International Journal of GEOMATE, July 2023, Vol. 25, Issue 107, pp.33-41
ISSN: 2186-2982 (P), 2186-2990 (O), Japan, DOI: https://doi.org/10.21660/2023.107.3658
Geotechnique, Construction Materials and Environment

ISOTOPIC RATIOS AS A TOOL FOR STUDYING SOURCES OF COPPER, LEAD, AND ZINC IN NATURAL AND URBAN ENVIRONMENTS: A REVIEW

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ABSTRACT: The study of natural and anthropogenic geochemical processes is important for identifying and preventing sources of environmental pollution. Isotopic ratios are used for lead (Pb) analysis in the environment, which is important because Pb is a toxic anthropogenic metal. Copper (Cu) and zinc (Zn), however, are ubiquitous metals, essential or toxic to organisms depending on their concentration, therefore research into their concentrations is useful for health risk assessments. This review presents the state of the art in Cu, Pb and Zn isotope studies applied in natural and urban environments. Although the study of Cu and Zn isotopes remains less developed than more that of lead isotopes, we can assess their relevance as a tracer of metals in the environment. We present the principles of isotope measurements from collecting samples to mass spectrometry analysis. To understand the fate of Cu, Pb, and Zn released into the environment by anthropogenic activities, we summarize the main processes governing the distribution of these metals in different environmental matrices. The matrices include atmospheric aerosols, dust, lake and river sediments, soils and other natural and artificial materials. The focus of the review is on the isotope fractionation affects which can modify the initial signature of the various sources. We suggest that the signatures of isotopes are defined for the main natural and anthropogenic sources of Cu, Pb, and Zn in the environment. This literature review points out current knowledge gaps and proposes future directions to make Cu, Pb, and Zn isotopes a relevant tracer of the sources and fates in the natural and urban environments.

Keywords: Copper, Lead, Zinc, Isotopes, Pollution

1. INTRODUCTION

Technogenesis is associated with intense geochemical changes in the environment, the concentration of chemical elements, and their dispersion. Technogenic flows of chemical elements in the natural and urban environment can have a negative impact on plants, animals, and humans.

Heavy metals accumulate in the human body through various routes of exposure (ingestion, inhalation, and dermal contact) causing constant risks of harm to the health of adults and children, including carcinogenic risks [1]. Metal-induced intoxication negatively affects the central nervous system, damages blood components, and impairs lung, liver, kidney, and other vital organ functions [2].

Copper is an essential micronutrient for humans, but its effects can be both positive and negative. It can accumulate in the liver, kidneys, brain, and eyes. Copper can accumulate in the liver and brain, causing changes in the structure and function of these organs [3]. Various studies have been conducted on the effects of copper on fertility, cancer formation, and causing liver cirrhosis in children. But the data are limited, and it is impossible to make definitive conclusions [4].

Lead is thought to be a particularly dangerous pollutant. Humans are exposed to it daily through the skin, respiratory, and digestive systems [5]. This element has severe toxic effects on humans and ranks second on the US Environmental Protection Agency's (USEPA) list of priority hazardous substances. It has previously been found that lead poisoning can adversely affect the reproductive systems of animals and humans [6]. Respiratory system disorders, effects on human hematological functions such as decreased hemoglobin in the blood [7], central nervous and cardiovascular system dysfunction, and kidney disorders are possible [8]. Unlike Pb, Zn is important for the human body. Zinc deficiency can negatively affect the central nervous, and the immune and reproductive systems. Severe Zn poisoning is rarely touched upon in the literature, however, it can lead to liver, kidney, and gastrointestinal tract disorders, and anemia against copper deficiency in the body. It occurs, for example, when taking zinc supplements due to a competitive absorption relationship within enterocytes mediated by metallothionein [9, 10].

Despite the fact that Cu, Pb, and Zn are natural elements in the continental crust, their significant accumulation in natural environments is anthropogenic in nature and is due to rapid urbanization, industrial growth, and increased traffic [11].

2. RESEARCH SIGNIFICANCE

Copper, Pb and Zn have stable isotopes that can be used to identify the sources of urban pollution. A growing number of studies show that using the isotopic signatures of Cu, Pb, and Zn is a promising ecological indicator to assess the anthropogenic influence on natural and urban environments.

