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Magnetite contamination of urban soils in European Russia

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ABSTRACT

Urban soils are enriched in magnetite (Fe_3O_4), thanks to aerial emissions of industry, energy and cars emission. Magnetite contamination of urban soils in Russia has both common features of the world and its specificity. The magnetite content through the magnetic susceptibility is used as an indirect indicator of the contamination degree of urban soils with some heavy metals. In the cities of Russia: Moscow, Cherepovets, Perm and Chusovoy, magnetite soil pollution is in agreement with some of the heavy metals pollution. The correlation coefficients between magnetic susceptibility and mobile forms contents are higher than coefficients with a total contents of heavy metals. The volume magnetic susceptibility, measured in the field conditions, is less correlated with the pollution of urban soils with heavy metals than an express specific magnetic susceptibility, which is determined in the laboratory. In Moscow and Chusovoy, magnetic susceptibility of soils is high in the territory of the old town and it is the lowest in the field of new buildings. Soil magnetic susceptibility is indicator of Cu, Zn and Pb in Moscow. Soil magnetic susceptibility is indicator of Pb, Zn and Cr in Cherepovets. In Chusovoy, the oxidation degree of the magnetite is low, and a stoichiometric index of magnetite is high; soil magnetic susceptibility is indicator of Mn, Zn and Cr. In Perm, the magnetic susceptibility of magnetite in the soils is low, but it is highly variable; soil magnetic susceptibility is indicator of Ni, Zn and Cr.

Introduction

Urban contaminated soils are different from background unpolluted soils, particularly in the forest zone. In urban soils pH-values are higher, often the particle size distribution is easier and organic content is higher [1]. Soil are contaminated with organic and inorganic pollutants, there are high concentrations of heavy metals and metalloids among the latter ones.

Mineralogical composition of soils is changed, especially composition of iron minerals. There is the most noticeable enrichment by technogenic magnetite Fe_3O_4 among them, the content of which reaches 4.3% or more [2], while in the background soils of forest and steppe zones its content does not exceed 0.05% [3]. The reason is, that many of the aerial waste industry (factories ferrous and non-ferrous metallurgy, metal processing plants), coal-fired power plants, as well as vehicles emissions contain magnetite particles [4,5].

Magnetite in urban soils is studies to solve two questions. 1) The sources of urban soils pollution are distinguished according to the characteristic of the magnetite particles. By the number of magnetite was evaluated by magnetic susceptibility. 2) We can judge about the degree of soil contamination with heavy metals by the content of magnetite, which was evaluated by magnetic susceptibility.

The first problem is due to the fact, that in different cities the pollution of urban soils by magnetite has its own features. Soils of Chinese cities are strongly enriched in magnetite due to aerial emissions of ferrous metallurgy and thermal coal-fired power plants [6–9]. In Poland, cities in Silesia are the most polluted by magnetite, where there are many steel plants [10,11]. In England, sites, enriched in magnetite at an early stage of the industrial revolution, are remained in London and Manchester [12,13]. In vast Russia territory, there are cities with very different industrial specialization. Pollution degree of magnetite and technogenic magnetite properties in urban soils are highly variable. The properties of magnetite are studied by different methods of analysis: Mössbauer spectroscopy, electron microscopy, different types of magnetic analysis.

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The second problem is solved by the fact, that the magnetic susceptibility reflects the degree of soil contamination by magnetite. But other mineral pollutants, especially heavy metals, enter soils by aerial path together with magnetite. Therefore, the magnetic susceptibility is used as an indirect criterion for urban soil pollution by some heavy metals [14,15]. Measurement of magnetic susceptibility is a fast, cheap and high sensitive method for mapping of urban soil contamination and identification of pollution sources.

Sites with high magnetic susceptibility are enriched in heavy metals. Indicator role of magnetite has been well studied in different cities around the world [10,12]. Maps of the magnetic susceptibility are used to identify the locations of the local high pollution, requiring urgent remediation. Thus, magnetite in urban soils is of interest as an indicator of soil contamination with heavy metals.

In the most populated European part of Russia, contaminations of urban soils by magnetite and heavy metals are the most studied.

Purposes: to compile information on research methods, content and properties of magnetite and its technogenic indicator role in urban soils of European Russia.

Methods of magnetite analysis in soils

Methods of magnetite analysis can be divided into two groups, depending on the purpose of study. The first group of methods is the assessing the "quality" of magnetite particles. Mössbauer spectroscopy, electron microscopy, thermal-magnetic analysis, determination of frequency-dependent magnetic susceptibility, the degree determination of magnetite solubility by ammonium oxalate and others methods consist the first group. Properties determination of magnetite particles can detect pollution sources of urban soils.

