catacomb culture of the middle of the third millennium BC [5]. The mound height is about two meters (Fig. 1).

The profile of the recent chestnut soil (Kastanozem) is located 30 m to the south of the mound. The burial mound is remote from roads and other industrial objects. The distance to the nearest city (Volgograd) is 108 km in the southwest direction. To study a local anthropogenic signal (i.e., isotope ratios of lead in Russian leaded gasoline), the surface (0- to 5-cm) layers of contaminated roadside soils were investigated at different distances (2, 5, and 10 m) from the Moscow–Volgograd M6 highway, 39 km to the north-northwest of Volgograd (sampling site coordinates 49°00' N, 44°11' E).

Soil samples were taken from all genetic horizons as grab sample covering the entire vertical extent of the horizon. Samples were dried at 40°C, sieved through a 1-mm nylon sieve, and subjected to standard chemical analyses: determination of particle size distribution and contents of humus, soluble salts, gypsum, and carbon-

ates [1], as well as determination of the content and isotopic composition of total ( $Pb_{tot}$ ) and mobile (acid-soluble  $Pb-HNO_3$  and carbonate-bound  $Pb_{carb}$ ) lead.

To determine the total content of a wide range of elements and the isotopic composition of total lead, soil samples (in duplicate) were digested in a mixture of concentrated hydrochloric and nitric acids in Savillex teflon beakers at 90°C and then treated with hydrogen peroxide and nitric acid to remove organic matter [28]. All operations were conducted with acids of the highest purity in the clean room of the Isotope Laboratory, Géosciences Environnement Toulouse (GET), France.

Acid-soluble lead ( $Pb-HNO_3$ ) was extracted with 0.5 N  $HNO_3$  [23]. Merck Suprapur 65%  $HNO_3$  was used for the preparation of the solution. The soil : solution ratio was 1 : 10. The suspension was shaken in plastic centrifuge tubes for 24 h. The solution was separated by centrifugation at 4000 rpm for 15 min and filtered through PVDF membrane filters (Life Science) with a pore size of 0.45  $\mu m$ .

The lead bound to carbonates ( $Pb_{carb}$ ) was extracted with a 1 M  $CH_3COONa$  solution, the pH of which was adjusted to 4.5 by adding of acetic acid [40]. The soil sample in a centrifuge tube was treated with the prepared reagent at a ratio of 1 : 10, shaken for 5 min, and centrifuged at 3000 rpm for 15 min; the liquid phase was separated for further analysis by filtering through a membrane filter (0.45  $\mu m$ ).

The concentrations of elements and the isotopic composition of lead were determined by inductively

**Table 1.** Profile characteristics of submound and recent soils

Parameter	Buried solonetzic solonchakous chestnut soil, K2sl,sk, profile D-711	Recent nonsaline dark-chestnut soil, K3, profile D-710
Humus layer (horizons A1 + B1), cm	27	35
Depth of effervescence, cm	27	33
Occurrence depth of soluble salts, cm	35	No
Occurrence depth of gypsum, cm	40	No
Weighted average content of CaCO <sub>3</sub> in the 0- to 100-cm layer, %	5.6	2.1
Weighted average content of soluble salts in the 0- to 100-cm layer, %	0.48	0.03
Weighted average content of gypsum in the 0- to 100-cm layer, %	1.03	0.31

coupled plasma mass spectrometry using Q-ICP-MS Agilent 7500A (Géosciences Environnement Toulouse (GET), France) and ICP-MS Thermo Xseries II (Stockholm University) instruments. Quality control of elemental analysis was performed using an internal (In/Re) standard and a soil standard (SRM San Joaquin Soil 2709, US National Institute of Standards and Technology). The relative standard deviation (RSD, %) for the determination of lead concentration was <10%. In the standard soil, recovery of about 84%, 87%, and 78% of the certified values were determined for Pb, Ti, and Ca, respectively. The standard SRM 981 (common lead) from the US National Institute of Standards and Technology was used for mass bias correction. Before the calculation of isotope ratios, the intensities of <sup>206</sup>Pb, <sup>207</sup>Pb, and <sup>208</sup>Pb were corrected against blank runs. The RSD of isotope ratios were as follows: 0.27% (<sup>207</sup>Pb/<sup>206</sup>Pb) and 0.27% (<sup>208</sup>Pb/<sup>206</sup>Pb) for total lead (29 determinations); 0.93% (<sup>207</sup>Pb/<sup>206</sup>Pb) and 0.91% (<sup>208</sup>Pb/<sup>206</sup>Pb) for acid-soluble lead (22 determinations); and 1.35% (<sup>207</sup>Pb/<sup>206</sup>Pb) and 1.08% (<sup>208</sup>Pb/<sup>206</sup>Pb) for carbonate-bound lead (48 determinations).

## RESULTS AND DISCUSSION

There is an opinion that soils hardly could be used as archives to study the history of lead contamination because of the possible migration, redistribution, and removal of the metal from the soil profile [75]. However, the soil and climatic conditions in the dry steppe zone (little precipitation, high pH, presence of carbonates in the soil) are apparently favorable for the immobilization of lead and hamper its leaching from the soil profile. This should favor the conservation of paleosol features reflecting paleoenvironmental conditions at the times of soil burial.