The aim of this review is to present an overview of literature published on the use of Cu, Pb and Zn isotopes as a tool for studying pollution sources in natural and urban landscapes.

3. COPPER, LEAD AND ZINC ISOTOPES

Natural copper comprises two stable isotopes, ^{63}Cu (69.17%) and ^{65}Cu (30.83%), and 27 known radioisotopes, five of which are particularly interesting for molecular imaging applications (^{60}Cu, ^{61}Cu, ^{62}Cu and ^{64}Cu) and target radiation (^{64}Cu and ^{67}Cu). Table 1 represents data about half-life and decay mode of Cu isotopes.

Table 1 Main characteristics of Cu radioisotopes

Isotope	Half-life	Decay mode
^{60}Cu	23.7 min	β^+ (93%) γ (7%)
^{61}Cu	3.32 h	β^+ (60%) γ (40%)
^{62}Cu	9.7 min	β^+ (98%) γ (2%)
^{64}Cu	12.7 h	β^+ (19%) γ (43%) β^- (38%)
^{67}Cu	61.83 h	β^- (100%) γ (52%)

Lead has four stable isotopes with mass numbers 204, 206, 207, and 208. Six ratios of lead isotopes are used in practice as indicators of traceability. Lead isotope ratios are expressed in the respective ratios of ^{206}Pb, ^{207}Pb, and ^{208}Pb of primary and radiogenic origin to the primary natural isotope ^{204}Pb ($^{206}Pb/^{204}Pb$, $^{207}Pb/^{204}Pb$, and $^{208}Pb/^{204}Pb$), as well as the ratios of the first three isotopes ($^{208}Pb/^{206}Pb$, $^{207}Pb/^{206}Pb$, $^{208}Pb/^{207}Pb$ or $^{206}Pb/^{207}Pb$). Due to the fact that ^{204}Pb is a stable isotope, isotope ratios including ^{204}Pb can be used for geochronological studies. Lead enrichment factors and $^{206}Pb/^{207}Pb$ ratios can be used to distinguish natural (i.e., geogenic) sources of atmospheric Pb from anthropogenic ones. Lead isotope ratios can be used for the direct identification of Pb sources and the investigation of Pb contamination pathways in various natural environments such as soil, atmospheric particles, river and lake sediment, coal, and ash. Table 2 shows main characteristics of Pb isotopes.

Table 2 Main characteristics of Pb radioisotopes

Parent isotope	Isotope	Half-life (years)
-	^{204}Pb	$>1.4 \times 10^{14}$
^{238}U	^{206}Pb	4.468×10^{9}
^{235}U	^{207}Pb	7.038×10^{8}
^{232}Th	^{208}Pb	1.405×10^{10}

Zinc has five stable isotopes, (^{64}Zn, ^{66}Zn, ^{67}Zn, ^{68}Zn and ^{70}Zn), with a natural content of 49.2, 27.8, 4.0, 18.4 and 0.6%, respectively. However, zinc isotope ratios such as $^{66}Zn/^{64}Zn$ ($\delta^{66}Zn$) can provide useful information about Zn sources in environmental samples when each Zn source has a particular isotope ratio [12]. Table 3 presents selected elemental properties of Cu, Pb, and Zn relevant for stable isotope research.

Table 3 Element and selected elemental properties

Element symbol	Number of stable isotopes	Mass of the isotope commonly used in the delta value or the most abundant isotope	Potential influence of radiogenic (RAD) and mass-independent fractionation (MIF) on the stable isotope system
Cu	2	65	-
Pb	4	208	RAD
Zn	5	66	MIF

4. COPPER, LEAD AND ZINC ISOTOPE ANALYSIS METHODS

Inductively coupled plasma mass spectrometry (ICP-MS) or thermal ionization mass spectrometry (TIMS) are used to study the isotopic composition of Cu, Pb, and Zn [13]. ICP-MS includes quadrupole (ICP-QMS) and sector field (ICP-SFMS) instruments, which are equipped with single (SC) or multiple manifold (MC) detection and time-of-flight-based mass analyzers (ICP-TOF-MS). As the accuracy of the methods becomes an increasingly important issue in isotope ratio analysis, the most accurate and convenient method of analysis must be chosen. Table 4 shows the main strengths and weaknesses of selected methods.