The second group includes determination methods of the magnetite amount, which makes it possible to associate the magnetite amount with the amount of other magnetite mineral pollutants, especially heavy metals.

Definition of magnetite particles properties

Mössbauer spectroscopy

The most reliable method of determining the amount and properties of magnetite in soils is Mössbauer spectroscopy, especially when the sample is cooled, often it is cooled to liquid-nitrogen temperature (77-78° K), and sometimes to helium temperature (4.7° K). Currently, the Russian Mössbauer analysis of soils is usually carried out at room temperature when you can reveal the magnetite presence if over 0.2–0.3%. Due to the high amount of magnetite in urban soils is usually sufficient shooting at room temperature. Thus, magnetite content reaches 2.4% in Perm soils; in Chusovoy soils, where there is a powerful steel plant, comes to 4.4%. Magnetite content in contaminated soils exceeds the content of other iron oxide - hematite [2].

The parameters of the Mössbauer spectra contain information about the "quality" of the magnetite particles. It is important to measure ν, characterizing the number of vacancies in the lattice of non-stoichiometric magnetite [16]:

$Fe^{3+}[Fe^{2+}_{1\text{-}3\nu}Fe^{3+}_{1+2\nu}\square_{\nu}]$,.

where: Fe^{3+} is the form of iron in the tetrahedral sublattice A, $[Fe^{2+}_{1\text{-}3\nu}Fe^{3+}_{1+2\nu}\square_{\nu}]$ is the form of iron in the octahedral sublattice B, $\square$ are vacancies in sublattice B.

Quantitatively vacancy part ν can be determined from the ratio

$S_A / S_B = (1 + 5\nu) / (2\text{-}6\nu)$,

S_A and S_B are Sextets Squares for sublattices A and B [16]. This equation is easily converted to the following:

$\nu = [2\ (S_A/S_B) - 1)] / [5 + 6\ (S_A/S_B)]$.

Knowing vacancy part ν, we calculate the ratio of magnetite stoichiometry based on the ratio of Fe in different oxidation states in the sublattice B:

$K_{stoichiometry} = (1\text{-}3\nu) / (1{+}2\nu)$.

$K_{stoichiometry}$ index varies from 1 at the stoichiometric magnetite to 0 at completely oxidized magnetite, that is, maghemite γFe_2O_3.

The degree of magnetite stoichiometry was determined in urban soils of Perm and Chusovoy.

Electron microscopy

This is the method of magnetic fraction analysis, which is derived from an aqueous slurry of soils by a permanent magnet (simplified magnetic separation is realized). Most often, the magnetic fraction is studied by the scanning electron microscope, although the transmission electron microscopy, combined with micro-diffraction of electrons, has an advantage: the ability to identify minerals accurately. For example, it is possible to identify the minerals formed in the course of weathering on the surface of technogenic magnetite [17].

Scanning electron microscopy of the magnetic fraction particles of urban soils showed, that a particular particle shape (hollow spherules) dominates in technogenic magnetite, although they have the large size from 1 to 500 μm [3,18,19]. They are confined to the sand and silt fractions of soil. The spherical shape is formed by high-temperature formation of magnetite [3,6]. Spherules of industrial origin appear in the processes of smelting metals, in the ash and slag of thermal coal-fired power stations, during welding, etc. The chemical composition of the spherules is not constant, it varies depending on the production technology.

Thin-walled spherules are unstable; they partially fall into the ground in the time-crushing manner and in the form of fragments [3,20]. This causes a higher chemical activity and solubility of technogenic magnetite than lithogenic one.

Scanning electron microscopy of magnetic fraction particles was used for the study of the Moscow urban soils. Transmission electron microscopy was used to study the contaminated soil in the town of Cherepovets.

The frequency-dependent magnetic susceptibility

An important parameter is the particle size; magnetite reactivity depends on it, that is, its activity and solubility in urban soils. Particle size affects the magnetic structure of magnetite [21]. Most fine magnetite particles (~0.01–0.07 mm) have super paramagnetic properties (SP); then stable single-domain particles (SSD) with a diameter of about 0.07–1.0 μm follow, pseudo single-domain (PSD) with a diameter of about 1.0–12 μm, and finally most large multi-domain (MD) particles with a diameter of about 12–100 μm [20,22]. To judge the structure of magnetite particles, we can easily measure a magnetic indicator, which is frequency-dependent magnetic susceptibility χfd [23]. This indicator (%) was determined from the expression [8]:

$\chi fd = [(\chi lf - \chi hf) / \chi lf] \cdot 100\%$,

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