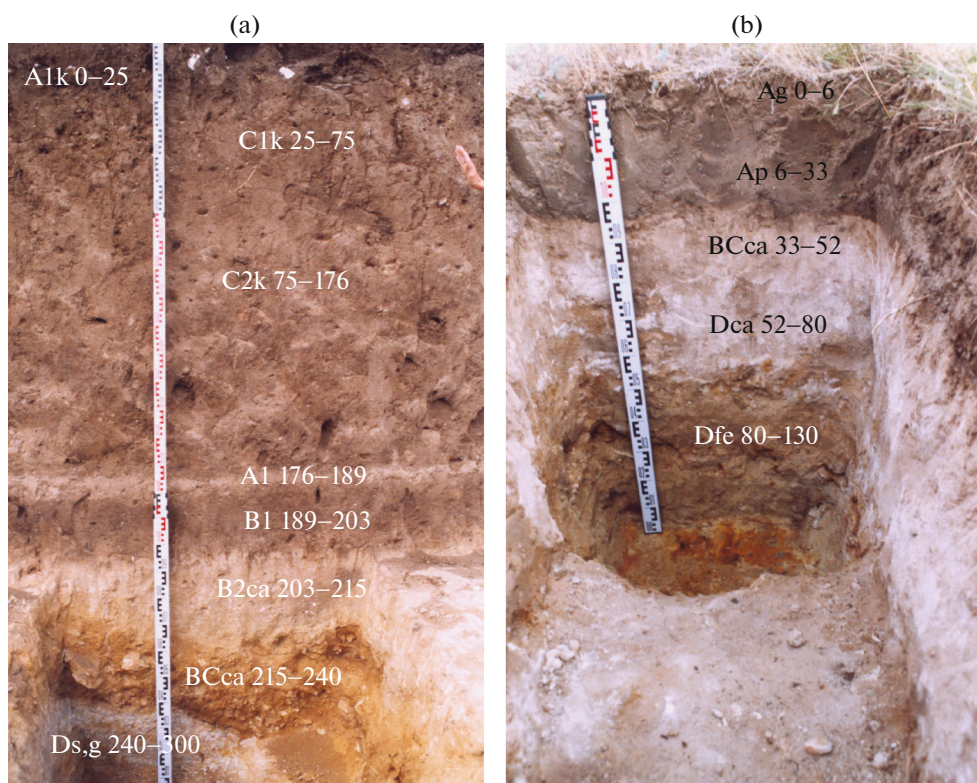
**Soil parameters and climatic reconstructions.** The profiles of the burial mound, buried and remote recent soils are shown in Fig. 2. The characteristics of soils are given in Tables 1 and 2. The buried soil was identified as a solonetzic solonchakous chestnut soil (Kasta-

nozems). The recent remote soil is a shallow loamy nonsaline dark-chestnut soil on sandy deposits. The detailed description of profiles is reported in [5]. In lithological terms, the studied soils are sandy and silty cover loess-like loams. The underlying rocks are deluvial deposits of heterogeneous composition (ferruginized loamy sands and sands with gravels, and sandstone and limestone fragments). In the case of modern soil, the underlying rocks have a lighter texture than in the case of paleosol (Table 2). Compared to the buried chestnut soil, inventory of carbonates, salts, and gypsum in the 0- to 100-cm layer of the recent dark chestnut soil decreased 2.7, 16, and 3.3 times, respectively (Table 1). The comparison of the buried and recent soils shows that the climatic conditions in the region during the Catacomb time were more arid than nowadays. According to previous studies in the Lower Volga region [2, 3, 5, 15], the most arid conditions were from the late third to the first quarter of the second millennium BC. Significant evolutionary transformations of soils took place due to changes in climatic conditions from relatively arid to more humid during the last 4500 years. Saline solonetzic chestnut soils evolved to nonsaline dark chestnut soils with a possible intermediate stage of chestnut-like soils.

Climatic factors, together with the position of the soil in the microrelief (associated with depressions or elevated areas), determine the soil subtype and the characteristics of soil profiles: texture, contents of iron and manganese hydroxides, organic matter, carbonates, and the depth of calcareous and hydroxide-enriched horizons. These parameters affect the mobility of lead and its distribution along the soil profile. Climate cooling and increase in precipitation could favor the changes of soil moisture conditions and, probably, some increase of lead mobility in the recent soil compared to the paleosol.

**Lead concentrations and forms in soils.** Along with the total lead content in the soil, the content of lead forms with different mobility and biological availability are important to be analyzed. Since anthropogenic lead accumulates mainly in less tightly bound forms [16, 72], the content of these forms and their isotopic





**Fig. 2.** Profiles of (a) the mound Perekopka 5 and the submound solonetzic solonchakous chestnut paleosol, and (b) the remote recent dark-chestnut soil.

composition are more sensitive indicators of contamination than the total lead content. To extract lead forms readily available to living organisms, we used a mixture of sodium acetate and acetic acid, which is usually used for the extraction of carbonates from soils and sediments. The classical Tessier method [70] is

based on use of 1 M  $\text{CH}_3\text{COONa}$  with pH 5.0. Later on, it was shown [40] that a more complete dissolution of carbonates is reached at pH 4.5, if their initial content does not exceed 50%. In our case, single extraction was used, which was not a step in the series of consecutive extractions, as was described in the

**Table 2.** Chemical properties and particle size distribution in submound and recent soils

Horizon, depth, cm	Humus, %	pH <sub>water</sub>	CaCO <sub>3</sub>	CaSO <sub>4</sub>	Contents of fractions, %		Total salts, %
			%	%	<0.001 mm	<0.01 mm	
Mound soil and buried solonetzic solonchakous chestnut paleosol (profile D-711)							
A1k, 0–25	2.52	7.6	2.8	0.12	8	23	0.05
C1k, 25–75	–	8.0	2.1	0.39	13	31	0.05
C2k, 75–176	–	7.9	1.0	0.40	9	30	0.20
A1, 176–189	0.65	7.5	0.5	0.62	6	23	0.26
B1, 189–203	0.91	7.5	0.8	0.50	21	41	0.23
B2ca, 203–215	0.86	7.8	5.9	0.57	20	42	0.41
BCca, 215–240	0.55	7.9	7.2	1.01	13	27	0.35
Ds,g, 240–300	–	7.8	8.0	1.55	12	23	0.78
Recent nonsaline dark-chestnut soil (profile D-710)							
Ag, 0–6	1.84	6.9	0.5	0.15	17	42	0.08
Ap, 6–33	1.97	7.0	1.0	0.28	19	37	0.04
BCca, 33–52	1.41	8.1	5.7	0.40	6	13	0.03
Dca, 52–80	–	8.0	2.6	0.35	6	8	0.03
Dfe, 80–130	–	8.1	0.0	0.27	3	4	0.03

above-mentioned methods [40, 70]; therefore, it extracted not only carbonate-bound lead, but also (partially) lead exchangeably and specifically sorbed by different soil components. Metals extractable by 1 M  $\text{CH}_3\text{COONa}$  with pH 4.5 compose a small portion of the total lead in the soil. However, they are readily available to living organisms, because they can be mobilized, when pH changes under the effect of root and microbial exudates. To be short, we shall refer to this form as “carbonate-bound”.

The second form (hereafter “acid-soluble” form) was extracted with 0.5 N nitric acid. This extraction gives results [23] analogous to the extraction with 0.43 N  $\text{HNO}_3$  (ISO 17586:2016) [32], which is officially recommended by the International Standard Organization (ISO). The method extracts (in the pH range 0.5–1) the potentially available metal fraction, i.e., the maximum amount that can be released from the soil under (predefined) worst-case conditions according to the ISO definition [31]. The extraction principle involves the solubilization of metal cations due to the competitive desorption by protons and the partial dissolution of Al, Fe, and Mn hydroxides, on which the metals are adsorbed. The exchangeable and carbonate-bound metals are also mobilized. The terms “labile” and “geochemically reactive” forms are also used for this form in international literature. It is assumed that this pool is in a dynamic equilibrium with the liquid phase, which is regulated by adsorption/desorption and precipitation/dissolution processes. Under specific conditions, it can be mobilized during a short time period (seconds to days) and is potentially available to living organisms. It contains “actually available” forms, i.e., the forms that can be mobilized by specific living organisms under real conditions [23].

