RESEARCH PAPER

MAGNETIC PARTICLES IN SOILS AND EPIPHYTES IN THE ZONE OF INFLUENCE OF A FERROUS METALLURGY FACTORY IN THE CITY OF PERM

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ABSTRACT. The intensification of industrial production leads to an increase in the technogenic impact on the environment. Minerals containing iron are sensitive to many environmental processes and analysis of the composition of magnetic particles is relevant in the study of environmental pollution. This study focused on urban soils of near-trunk circles and epiphytic mosses on *Populus nigra* L. in the territory of Motovilikhinsky district of Perm, where a metallurgical plant is located. In this work, using electron probe microanalysis and scanning electron microscopy, we analyzed the magnetic susceptibility (MS), morphology, and chemical composition of magnetic particles isolated from urban soils and epiphytic mosses. The content of heavy metals in the studied soils exceeds the clarkes of chemical elements (CCE) in the upper continental crust: Cr - 286 times, Mn - 15 times, Fe - 11 times, Ti - 4 times, Mg - 4 times. The study of the chemical composition of epiphytes made it possible to assess the contribution of aerial sources to soil pollution. The concentrations of metals in the magnetic particles of epiphytes also exceed the Clarke values: Cr - 3257 times, Fe - 8 times, Ti - 7 times, Mg - 4 times. The similarity of the morphology and chemical composition of the magnetic particles of soils and epiphytes indicate common sources of pollution. A comprehensive assessment of the state of the territory may include magneto-geochemical monitoring of the soil cover and monitoring of the magnetic state of epiphytes on *Populus nigra* L.

KEYWORDS: magnetic susceptibility, heavy metals, urban soils, epiphytic mosses, aerial pollution, electron microscopic analysis

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INTRODUCTION

The soils of industrial cities are often polluted with technogenic magnetic particles (TMP), including technogenic magnetite (Fe_3O_4) - iron oxide, the content of which in urban soils can reach more than 3-4% (Vodyanitskii 2010), while in the background uncontaminated sod-podzolic soils it does not exceed 1% (Babanin et al 1995). Aerial magnetic pollution of soils is caused by emissions from ferrous and non-ferrous metallurgy plants, thermal power plants, exhaust gases and particles of braking elements of cars (Sheshukov, Mikheenkov, Nekrasov, Yeghiazaryan 2020; Winkler 2020; Kirana et al. 2021; Narayana 2021; Wang et al. 2021). The value of MS in urban soils polluted with TMP increases significantly. During high-temperature technogenic processes, some of the Fe ions in the lattice of technogenic magnetite are replaced by other cations, which makes it possible to identify the increase in the magnetic susceptibility of soils with an increase in the degree of their contamination with heavy metals (Vasiliev, Lobanova 2015; Bobrova 2021; Narayana 2021; Zhang et al. 2022).

Pollution of the environment with toxic chemical elements that comprise TMP determines high levels of ecologically conditioned diseases (Kopylov 2013) and can be identified through epiphytic mosses (Varduni 2015; Sukhareva 2018; Ananyan 2020; Mostalygina 2020; Bobrova 2021).

Biomonitoring methods are widely introduced into the practice of ecological and geochemical research in urban areas (Varduni 2015; Gatziolis et al. 2016; Jiang et al. 2018; Koroleva 2020; Messager et al. 2021; Kropova et al. 2022; Zhang et al. 2022). The study of the elemental composition of epiphytes is often used to assess the degree of aerial pollution of ecosystems with heavy metals (Tarkhanov 2016; Ananyan 2020; Mostalygina 2020; Evseev et al. 2021; Kataeva, Belyaeva 2021; Nuguyeva, Mammadov 2021).

The city of Perm is home to Motovilikhinsky plants, the oldest industrial metallurgical enterprise in the Urals. Emissions of this enterprise have a negative impact on the environment primarily in Motovilikhinskiy district. However, the similarity of magnetic particles in the composition of soils and epiphytes of the city of Perm has not been assessed. Data on the content, morphology, and chemical and mineralogical composition of magnetic particles in epiphytes are also still missing. This information will make it possible to assess the contribution of technogenic magnetic particles to the aerial pollution of urban soils, which determines the relevance of the performed research.