4.1 Thermal Ionization Mass Spectrometry

Thermal ionization mass spectrometry (TIMS) is a classical method for the high-precision

Table 4 Advantages and disadvantages of methods

Method	Advantages	Disadvantages
TIMS	Accuracy, Average mass fractionation Transmission of ions from source to collector	Separation of an element Time of analytical procedure Mass fractionation
ICP-QMS	Sensitivity Size Operation process Time of registration	Upper limit Resolution Acquisition Mass accuracy
TOF	Dynamic range Mass accuracy and resolution Scan speed	Vacuum system Instrument size

measurement of the isotopic composition of a wide range of elements of the Pb or Cu type [14]. This method requires a preliminary preparation of the chemical sample. The sample analyzed by TIMS, must be chemically pure in order to eliminate the suppressive effect of ionization by impurities in the sample.

4.2 Inductively Coupled Plasma Mass Spectrometry

Inductively coupled plasma mass spectrometry with quadrupole-based (ICP-QMS) involves only the dissolution of the sample, and it takes a few minutes to reach its ultimate accuracy. Although lead isotope ratios have traditionally been measured using thermal ionization mass spectrometry (TIMS), multicollector inductively coupled plasma mass spectrometry (MC-ICP-MS) is increasingly displacing it [15].

Inductively coupled plasma mass spectrometry with sector field (ICP-SFMS) is an excellent method for the sensitive and accurate measurement of isotope ratios in complex matrices, such as soils, without sample pretreatment. ICP-SFMS can reliably distinguish between anthropogenic and geogenic metal sources. The accuracy of multicollector sector field instruments can reach 0.002% [16].

The operation of time-of-flight-based mass spectrometry (TOF) analyzers is based on the dependence of ion velocity on their mass. The secondary defragmentation of ionized particles is significantly reduced due to the lower influence of electric and magnetic fields on the ions. Since the field-free region of a TOF mass spectrometer is a hollow stainless-steel tube, the transmission efficiency is one of the highest among all mass analyzers and indicates an excellent sensitivity [17].

5. COPPER, LEAD, AND ZINC ISOTOPES IN THE ENVIRONMENT

5.1 Copper, Lead, and Zinc Isotopes in Aquatic Sediments

Natural phenomena, such as geological weathering, precipitation, and wave erosion, play a special role in the distribution of chemical elements in aquatic ecosystems. Anthropogenic activities such as rapid industrialization and urbanization facilitate the accumulation and deposition of heavy metals in aquatic sediments [18]. Stable isotope analysis in sediments is a useful method for studying the history of heavy metal pollution.

5.1.1 Copper isotopes in lake and river sediments

It was found that $\delta^{65}Cu$ of the organic fraction is heavier in the upper layer of the sediment core and shifts toward lighter values at lower layers, and this isotopic shift coincides with the assumed transition from predominantly atmospheric Cu input to fluvial transport [19]. A study of organic-rich Black Sea sediments [20] revealed that the modern non-lithogenic flux of oceanic Cu is homogeneous in many sediments. The signature of the highly copper-enriched Black Sea sediments ($\delta^{65}Cu_{auth}$ + 0.3‰) does not match the open ocean signature (by about +0.6 to +0.9‰). The heavy Cu isotope in the aqueous phase of river and seawater is explained by the mostly organic complexation of the heavy isotope in the dissolved phase.

5.1.2 Lead isotopes in lake and river sediments

There are a number of studies on Pb isotopes in aquatic sediments determining the level of pollution and its possible source. Lead is transported by river water mainly in suspended forms, so the global flow of Pb to the ocean from the Amazon, Ganges, Brahmaputra, and Mekong basins can be considered as functions of solid $^{206}Pb/^{204}Pb$ [21]. However, the data indicate that anthropogenic lead is almost absent in river sediments because it is not formed due to bedrock erosion but is adsorbed on the surface of suspended solids transported by the river.

An isotopic analysis of lake sediments in Lake Tanganyika [22] found that compared to the littoral zone of the lake, the offshore area is a more sensitive and reliable recorder of environmental changes in the lake basin. Temporal changes in trace element fluxes are increased by erosion. They are associated with possible changes in land use, rather than with the additional input of industrial elements. The spatially different, but predominantly stable, Pb isotope compositions at two sites over time indicate that Pb comes from relatively different sources (the result of elevated atmospheric lead levels at the offshore site compared to the nearshore site). Lake researchers in Stockholm [23] identified water body contamination at the local level, as obvious contamination was found in the central area, while small lakes around the city center were the least affected by negative anthropogenic activity (with typical lead ratios of $^{207}Pb/^{206}Pb$ 0.85-0.89 and $^{208}Pb/^{204}Pb$ 36-38).