**Total lead.** Our results showed that in the two upper horizons, the total lead contents of the buried and recent (remote from roads) soils did not differ significantly. However, the lead concentrations in the deeper part of the recent soil profile were lower than in the corresponding horizons of the buried soil; i.e., the increase in lead concentration from bottom to top in the profile was more visible in the recent soil (Fig. 3a).

The share of anthropogenic lead in the soil is frequently determined using its ratio to “lithogenic conservative” elements, i.e., elements that are genetically bound to the parent rock, do not migrate during weathering, and the concentrations of which depend little on the anthropogenic impact (e.g., Ti, Sc, Y, and Zr) [39]. Our results showed that the Pb/Ti, Pb/Zr, and Pb/Y ratios (Figs. 3b–3d) were characterized by constant and similar values in the profiles of the buried and recent soils, except for underlying rocks. The behavior of the Pb/Sc ratio was the same (not shown in Fig. 3). At the same time, in the upper horizon of the roadside soil the ratios were significantly higher than in the upper horizons of the buried as well as the

recent remote soil, i.e., 6, 4, and 5 times higher for the Pb/Ti, Pb/Y, and Pb/Zr, respectively, which was most probably related to the input of anthropogenic lead from the leaded gasoline.

The high values of the total lead content as well as Pb/Ti, Pb/Zr, Pb/Y (Figs. 3a–3d), and Pb/Sc ratios in underlying rocks (Ds,g horizon) of buried soils should be noted. They approached the values observed in the roadside soils. The anomalous values of these characteristics in the Ds,g horizon could be due to the spatial heterogeneity of soil-forming and underlying rocks and differences in their mineralogy (see below).

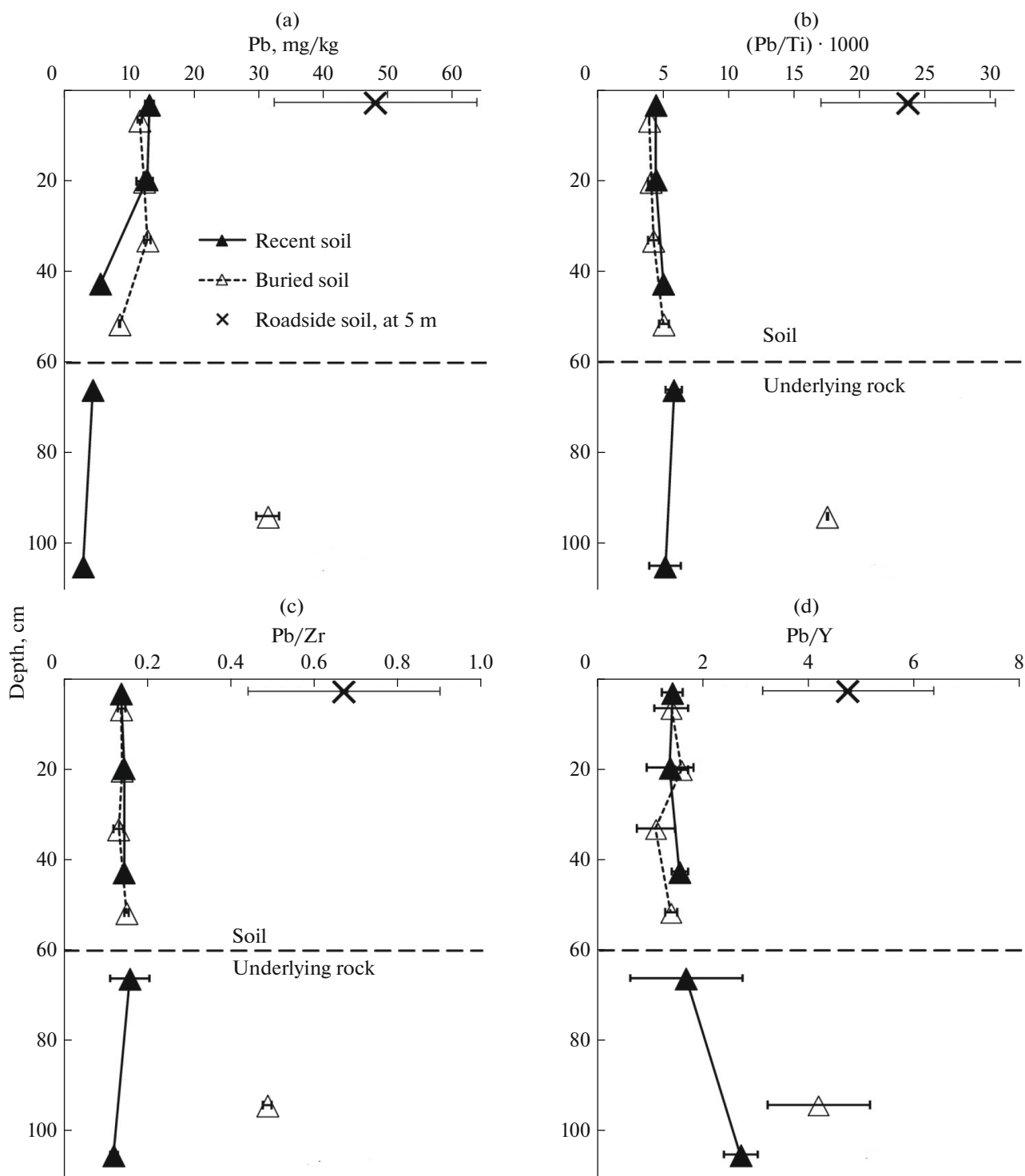
**Carbonate-bound lead.** Our study showed a high correlation between Ca extractable by 1 M  $\text{CH}_3\text{COONa}$  with pH 4.5 ( $\text{Ca}_{\text{carb}}$ ) and carbonates ( $R^2$  is 0.95 for all soils, 0.99 for the recent soil, and 0.94 for the buried soil). This close correlation makes it possible to use  $\text{Ca}_{\text{carb}}$  as a proxy for carbonates.