The goal of the study was to assess the content, morphology, and ecological and geochemical state of magnetic particles in the composition of soils and epiphytic mosses of the black poplar in Motovilikhinsky district of Perm. The research focused on the soils of near-stem circles of *Populus Nigra* L. and epiphytic mosses *Pleurozium schreberi* (Brid.) Mitt.

MATERIALS AND METHODS

Magnetic susceptibility of soils was measured in sections of 100-150 m long and 5-7 m wide, located parallel to Vosstaniya Street (st.) at a distance of 500-540 m from Motovilikhinsky plants (Fig. 1).

Samples of epiphytes were taken from the surface of the *Populus Nigra* L. trunks at a height of 1.5 m using a plastic knife. At the same time, soil samples were taken in 10 locations around the trunks from a depth of 0-5 cm. The collected samples were dried at room temperature. Soil samples were ground in an agate mortar and passed through a sieve (diameter 1 mm), and moss samples were mechanically dispersed to the state of dust in double polyethylene bags using fingers.

The MS of soils was determined using a kappameter KT-6 manufactured by SATISGEO (Czech Republic) with the instrument sensitivity of 1×10^{-5}SI. The magnetic phase of the samples was extracted with a permanent ferrite magnet (Vasiliev et al. 2020).

The microstructure of the magnetic phase particles was studied using an FEI Quanta 650 FEG high-resolution scanning electron microscope with an EDAX Octane Elite energy dispersive spectrometer (Thermo Fisher Scientific, USA). The microscope is characterized by a 5-1000000 magnification and can operate in variable pressure (pressure range 10-200 Pascal) and high vacuum (10^{-2}-10^{-4} Pascal) modes. The resolution of the spectrometer is 125 electron volts (Gordeev 2017).

The ecological and geochemical assessment of the elemental composition of soils and particles of the magnetic phase was carried out by comparing the content of the element in the sample with geochemical constants, represented by the average content of elements in the upper continental crust (Wedepohl 1995). The MS of the studied soils was compared with the background values for the territory of the city of Perm, which are in the range of 0.43-0.62×10^{-3} SI (Vasil'ev, Lobanova 2015).

RESULTS AND DISCUSSION

Very high median values of MS are typical for the soils of streets with heavy traffic located at a distance of 500 m from Motovilikhinsky plants. Soil MS values vary over a wide range, from 3.13 to 11.2×10^{-3} SI, with an average median value of 5.6×10^{-3} SI and a coefficient of variation of 40 percent.

The volumetric magnetic susceptibility of soils is more than 10 times higher than the local background (0.43-0.62×10^{-3} SI), which indicates soil contamination with magnetic particles.

Clastic particles ranging from 1 μm to 600 μm in size dominate in the highly magnetic phase of the soil near