Lead isotopy for source identification was examined on an 80 km long transect with a conditional center at a copper smelter in the town of Karabash, Ural Mountains, Russia [24]. Lead concentrations in core sediments from the 10 lakes were generally low at their base and sharply increased in their upper layers, which coincides with the beginning of large-scale smelting process in 1910. The lead isotope ratios obtained for ^{204}Pb, ^{206}Pb, ^{207}Pb, ^{208}Pb for the lower layers of sediments (the pre-industrial period) were significantly different from the upper ones. The upper layers of 10-14 cm intervals have isotope ratios typical for smelter dusts.

5.1.3 Zinc isotopes in lake and river sediments

Core sediments obtained from stabilized lakes may reveal a history of Zn deposition due to natural weathering and human activities. However, the factors controlling variations in Zn isotopic composition in lake sedimentary rocks, cores, and upper intervals have not been fully established and are under discussion [25].

Studies of marine sediment in Tokyo Bay [26] proved the hypothesis of anthropogenic sources based on $\delta^{66}Zn$ variations, which cause elevated zinc concentrations in the water. To establish the sources of elevated zinc levels in Shinji Lake, estimating the transport of Zn from mainland China to the aquatic environment of Japan, it was found that the main source is sewage discharge, while the contribution of Zn from the mainland is insignificant [27].

Zn isotope composition was analyzed for 21 snowpack samples in South Ural, Russia in connection with a copper smelter. Values of $\delta^{66}Zn$ for snow dust varied from -4.0 to 2.5‰ with maximum fluctuations characteristic of technological materials used as a source of contamination (Cu concentrates, fly ash smelting). It was found that the pollutant particles came from the technogenic source at a distance of up to 95 km from the smelting production area [28].

5.2 Copper, Lead and Zinc Isotopes in Soil

Soil is a critical subsystem of biogeochemical cycles such as nutrient recycling, energy exchange, slowing greenhouse gas fluxes, and carbon recycling. Therefore, it is important to monitor the concentration of heavy metals in soil and their additional inputs due to agricultural activities, rapid urbanization, and industrialization. Elevated concentrations of Cu, Pb, and Zn in soils are a serious problem affecting both developed and developing countries. The method for estimating Cu, Pb, and Zn isotopic ratios in soils is a useful tool for identifying metal origins.

5.2.1 Copper isotopes

Copper isotope studies of soil isotope composition generally focus on plant uptake [29]. The analysis of Cu isotopes in soils and plants can be used to assess the intensity of contamination from Cu ore mining and processing areas, provided that the isotope composition of ore processing products differs from the isotope composition of uncontaminated soils and plants. Table 5 shows different Cu isotope ration in leaves.

Table 5 Copper isotope ratios in plant leaves

Location	Specie	$\delta^{65}Cu$	Ref.
France, Saint Mont	*Vitis vinifera*	0.20±0.07	[29]
USA, hydroponic	*Solanum lycopersicum*	-0.5±0.3	[30]
	Avena sativa	-0.3±0.2	
USA, St. Louis	*Elymus virginicus*	-0.30	[31]

5.2.2 Lead isotopes

Despite the fact that the mobility of Pb in soil can increase with high concentrations of organic compounds, this metal is considered immobile and persistent in soils. The isotope composition of lead is not subject to physical or chemical processes and measuring this is an effective method to determine the origin of lead in various soils. A combination of EFs, PCA, APCS-MLR and a binary Pb isotope mixing model was successfully implemented to search for sources of soil contamination in urban parks in Xiamen City, China. The sources of anthropogenic lead according to the $^{206}Pb/^{207}Pb$ and $^{208}Pb/^{207}Pb$ isotope models were arranged as follows: natural (49%) > coal combustion (45%) > transport emissions (6%) [32].

The Pb isotope composition of uncontaminated soils can be generally more radiogenic ($^{206}Pb/^{204}Pb$ ~ 18.5-19.5) as most of the Pb comes from weathered bedrock, and the Pb isotope composition is mainly affected by the decay of ^{238}U to ^{206}Pb [33]. Table 6 shows different Pb isotope ratio in soil of different regions.