The content of  $\text{Pb}_{\text{carb}}$  in the soil correlated with the contents of carbonates ( $R^2$  is 0.95 for all soils, 0.90 for the recent soil, and 0.95 for the buried soil) and carbonate calcium  $\text{Ca}_{\text{carb}}$  ( $R^2$  is 0.82 for all soils, 0.84 for the recent soil, and 0.90 for the buried soil). The content of  $\text{Pb}_{\text{carb}}$  in the buried and remote recent soils varied from 1.7 to 14% of the total lead content, with the maximum absolute and relative concentrations in calcareous horizons (Fig. 4). In the upper horizon of the roadside soils, this form made up  $9.6 \pm 1.5\%$  at 10 m from the road and  $26 \pm 9\%$  at 5 m from the road, which was significantly higher than in the upper horizon of the remote recent and buried soils (Fig. 4b) and was probably related to the input of anthropogenic lead into the roadside soil from leaded gasoline.

The absolute and relative contents of  $\text{Pb}_{\text{carb}}$  in the upper horizons of the remote recent soil were slightly higher than in the buried soil (Figs. 4a, 4b). In addition, at a similar content of carbonates (and  $\text{Ca}_{\text{carb}}$ ) in the upper horizons of the remote recent and buried soils (Table 2, Fig. 4c), higher  $\text{Pb}_{\text{carb}}/\text{carbonates}$  and  $\text{Pb}_{\text{carb}}/\text{Ca}_{\text{carb}}$  ratios characterizing the degree of Pb accumulation on soil carbonates were observed in the upper horizons of the remote recent soil. The highest  $\text{Pb}_{\text{carb}}/\text{Ca}_{\text{carb}}$  ratio was observed near the highway (Fig. 4d).

**Acid-soluble lead** ( $\text{Pb-HNO}_3$ ) can include lead bound to soil organic matter and occluded by aluminum, iron, and manganese hydroxides, as well as bound to carbonates. Its share in the buried and recent soils varied from 13 to 49% ( $\text{Pb-HNO}_3$  was not determined in roadside soils). In the two upper horizons of the recent remote soil, the absolute concentrations of acid-soluble lead and its share in the total pool were significantly higher than in the buried soil and abruptly decreased with depth. In contrast, the maximum relative and absolute contents of this form in the buried soil were found in the calcareous B2ca horizon rather than in the upper horizon (Figs. 5a, 5b).