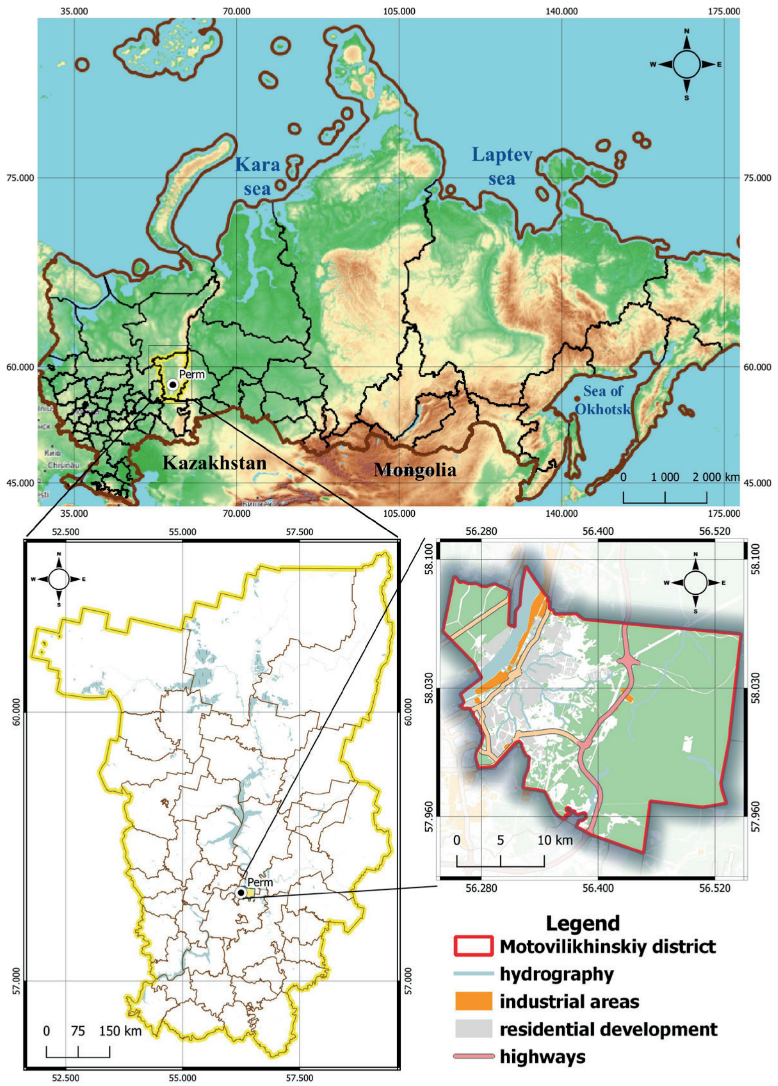

Fig. 1. Study area map

the trunks of black poplar on Vosstaniya street. Some particles are spherical (Selected Area 3, Fig. 2). The areas of energy dispersive analysis are indicated in the figures by squares. Magnesium ferrites in the form of spherules are usually found in dusty emissions from ferrous metallurgy enterprises (Makarov, Osovetsky, Antonova 2017; Vasiliev et al. 2020).

The peaks of Fe^{+2} and Fe^{+3} atoms on the energy dispersive spectra correspond to magnetite- maghemite (Fig. 3).

Individual sections of the sample are characterized by Fe content from 6.5 to 49.9%. Some elements such as Ti, Cr and Mn are not present in all particles (Table 1).

The concentration of metals in the composition of magnetic particles exceeds CCE in the upper continental crust according to K.H. Wedepohl (1995): Cr - 286 times, Mn - 15 times, Fe - 11 times, Ti - 4 times, Mg - 4 times (Fig. 4).

Magnetic particles in the composition of the soil along Vosstaniya street in Motovilikhinskiy district are characterized by an intensive accumulation of Cr (CC = 1209 units). Some magnetic particles are enriched in Ti. The content of Fe at all points of the energy-dispersive analysis of magnetic particles is above CCE.

The heterogeneous content of Mn in the composition of magnetic phase particles allows us to consider this metal as a soil pollutant. The accumulation of Mn in soils

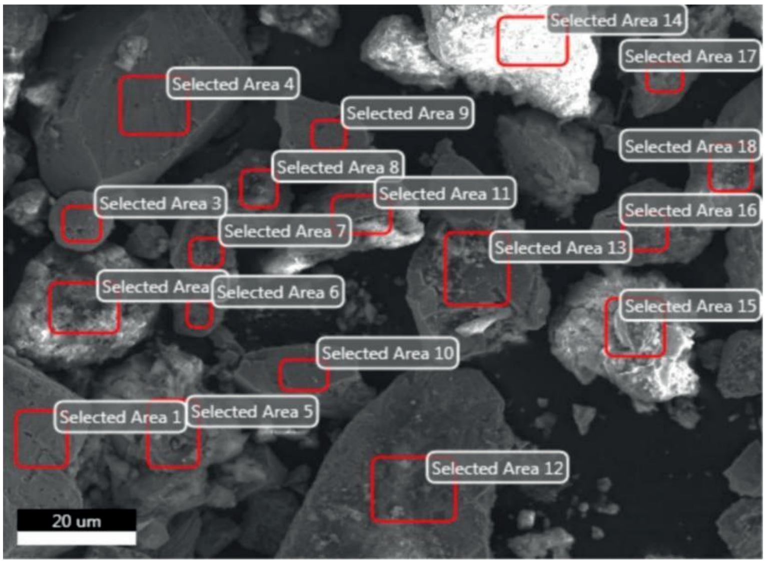

Fig. 2. Microphotograph of the highly magnetic phase particles in the soil on Vosstaniya street

