Science of the Total Environment 642 (2018) 63–76

Contents lists available at ScienceDirect

Science of the Total Environment

journal homepage: www.elsevier.com/locate/scitotenv

# Contamination of soils by potentially toxic elements in the impact zone of tungsten molybdenum ore mine in the Baikal region: A survey and risk assessment

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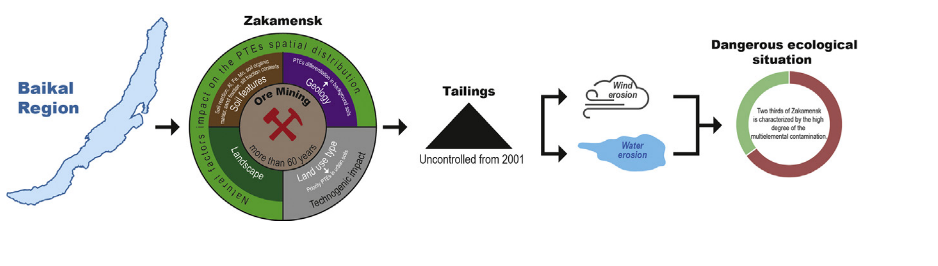
## HIGHLIGHTS

- Environmental consequences of long-term W–Mo ore mining operations were evaluated.
- Very high levels of W-Mo-Bi-Sb in the urban soils of the mining center were revealed.
- Ore and accompanying element content in soils depends on their delivery from tailings.
- Uncontrolled tailings cause catastrophic environmental effects.

## GRAPHICAL ABSTRACT




## ARTICLE INFO

*Article history:*
Received 25 January 2018
Received in revised form 22 May 2018
Accepted 4 June 2018
Available online xxxx

*Keywords:*
Deposits of nonferrous metals
Priority pollutant
Mining impact
Environmental geochemistry
Technogenic anomalies

## ABSTRACT

Mining of mineral resources exerts strong impact on the environment and leads to irreversible changes in vegetation, soils, atmosphere, surface and ground waters. The aim of this study is to assess the modern geochemical state of soil cover in Zakamensk, a city located in Buryat Republic (Russia) and known as one of the biggest ore mining center in the former Soviet Union. The center was operating for 68 years and closed 17 years ago. Soil-geochemical survey was conducted in 2012 and included collection of 103 soil samples in Zakamensk and 27 samples in the background areas. The bulk contents of 16 potentially toxic elements (PTEs) in the soil samples were determined by mass spectrometry and by atomic emission spectrometry with inductively coupled plasma.

Background sites are characterized by increased concentrations of ore elements W and Mo. The mineral deposit development and physical and chemical weathering of tailings' material have led to a sharp increase in Bi, Cd, Cu, Mo, Pb, Sb, W and Zn levels in the soils of different land-use areas. Near the tailings, the concentration of Sb in soils was 356 times higher than in the background area; Cd – 70 times; Mo, Bi, Cu, and W – 42–55 times; Pb and As – 34–37 times; and Zn and Sn – 6–12 higher. In the north of the city a prominent anomaly of PTEs occurs in sandy sediments of the Modonkul floodplain. It was formed due to the washout and subsequent sedimentation of suspended matter carried by the Modonkul River from the Barun–Naryn, the Dzhida, and emergency tailings. So, the anthropogenic activities are the most important source of ore and accompanying elements in the urban soils. High levels of accessory elements also depends on natural factors such as physicochemical properties of soils, position in the landscape, and genesis of parent materials. The environmental assessment of topsoils in Zakamensk showed that Pb, Sb, Cd, and As concentrations exceeds the Russian MPCs by 1.7–7.8 times, which creates a significant hazard for the environment and adversely affects human health.



## 1. Introduction

Mining industry is one of the largest sources of potentially toxic elements (PTEs) in the environment that leads to irreversible changes in

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https://doi.org/10.1016/j.scitotenv.2018.06.042
0048-9697/

water, soils, microorganisms, atmosphere, and vegetation (Hudson-Edwards et al., 2011; Lavid et al., 2001; Serbula et al., 2012; Kosheleva et al., 2016; Timofeev et al., 2016). The extraction of mineral ores and their processing are accompanied by the release of >10 billion tons waste annually (Adiansyah et al., 2015). These wastes are stored in tailings and pose considerable risk to human and environmental health (Acosta et al., 2011; Anawar et al., 2011; Dudka and Adriano, 1997; Li et al., 2014; Sánchez-López et al., 2015; Yang et al., 2012).

The modern stage of environmental and geochemical studies in mining areas is characterized by a great number of works devoted to various aspects of the impact of mining industry on the environment and humans. Special surveys were performed in order to predict environmental consequences of tailing destruction (Acosta et al., 2011; Anawar et al., 2011; Kohfahl et al., 2010; Mudd, 2007; Owor et al., 2007; Pellegrini et al., 2016; Rey et al., 2013). Migration and precipitation of dust particles emitted to the atmosphere from the mining centers and their influence on human health were examined (Drahota et al., 2017; Li et al., 2015; Rout et al., 2015). Considerable attention was paid to the element migration in the soil–plant–living organisms system (Alloway, 2013; Antoniadis et al., 2017; El Azhari et al., 2017; Ghaderian and Ghotbi Ravandi, 2012; Santos et al., 2012; Wahsha et al., 2012). Spatial distribution patterns of heavy metals in the soil cover as the main depositing medium and their vertical distribution in the soil profile were investigated (Candeias et al., 2011; Garcia-Sanchez et al., 2010; Gomez-Alvarez et al., 2007; Kosheleva et al., 2015a; Lü et al., 2018; Timofeev et al., 2016).