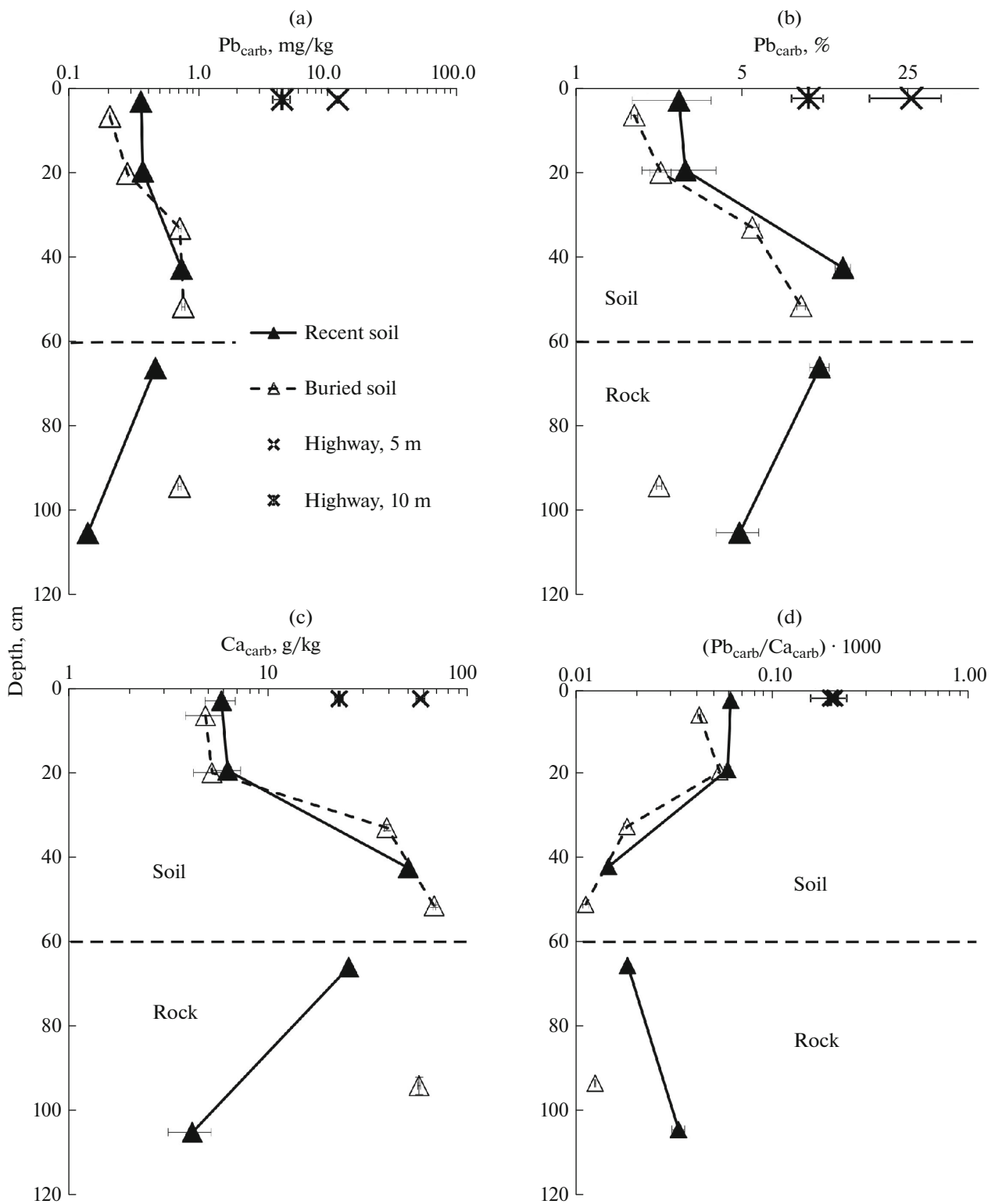




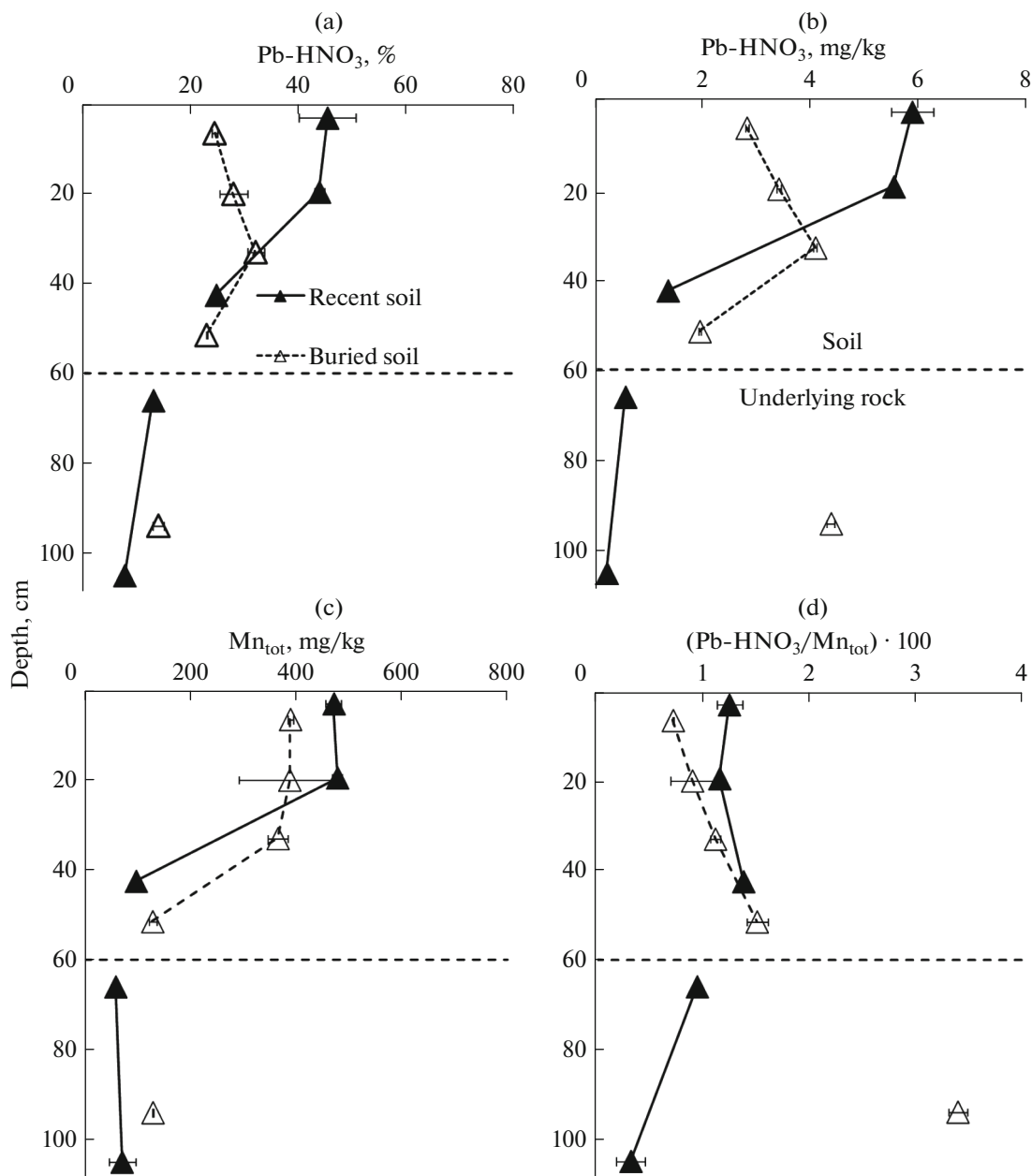
**Fig. 3.** (a) The total lead content and the (b) Pb/Ti, (c) Pb/Zr, and (d) Pb/Y ratios in the profiles of the recent (remote and roadside) and buried soils. The roadside soil was sampled in the 0- to 5-cm layer at 5 m from the Moscow–Volgograd M6 highway. Mean values for horizons  $\pm$  standard deviations are given. Dashed line denotes the approximate boundary between the soil and the underlying rock. The depth of the buried soil was calculated from the contact line between the buried and mound soils.

Numerous studies showed a close correlation of lead with iron and manganese hydroxides [36]. We did not determine the contents of iron and manganese hydroxides themselves, but a positive correlation was revealed

between the share of acid-soluble lead and the content of total manganese  $Mn_{tot}$  ( $R^2$  was 0.71 for all soils, 0.88 for the recent soil, and 0.49 for the buried soil). The concentration of manganese in the top horizons of the



**Fig. 4.** (a) Content of carbonate-bound lead  $Pb_{carb}$  and (b) its share in total lead, %; (c) the content of carbonate-bound calcium  $Ca_{carb}$  and (d) the  $Pb_{carb}/Ca_{carb}$  ratio in the recent (remote and roadside) and buried soils. The roadside soil was sampled from the 0- to 5-cm layer at the distance of 5 and 10 m from the Moscow–Volgograd M6 highway.



**Fig. 5.** (a) The relative and (b) absolute content of acid-soluble lead Pb-HNO<sub>3</sub>, (c) the total Mn content, and (d) the ratio of acid-soluble lead to total Mn in the profiles of the recent (remote) and buried soils.

recent soil was higher than in the buried soil (Fig. 5c), which could result in a higher content of Pb-HNO<sub>3</sub> (Figs. 5a, 5b). However, the relative accumulation of lead (ratio of Pb-HNO<sub>3</sub> to the total manganese in the soil) was higher in the recent soil (Fig. 5d).

The high absolute and relative content of carbonate-bound and acid-soluble lead in the upper horizons of remote recent soil compared to the paleosol could be explained by an enrichment with anthropogenic lead entering the soil in mobile forms.

However, natural factors can also affect the forms of lead in the soil. So, buried soils isolated from the atmo-

spheric impact are obviously less subjected to weathering than recent soils. In addition, the recent soils were developed under more humid conditions favorable for weathering than the soils formed 4500 years ago. The release of strongly bound Pb and its conversion to more mobile forms could occur with the destruction and transformation of the crystal lattices of minerals in the course of weathering. This could result in a higher content of mobile lead in the upper horizons of the remote recent soil than in the buried paleosol (Figs. 4, 5). Unfortunately, the presence of carbonates, gypsum, soluble salts makes it difficult to assess the degree of

weathering using commonly used chemical indices [13]. Nevertheless, differences in the intensity of weathering processes in the exposed and buried soils are expected and can affect the speciation of Pb and its mobility.