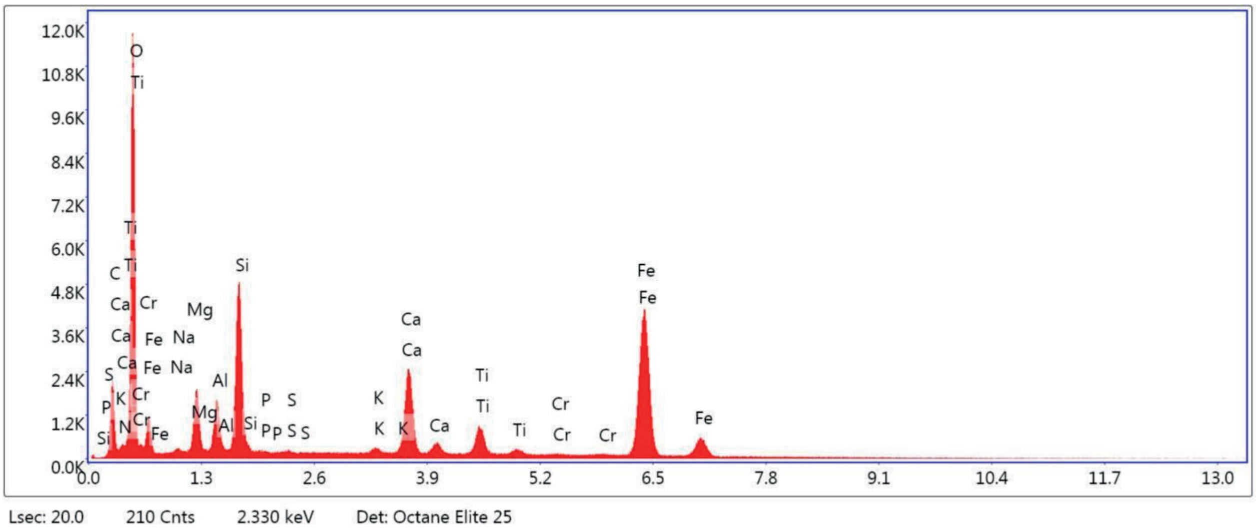

Fig. 3. Energy-dispersive spectrum of the magnetic phase particles in the soil on Vosstaniya street, point number 13

Table 1. Chemical composition of the magnetic phase particles in the soil on Vosstaniya street

Chemical element	CCE, %	Spectrum number																	
		№1	№2	№3	№4	№5	№6	№7	№8	№9	№10	№11	№12	№13	№14	№15	№16	№17	№18
Fe	3.089	48.5	15.9	44.8	44.4	17.4	46.7	25.7	8.1	43.6	49.9	23.7	17.8	24.2	6.5	26.3	38.7	24.8	15.1
Mg	1.351	2.6	3.4	2.1	2.5	4.0	2.3	2.6	1.1	2.5	2.5	7.7	6.2	4.4	7.7	3.1	5.3	6.4	5.2
Mn	0.0527	–	–	0.5	–	0.5	–	–	–	–	–	0.6	1.1	–	–	–	–	–	–
Ti	0.3117	1.5	0.2	–	0.8	2.8	0.9	2.7	0.1	1.0	–	0.6	0.1	2.4	0.1	0.3	–	–	0.2
Cr	0.0035	0.1	0.1	–	0.1	0.1	2.4	–	0.0	–	–	4.2	–	0.1	–	–	0.6	–	–