Tungsten is one of the main alloying elements widely applied in machine and vehicle production. For >60 years Zakamensk, a city located in the Republic of Buryatia (south-central region of Siberia, Russia), had been the main mining center for this element. In the former Soviet Union during some years the plant in Zakamensk produced >80% of the tungsten concentrate (Zinov'eva et al., 2011). Rapid industrial development of the mineral field led to uncontrolled waste disposal from the Dzhida tungsten–molybdenum plant (DTMP), which posed a serious threat to the environment in the area of >450 ha declared as environmental emergency (MNR RB, 2011). The modern literature on Zakamensk includes the data on the geology (Gordienko et al., 2012; Simonov et al., 2014), the information on chemical composition of the industrial wastes (Khodanovich et al., 2002a) and the formation of secondary minerals in tailings (Yurgenson et al., 2008), and also the results of the public health evaluation (Imetkhenov et al., 2015; Prusakov et al., 2005). In 2004–2005, as a result of a comprehensive environmental and geochemical survey of Zakamensk (which included also the study on the distribution of contaminants in herbaceous vegetation) the maps of the total contamination index for the soil and snow covers, as well as their contamination by particular elements were compiled (Smirnova and Plyusnin, 2013).

However, there is still a number of problems that should be solved by further studies. Since the study object is located in the area with high natural lithological and geochemical heterogeneity the application of special approach taking into account different chemical composition of background soils developed on various parent rocks is required. The previous studies on environmental assessment also did not specify geochemical specialization of land-use areas that might differ in pollution levels and in the priority contaminants lists. Moreover, the northern part of the city, where Modonkul deposit of contaminated sands has been recently formed, and the area around the emergency tailing remediated in 2011 within the framework of a governmental program have not been examined yet. Identification of major landscape-geochemical and anthropogenic factors controlling the redistribution and accumulation of PTEs is in the focus of this type of studies.

The aim of our study was to assess the present state of soil cover in the area of the Zakamensk mining center, after the DTMP was closed. The following particular tasks had to be solved:

- determination of the enrichment of surface layers of the technogenically disturbed soils in different land-use areas of the city with PTEs in comparison with their levels in background soils developed on different parent materials;
- examination of spatial patterns in the PTEs distribution in relation to soil and landscape-geochemical factors; and
- environmental and geochemical assessment of the soil pollution within the DTMP impact zone and its subdivision into the areas with different levels of soil contamination.

## 2. Study area

### 2.1. Natural setting

The city of Zakamensk (45 $km^2$) emerged in the narrow Modonkul River mountain valley, 460 km to the southwest of the Ulan-Ude city (Fig. 1a). The height amplitude in elevations between the tops of the ridges and the river bottoms in this area reaches 400–450 m (Zinov'eva et al., 2011). The Modonkul River is a right tributary of the Dzhida River, draining the southern part of the Mongolian–Siberian mountainous region, at the boundary between two large geological structures represented by the calcareous–terrigenous Lower Paleozoic deposits of the Dzhida synclinorium and granitoid intrusions of the Modonkul massif (Papov, 2007). The large ore-containing fault zone (with the Pervomaisk, Inkursk, and Kholtoson ore fields) extending in the northwestern direction was shaped in the Early Paleozoic.

The climate is strongly continental: the winters are long and cold (up to −49 °C) with little snow and the summers are relatively warm (the $T_{July} = +15.6$ °C) and short (Fig. 1b). The mean annual precipitation is about 250–300 mm. Southwestern winds predominate during the warm season, and northern and northwestern winds predominate during the cold season (Fig. 1c). Local weather conditions are characterized by frequent temperature inversions, causing air stagnation in the depressions, and a considerable number of calm days favoring atmospheric dust and associated pollutants deposition and their accumulation in the depositing media.

On tops of the local hills and on the ridges' slopes, shallow soddy and soddy-calcareous soils are formed under forest vegetation (Nogina, 1964) which is dominated by Siberian larch (*Lárix sibírica*) and birch (*Bétula platyphýlla*) trees with rhododendron (*Rhododendron dauricum*) and dog rose (*Rosa aciculáris*) shrubs and bog bilberry dwarf shrubs (*Vaccínium uliginósum*) (Papov, 2007). The river valley bottoms are occupied by anthropogenically disturbed meadow and meadow-marsh cenoses and also willow thickets developing on soddy forest and alluvial meadow soils (Nogina, 1964).

### 2.2. Technogenic impact

From 1934 to 2001, the DTMP extracted molybdenum from the Pervomaisk ore field, tungsten from the Inkurskoe and Kholtoson primary ore fields and placers, and gold from the Myrgensheno and Ivanovka deposits. Mineral composition of the Pervomaisk ore is represented by molybdenite, fluorite, muscovite, feldspar, pyrite, beryl, galena, sphalerite, copper pyrite; that of Inkurskoe and Holtoson – by hubnerite, scheelite, pyrite, sphalerite, galena, copper pyrite, fluaurite. The extracted ores contained high levels of the PTEs, such as As, Be, Bi, F, Mo, Pb, W, Zn, and some others (Zinov'eva et al., 2011). During the operation of the DTMP, 44.5 million tons of waste was accumulated in the Dzhida filled tailing and the Barun-Naryn sludge pond and also in the emergency tailing (Fig. 2).

The tailings are composed of feldspar-quartz debris with an admixture of micas, fragments of amphibole, epidote, fluorite, sulphide, hubnerite, scheelite and beryl grains (Smirnova and Plyusnin, 2013). Because of the rock comminution, the grain-size composition of the wastes entering tailings consists mostly of very fine sand and coarse