Metal speciation in the soil can also vary because of the transformation of organic matter. The close relationship between lead and soil organic matter is well known [36]. The content of organic carbon in the paleosol is significantly lower than in the recent soil (Table 2). The previous studies [3] showed that buried soils and their recent analogues differ not only in the content of organic carbon (it is always higher in recent soils), but also in the proportions of the main groups of humic substances: humic acids (HAs), fulvic acids (FAs), and humin (HM). These characteristics are determined both by the peculiarities of soil formation before the moment of their burial (climate and relief), and the processes of diagenesis after burial. It has also been shown that the transformation of humic substances in paleosols results in the modification of their molecular structure and the degree of aromaticity of HAs [3]. The mineralization and transformation of soil organic matter during diagenesis may lead to the destruction and reorganization of metal bonds with the functional groups of organic substance and change the ratio of mobile and tightly bound forms of lead in soil.

Thus, it is difficult to unambiguously explain the higher content of mobile (acid-soluble and carbonate-bound) lead forms in the remote recent soil compared to the paleosol by the impact of the anthropogenic factor alone. Differences in the conditions of soils formation, spatial heterogeneity, diagenesis and weathering can also affect the mobility and forms of lead in these soils.

**Lead isotopic composition.** The basic principles of the isotope geochemistry of lead are described in the literature [6, 7]. There are four stable lead isotopes:  $^{204}\text{Pb}$  (1.4%),  $^{206}\text{Pb}$  (24.1%),  $^{207}\text{Pb}$  (22.1%), and  $^{208}\text{Pb}$  (52.4%) (tabulated distribution of isotopes in the nature is given in parentheses [59]). Isotopes  $^{206}\text{Pb}$ ,  $^{207}\text{Pb}$ , and  $^{208}\text{Pb}$  are the final products of the radioactive decay of  $^{238}\text{U}$  with a half-life ( $T_{1/2}$ ) of  $4.47 \times 10^9$  years,  $^{235}\text{U}$  ( $T_{1/2} = 7.0 \times 10^8$  years), and  $^{232}\text{Th}$  ( $T_{1/2} = 1.4 \times 10^{10}$  years) respectively; the  $^{204}\text{Pb}$  isotope is not radiogenic. The content of  $^{204}\text{Pb}$  in an object (rock, mineral) remains constant over time, while the content of radiogenic isotopes increases with different rates due to the radioactive decay of the parent radionuclides. Thus, the ratio of isotopes depends on the initial proportions of Pb, U, and Th and the time of their coexistence. In a closed system, not only the ratios of radiogenic to non-radiogenic isotopes (that is  $^{206}\text{Pb}/^{204}\text{Pb}$ ,  $^{207}\text{Pb}/^{204}\text{Pb}$ , and  $^{208}\text{Pb}/^{204}\text{Pb}$ ), but also the ratios of radiogenic isotopes themselves change regularly with time. Analysis of the temporal evolution of the  $^{207}\text{Pb}/^{206}\text{Pb}$  and  $^{208}\text{Pb}/^{206}\text{Pb}$  ratios [14, 66] shows their monotonous decrease with time during the past

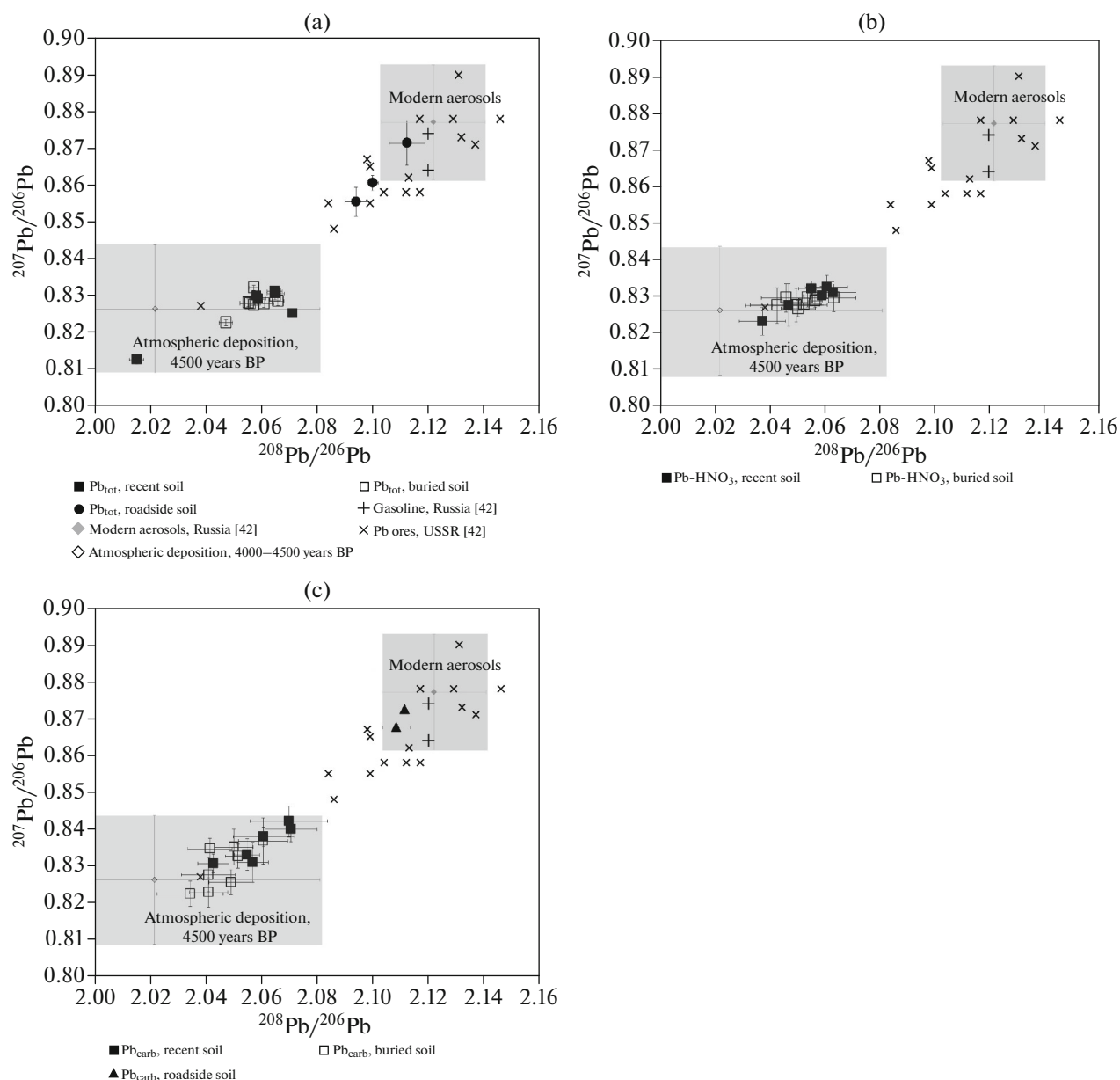
3.7 billion years. This makes it possible to use the ratios of radiogenic isotopes for dating rocks and ores. More radiogenic compositions are characterized by lower  $^{207}\text{Pb}/^{206}\text{Pb}$  and  $^{208}\text{Pb}/^{206}\text{Pb}$  ratios. These ratios are most frequently used in environmental sciences, because the sensitivity of the most accessible and efficient isotope analysis method based on Q-ICP-MS is insufficient for a reliable determination of the least abundant non-radiogenic isotope  $^{204}\text{Pb}$ . However, even without  $^{204}\text{Pb}$ , the probability of a correct determination of Pb sources remains sufficiently high (86%) [60].