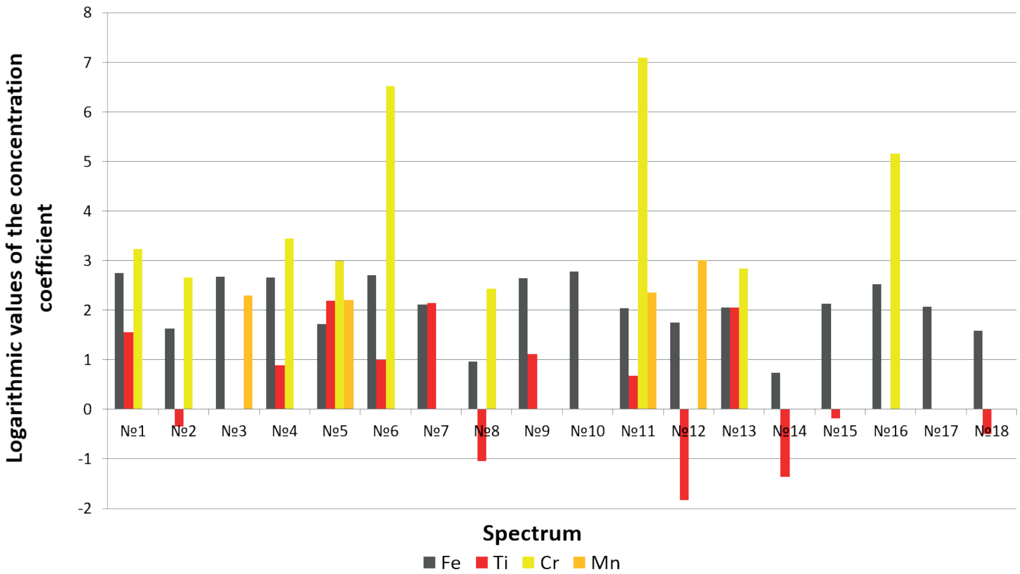

Fig. 4. Logarithmic values of the concentration coefficient (CC) of Fe and heavy metals in the soil, Perm

near metallurgical enterprises is a characteristic feature of the negative impact of this industry on environmental components, including soils.

Particles of detrital and spherical shapes ranging in size from 1 μm to 700 μm dominate in the highly magnetic phase of the moss sample from Vosstaniya street (Fig. 5).

Microprobe analysis of the highly magnetic phase of the epiphyte samples from Motovilikha district of the city of Perm revealed the content of Fe ranging from 4.9 to 38.0%, and Mg from 1.9 to 18.9%, while Ti and Cr also accumulated in some particles (Table 2).

The average concentrations of metals in the composition of magnetic particles exceed CCE in the upper continental crust: Cr - 3257 times, Fe - 8 times, Ti - 7 times, Mg - 4 times (Fig. 6).

The CC values for Mg in all cases are above 1.0, which indicates the presence of magnesium ferrites (Vasiliev, Lobanova 2015). The values of CC for Fe in all particles of the magnetic phase are high with the CC ranging from 1.6 to 12.3 units.

Thus, the accumulative role of the magnetic phase of epiphytes is confirmed by the high CC for heavy metals, particularly Ti (CC up to 6.7 units) and Cr (CC up to 8217.1 units). These elements are not found in all particles of the magnetic phase, which indicates their anthropogenic technogenic origin.

The concentration of Cr, Fe, Mg, Ni, and Ti in the magnetic phase particles is several times higher than CCE in the upper continental crust, which characterizes soil pollution as a polyelemental one.

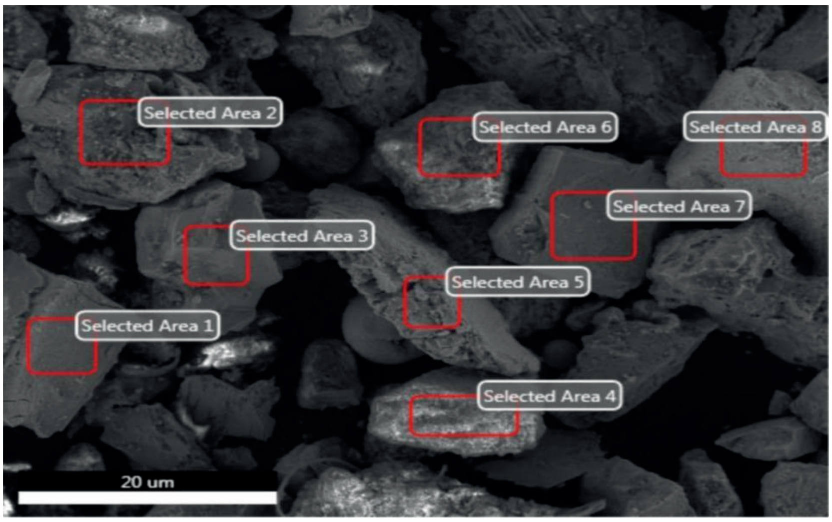

Fig. 5. Micrograph of the highly magnetic phase particles of epiphytes on Vosstaniya street

Table 2. Chemical composition of the magnetic phase particles in the composition of epiphytes on Vosstaniya street