5.2.3 Zinc isotopes

There are a variety of anthropogenic sources of zinc in the environment, many of which are industrial and agricultural. For the most part, studies of stable Zn isotopes in soils have been performed to assess the contribution and absorption of Zn by plants due to the use of Zn fertilizers. The isotope ratio method has been used to assess the extent of Zn uptake from manure, sewage sludge, and complex organic fertilizers into soil-plant systems, and to assess the contribution of these fertilizers to crop Zn nutrition [39]

5.3 Isotopes of Copper, Lead, and Zinc in Dust

5.3.1 Copper and zinc isotopes in dust

A number of researchers use Cu and Zn isotope ratios, (as well as Pb isotope ratios), to identify the sources of the metals. Studies conducted in Busan, South Korea, showed [40] that the isotope composition of Cu and Zn in road dust was associated with traffic-related sources, such as brake pads and tires. The results of measuring metal concentration and the Cu and Zn isotope composition of road dust can help identify and measure air pollution from fine particulate matter and metals in the fine fractions of road dust. The use of Cu, Pb, and Zn isotope ratios identifies pollution sources in various environments (Fig. 1).

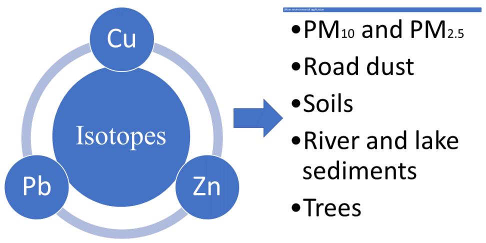

Fig. 1 Application of Cu, Pb and Zn isotope ratio in the urban environment

The research in the large metropolitan area of São Paulo, Brazil [41] with multi-isotope Cu-Pb-Zn diagrams successfully separated wear and tear from vehicles, including tires and brakes, exhaust fumes, industrial emissions, and improved the identification of sources of air pollution.

5.3.2 Lead isotopes in dust

Dust particles enriched with heavy metals are emitted by factories and in combustion processes (household furnaces, thermal power plants, waste incineration, motor vehicles). Heavy metals from road dust can easily enter the ambient air through resuspension processes as $PM_{2.5}$ and PM_{10} [42]. It was found that the concentrations of $PM_{2.5}$ and PM_{10} in the atmosphere of industrial cities often exceed health standards [43]. Lead isotope analysis identifies the sources of dust pollution, including atmospheric dust [45] from lead mining. There were [38] correlations between the $^{208}Pb/^{206}Pb$ and $^{207}Pb/^{206}Pb$ ratios in dust and isotope ratios in atmospheric particles $PM_{2.5}$, PM_{10}, coal fly ash, and atmospheric dust from a machinery plant, indicating that sources of Pb in atmospheric dust and vegetables are closely related to coal combustion and industrial emissions. Coal combustion, metallurgical dust, and vehicle exhaust appear to be major sources of Pb in $PM_{2.5}$ and PM_{10} particles in many countries [34]. Table 7 represents different Pb isotope ratio in the dust of different regions.

5.4 Studying the Copper, Lead, and Zinc Isotope Composition in Other Environmental Media

Due to their organic nature peat bogs effectively absorb trace elements from the atmosphere, providing valuable information on atmospheric inputs of metals, especially Pb. Ombrotrophic peat bogs have been used as archives of relatively high Pb contamination levels over the past 12,000 years, vertical peat profiles are the most widely studied [46]. Although Pb concentrations in peat profiles correspond to lake sediments, the isotope ratios are different. During the fen-to-bog transition there is a rapid decrease in the $^{206}Pb/^{207}Pb$ ratio (from >1.3 to about 1.2) with a further decrease in the high bog in the 0-20 cm intervals to 1.15, most likely due to the long-range transport of atmospheric lead in soil dust. This is more important in ombrotrophic peats than in lake sediments, which have an additional input of lead from watersheds. Intensive mining and processing of local Zn-Pb ores have been the main cause of the decrease in the $^{206}Pb/^{207}Pb$ ratio in the upper atmosphere for Wolbrom, Poland [47].