During the crystallization of the main lead ore mineral (galena PbS), U and Th are not incorporated into the crystal lattice, and feeding of the lead with radiogenic isotopes ceases. The isotopic composition of the lead extracted from ore deposits and getting involved in biogeochemical cycles in many cases differs from the composition of the lead of local rocks and soils [4]. This allows determining the source and scale of anthropogenic impact.

Results of analysis of the isotopic composition of total, acid-soluble, and carbonate-bound lead in the roadside, remote recent and buried soils (horizons A+B+BC) are shown in Fig. 6. Isotope ratios of the lead in Russian leaded gasoline, ore deposits of the former USSR, modern Russian aerosols [42], and pre-anthropogenic (4000–4500 years BP) atmospheric deposition reconstructed from European peat archives [4] are also shown. Fig. 6 demonstrates a significant shift in the isotopic composition of lead in modern aerosols compared to the pre-anthropogenic atmospheric deposition, moving toward the less radiogenic values typical for ore-lead in Russia and former republics of the Soviet Union, as well as Russian gasoline lead [42]. A less radiogenic isotopic composition is also revealed in the total and carbonate-bound lead from the upper horizons of roadside soils studied in our work. These observations indicate that the composition of lead in the modern atmospheric aerosols and the upper 5-cm layer of roadside soil is dominated by anthropogenic metal, the source of which is obviously ore-lead, including that from leaded gasoline (used in Russia since the 1930s and officially prohibited in 2003).

The isotopic composition of the buried and remote recent soils is characterized by more radiogenic ratios, overlaps with those of pre-anthropogenic deposition, and significantly differs from the composition of lead in roadside soil, gasoline, ore deposits, and modern aerosols. However, there is no statistically significant difference in the isotope ratios of lead (both total and acid-soluble) between the upper horizons of the buried and remote recent soils. This indicates that lead from natural sources dominates in the remote recent soil.

A small shift in the isotopic composition of the remote recent soil away from the buried one towards “anthropogenic” compositions is noted only for the



**Fig. 6.** Isotopic compositions of (a) total; (b) acid-soluble; and (c) carbonate-bound lead in buried soil, recent soil remote from roads (horizons A+B+BC), and roadside soils (0- to 5-cm layer); gasoline of Russian production; modern Russian aerosols (shaded zone: mean  $\pm$  standard deviation); and lead ores of the former Soviet Union [42]; as well as the composition of atmospheric deposition in Europe 4000–4500 years BP (shaded zone: mean  $\pm$  standard deviation) reconstructed from peat archive data [4].

most mobile carbonate-bound form of lead (Fig. 6c), which constitutes only a small portion of the total lead (1.7 to 14%). This shift, as well as a higher absolute and relative concentration of lead in the carbonate-bound form (Fig. 4), may indicate the presence of anthropogenic lead in the remote recent soil. However, the shift in composition is not large enough to be considered as a strong evidence of anthropogenic impact and significant contamination. In addition, the shift of lead isotopic composition in the soil can occur in the course of weathering because of the different stability of rock-forming and accessory minerals characterized by dif-

ferent lead isotope ratios. Erel et al. [17] showed that the soils subjected to stronger weathering had less radiogenic isotopic composition of lead. Our results are consistent with these observations; they also agree with our earlier study of the buried soils near the villages of Salomatino and Peregruznoe in Volgograd region [4].

It should be noted that the rocks underlying the buried soil (horizon Ds,g containing 8% carbonates; depth from the current surface 240–300 cm) are enriched with less radiogenic lead. The isotope ratios



of the total lead ( $^{207}\text{Pb}/^{206}\text{Pb} = 0.840$ ,  $^{208}\text{Pb}/^{206}\text{Pb} = 2.074$ , not shown in Fig. 6) strongly differ from the ratios in the overlying horizons of the soil profile. In addition, in D<sub>s,g</sub> horizon, the total lead content and the Pb/Ti, Pb/Y, and Pb/Zr ratios (Fig. 3), as well as the Pb/Sc ratio (not shown in Fig. 3), are significantly higher than in the overlying soil profile. The absolute concentration of mobile forms of lead in the D<sub>s,g</sub> horizon is also increased due to the high content of carbonates (Figs. 4a, 5b). The strong difference in the forms and isotopic composition of lead in the D<sub>s,g</sub> horizon compared to the whole profile is apparently related to the lithological heterogeneity of rocks in Perekopka. Thus, the soil-forming rocks are sandy and silty cover loess-like loams, while the underlying rocks mainly consist of deluvial deposits with heterogeneous composition. The soil is not bound genetically with the underlying rocks, and lead in the rocks and the overlying soil profile can have different sources and history. In this context, it is important to conceive that the content or isotopic composition of lead cannot unambiguously characterize its source as anthropogenic and should be considered in conjunction with other factors.