Chemical element	CCE, %	Spectrum number							
		№1	№2	№3	№4	№5	№6	№7	№8
Fe	3.089	37.12	17.88	32.16	4.86	31.10	11.70	38.04	7.98
Mg	1.351	1.98	5.07	2.76	18.87	1.90	5.73	1.98	3.04
Ti	0.3117	1.91	–	–	–	–	–	2.09	–
Cr	0.0035	0.45	–	–	1.10	28.76	0.00	–	–

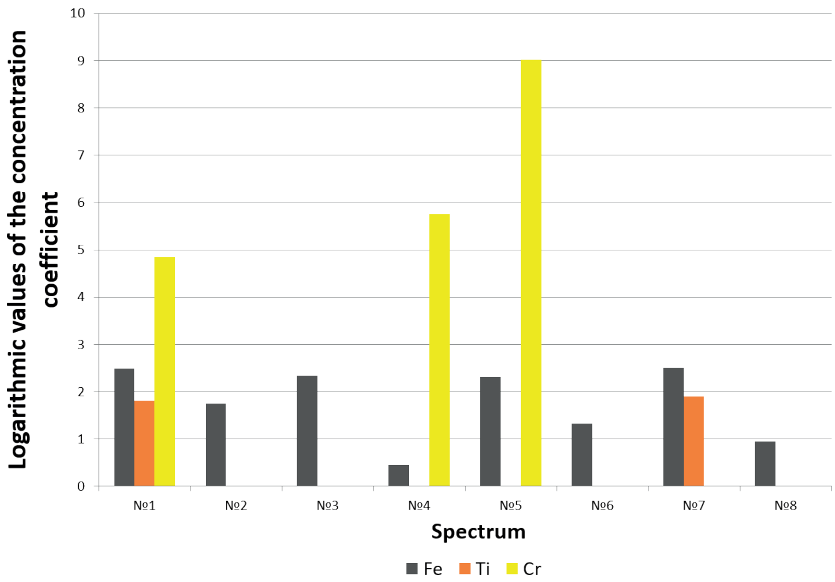

Fig. 6. Logarithmic values of the CC of Fe and heavy metals in epiphytes, Perm

The analysis of the chemical composition of epiphytes demonstrates similarity with the composition of the studied soils. The pollutants in the samples are represented by the same elements (Fe, Ti, and Cr) and contamination of both epiphytes and soils is highest near industrial enterprises, which suggests that epiphyte mosses can act as indicators of aerial pollution of the environment.

The results of our research coincide with the data obtained earlier. Foreign scientists have found that in epiphytic mosses and lichens, part of the internal volume of thalli consists of loose long-cell biogenic parts that form a cottony layer with a very high internal air space, which makes it easy to absorb and retain TMP for a long time. This was demonstrated using scanning electron microscopy and magnetic measurements (Winkler et al. 2019; Chaparro 2021). The concentrations of metals in moss pseudotissues are not so affected by local fluctuations in the level of metals in the soil (Jiang et al. 2018). Mosses have been widely used in several countries in Europe and China as biological monitors of metal pollution for decades because they easily accumulate pollutants over time, reflecting their long-term levels (Fernández et al. 2015; Zhang et al. 2022). As a result, numerous studies have successfully used elemental analysis of mosses to estimate the spatial distribution and sources of metals associated with urban and vehicular traffic. Also, epiphytic mosses were used to map metal pollution in urban areas (Gatziolis et al. 2016).

CONCLUSIONS

The soils near the streets of Motovilikhinsky district, located close to the territories of industrial enterprises (Motovilikhinsky plants), concentrate particles of a magnetite-like mineral complex – magnetite-maghemite, magnesium ferrites, etc. The magnetic susceptibility of soils in Motovilikhinsky district significantly exceeds the background values for the soil cover of the city of Perm. The content of Cr, Fe, Mg, Ni, and Ti in the composition of magnetic soil particles and epiphyte mosses significantly exceeds CCE in the upper continental crust.

Epiphytic mosses living on the bark of trees passively accumulate TMP. They are ubiquitous in the study area of the city and can be found even in the most polluted areas near factories. Epiphytic mosses have an advantage over urban soils as they are well dispersed in urban areas, which allows to use them for biomonitoring of environmental pollution where urban soils can be covered with asphalt, concrete, or fresh soil in the surface layer.

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