Table 6 Pb isotope ratio in soil in different regions

Location	$^{206}Pb/^{208}Pb$	$^{206}Pb/^{207}Pb$	$^{206}Pb/^{204}Pb$	$^{207}Pb/^{204}Pb$	$^{208}Pb/^{204}Pb$	Ref.
Russia	n.d.	1.171 ± 0.007	18.1 ± 0.2	15.5 ± 0.2	38.9 ± 0.5	[34]
Italy	0.4818±0.0007	1.1908±0.0002	n.d.	n.d.	n.d.	[35]
France		1.163	18.141	n.d.	38.15	[36]
Switzerland	0.485	1.191	18.670	15.672	38.509	[37]
China	0.475	1.1652	n.d.	n.d.	n.d.	[38]

Table 7 Pb isotope ratios in dust in regions

Location	$^{206}Pb/^{208}Pb$	$^{206}Pb/^{207}Pb$	$^{206}Pb/^{204}Pb$	$^{207}Pb/^{204}Pb$	$^{208}Pb/^{204}Pb$	Ref.
Russia	n.d.	1.173 ± 0.007	17.7 ± 0.1	15.13 ± 0.08	36.5 ± 0.2	[34]
U.K.	0.470 ± 0.003	1.137 ± 0.003	17.70 ± 0.05	n.d.	n.d.	[42]
France	n.d.	1.131	17.620	n.d.	37.39	[36]
Taiwan	n.d.	1.158	18.037	n.d.	n.d.	[45]
China	0.477	1.184	n.d.	n.d.	n.d.	[38]

As trees and other plants, including microalgae [48], absorb Zn, Pb and other heavy metals from soil, and atmosphere and accumulate them in their tissues, they can be used as effective bioindicators in the urban environment [49] and isotope composition of plant organs can provide a record of the biological and physicochemical processes that trace the path of an element from its source to organs such as the roots, leaves, and fruits.

Lead isotope composition can also be used as a biogeochemical indicator of heavy metals in tree rings, which absorb heavy metals through the deciduous, cortical, and root apparatus. The source of Pb adsorbed through the deciduous and root apparatus is the dry and wet deposition from atmospheric aerosols and the subsequent adsorption by plants [50].

It was found that trees absorb lead primarily through local root processes [51]. Mihaljevič et al. [52] examined annual tree rings from the Copper belt smelting area in Zambia and found young tree parts to have low $^{206}Pb/^{207}Pb$ ratios (<1.17), possibly due to the fact that Pb is produced in the youngest parts of tree species by absorption of suspended Pb in the bark rather than the roots. Isotopes are widely used in chemical and biological studies. Isotopes can also be used in forensic investigations, providing possible information on the origin, migration, and diet by human teeth [53]. The composition of Cu, Pb, and Zn isotopes can be an excellent hydrochemical indicator for both surface water and groundwater quality management. Several studies have analyzed lead isotope ratios in groundwater [54], finding that groundwater samples from aquifers in granitic massifs have the highest radiogenicity values of lead, which may be a possible dependence of weathering of different U- and Th-containing minerals.

6. CONCLUSION

The application of a multi-isotope approach using Cu, Pb, and Zn indicators may be key to identifying potential sources of metal pollution and to understanding environmental pollution and the contribution of copper, lead, and zinc in different environments, especially in urban and industrial areas. However, the isotope composition of copper, lead, and zinc in different environments has not been sufficiently studied.

Lead is a toxic metal, though copper and zinc are essential for life, in excess they may be toxic to organisms. In addition to natural sources, many human activities mobilize and spread large quantities of Cu, Pb, and Zn in the environment (e.g., industry and road traffic). Isotopic approaches, especially for lead, have proven their efficiency in tracing sources in the environment for decades. Compared to these isotopes, the value of tracing Cu and Zn isotopes, developed in the 2000s, is yet to be proven. This review compiles the major findings of previous studies in order to evaluate the ability of Cu and Zn isotope compositions to trace metal sources in natural and urban environments. Further research and additional information on isotope ratios from various potential sources of natural, industrial, and transportation activities will provide a better understanding and identification of sources of metal pollution.

7. ACKNOWLEDGMENTS

The research was found by the Russian Science Foundation (RSF), project number 22-17-20006 (https://rscf.ru/en/project/22-17-20006/) and Chelyabinsk Region.

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