The buried and recent soils of Perekopka vary in their characteristics and belong to different subtypes of chestnut soil. The recent nonsaline dark chestnut soil was apparently formed under more humid conditions than the buried solonchakous chestnut paleosol [5]. This could contribute to a higher mobility of lead in the recent soil profile, resulting in a removal of its most mobile forms from the upper horizon and a redistribution along the profile, which may slightly counteract the increase of concentration in the upper horizon due to anthropogenic atmospheric deposition. Our data on chestnut soils in Volgograd region (Salomatino) indeed showed that lead deposited with atmospheric fallout could migrate in the soil profile, although to a limited extent [48, 49]. There, the rate of downward migration of anthropogenic lead in the soil was determined from the profile distribution of the atmospherically-born short-lived radioactive  $^{210}\text{Pb}_{\text{ex}}$  isotope (which is not supported by the decay of soil  $^{226}\text{Ra}$ ). Such unsupported  $^{210}\text{Pb}_{\text{ex}}$ , formed in the atmosphere due to the decay of radon, is adsorbed on aerosols, and falls onto the soil with atmospheric deposition. Assuming that the chemical properties and behavior of different lead isotopes in geochemical processes are similar,  $^{210}\text{Pb}_{\text{ex}}$  can serve as a model for anthropogenic lead entering the soil, e.g., from the leaded gasoline. We showed that the rate of  $^{210}\text{Pb}_{\text{ex}}$  downward migration in the profile was variable: it was about 0.8 cm/year in the upper layer (above the calcareous horizon) of the recent chestnut soil; in the calcareous horizon,  $^{210}\text{Pb}_{\text{ex}}$  was accumulated and was not found below [48]. In deeper soil layers, the migration rate cannot be estimated by this approach because of the rapid decay of  $^{210}\text{Pb}$  ( $T_{1/2} = 22$  years). Further note

that the portion of the lead that can migrate relatively fast in the soil profile may be small. According to some studies [71, 72], the migration of gasoline lead in calcareous soils (Terra Rossa) follows two different mechanisms: its major fraction (about 95%) accumulates in the upper part of the profile and moves downward with soil particles very slowly ( $\sim 0.05$  cm/year), while the minor part (about 5%) moves with a rate of  $\sim 0.5$  cm/year, probably in the dissolved form.

Thus, our work showed that a significant contamination of recent soils with anthropogenic lead relative to a soil of the Bronze Age is locally and explicitly manifested only in the roadside soils. This contradicts to the conclusions derived for some remote soils in Sweden, [9], Norway [68], USA [20, 55], Germany [27], Scotland [8], Finland [69], France [28, 61], Switzerland [11, 45] that the Pb concentration in the modern soils exceeds the pre-anthropogenic level hundreds of times. Is this discrepancy between our and above-cited results due to a much lower level of atmospheric Pb deposition in the studied region?

Unfortunately, the reconstruction of historical atmospheric deposition in the steppe zone is difficult for lack of natural archives such as glaciers and ombrotrophic peat bogs. However, we can estimate the relative exceedance of modern deposition of Pb in Perekopka over the pre-anthropogenic background level by using our recent research on a dated ombrotrophic peat profile in the NW of the European part of Russia (Central Forest State Nature Biosphere Reserve, Tver region) [50]. The obtained results are in good agreement with European data and indicate that the maximum lead deposition in the Reserve took place in the second half of the 20th century (about 20 mg/(m<sup>2</sup> yr) and exceeded the natural level (2500–5800 years ago) by about 1000 times. Despite a significant decrease since the 1980s, Pb deposition in 2012 still exceeded the natural level by more than 50 times. On our request, recent (1990–2012) Pb deposition values for Perekopka were calculated by the Meteorological Synthesizing Center East (MSC-E), Moscow, using a regional heavy metal transport model (MSCE-HM) [30]. Modelled deposition decreased from 3 to 0.7 mg/(m<sup>2</sup> yr) during the period of 1990–2007 and was 1.3 mg/(m<sup>2</sup> yr) in 2012. Thus, the recent deposition in the region is close to the fallout reconstructed using ombrotrophic peat in Tver region (6, 1.5, and 1.1 mg/(m<sup>2</sup> yr) in 1991, 2007 and 2012 respectively). Our peat-based reconstruction of pre-anthropogenic lead deposition for Tver region ( $0.02 \pm 0.01$  mg/(m<sup>2</sup> yr)) is in good agreement with the estimates for Central and Northern Europe (0.005–0.01 mg/(m<sup>2</sup> yr) [9, 56, 65]); these figures may thus represent reference values also for the Perekopka region. Even if the pre-anthropogenic level is taken equal to 0.02 mg/(m<sup>2</sup> yr), the recent lead deposition in the studied region exceeded the pre-anthropogenic level 35 times in 2007, when the soil was sampled, and 150 times in 1990. Thus, a signifi-

cant exceedance of the recent Pb deposition above the natural level can be inferred also in this region.

Obviously, at a given level of atmospheric deposition, the relative addition of anthropogenic lead is significantly higher in organogenic soils (horizons) than in mineral soils. The publications cited above describe upper organic horizons of forest soils with an organic matter content of 50–90% [67], thus a low content of the mineral component and the associated lithogenic lead. Against this background, the relative role of atmospheric deposition as a source of Pb in soils increases. Thus, the increase in the concentration of lead and the change of its isotopic composition in atmospheric fallout immediately affect the content and isotopic composition of lead in the organic horizons of forest soils. Compared to forest soils, the chestnut soils studied in our work have much lower organic matter content (Table 2), and the shares of the mineral component and the natural lead inherited from the parent soil-forming rock are significantly higher. Against this different background, the addition of lead from anthropogenic sources can be imperceptible in terms of total content and detected only in the analysis of mobile forms.

## CONCLUSIONS

Our comparison of a submound soil and two recent soils (roadside and remote from roads, cities, and industrial centers) allows us to draw the following conclusions:

(1) Obvious signs of anthropogenic contamination were revealed in the upper horizon of the roadside soil within 10 m from the Moscow–Volgograd highway. These include high (compared to the remote recent and buried soils) concentrations of lead in all forms; higher Pb/Ti, Pb/Zr, Pb/Y (total) ratios; and a less radiogenic isotopic composition of lead (mobile and total) approaching the composition of lead in modern aerosols, lead ores, and Russian leaded gasoline;

(2) No significant differences in the content or isotopic composition of total lead were revealed between the upper horizons of the remote recent soil and the buried soil;

(3) However, possible signs of anthropogenic impact can be observed in remote recent soils by analysis of mobile metal forms. Anthropogenic lead entering the soil in a mobile form can accumulate in the soil profile by sorption on organic matter, carbonates, and Mn and Fe hydroxides. As a result, some shift in the carbonate-bound lead isotopic composition towards anthropogenic ratios was found. In addition, the absolute content and the share of mobile lead in the remote recent soil were higher than in the buried soil. However, the Pb partitioning between different forms in a soil can also be controlled by natural factors like the soil composition and the degree of weathering of the

mineral matrix, which differ between recent and buried soils.

Thus, our study revealed no significant contamination of a recent soil remote from roads, cities, and industrial centers relative to a soil buried 4500 years ago. Despite the absolute dominance of anthropogenic lead in the recent atmospheric deposition, its addition to a remote recent chestnut soil was insignificant compared to the background content of the soil lithogenic lead. An evident contamination of chestnut soils with lead was revealed only within tens of meters from a highway.

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