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Assessing urban soils' pollution in Moscow megalopolis by portable X-ray fluorescence analyzer

Olga Romzaykina[1], Marina Slukovskaya[1,2,3], Viacheslav Vasenev[1,4], Anna Paltseva[1,5], Dmitrii Sarzhanov[1], and Artyom Losev[1,6]

[1]Smart Urban Nature research center, Peoples' Friendship University of Russia, Moscow, Russia
[2]Laboratory of Nature-inspired Technologies and Environmental Safety of the Arctic, Kola Science Centre, Russian Academy of Sciences, Apatity, Russia
[3]I.V. Tananaev Institute of Chemistry and Technology of Rare Elements and Mineral Raw Materials, Kola Science Centre, Russian Academy of Sciences, Apatity, Russian Federation
[4]Wageningen University, Soil geography and landscape research group, Wageningen, Netherlands
[5]School of Geosciences, University of Louisiana at Lafayette, Louisiana, USA
[6]Department of Soil Science, Geology and Landscape Science, Institute of Agrobiotechnology, Russian State Agrarian University - Moscow Timiryazev Agricultural Academy, Moscow, Russia

The study of urban soils of large cities is complicated due to their heterogeneity and continued reconstruction. Large territorial coverage and administrative prohibitions in some areas led to the difficulty of conducting full-fledged field sampling campaigns and results in inaccuracy. Express methods of chemical elements' content analysis using portable XRF devices allows to quickly assess the pollution level, minimizing the most complicating factors of research. However, the results obtained using a pXRF analyzer require adjustment of the instrument readings as they can be affected by a set of factors such as humidity, sample heterogeneity, and inter-element interference. Modern models of pXRF analyzers allow automatic correction of instrument readings through the correction factors stored in the device's memory.
Our research focused on the development of such correction factors for the Olympus Vanta, one of the most common pXRF analyzers available today. Urban soils are characterized by high heterogeneity both in terms of potentially toxic metal (PTM) content, particle size distribution, and the proportion of organic matter in the soil. Overall 85 soil samples from three sites in the Moscow megalopolis with different levels of PTM pollution were collected for the device validation: the Repin's square in the city-center (high level), the RUDN University campus (medium level), and the urban forest in Moscow Timiryazev Agricultural Academy (low level).
Soil samples were collected from 0-10 cm depth, analyzed for moisture content and bulk density, dried, ground, sieved through a sieve with a 2 mm mesh diameter and analyzed by Olympus Vanta C device. Exposure time was 90 sec in the "Soil" mode. The ICP-OES measurements were taken by EPA 6010B. The carbon content was determined by Vario TOC Select (Elementar). Soil pH_{water} was determined by the potentiometric method. Further, all samples were divided into groups based on different particle size distributions: sand, loam, peat, and their mixtures. Finally, the samples were grouped by the PTM concentrations. International indices (IPI, $PI_{Nemerow}$, and PERI) were used to

assess the accuracy of complex soil pollution. The correction factors were calculated for five PTMs (Cu, Ni, Zn, Pb, Cd).

For sand, the pXRF-measured concentration corresponded to the ICP-OES result with the conversion factor K=1. The surplus of pXRF readings for samples with peat domination was 1.5-2, but the addition of mineral substrates (sand and loam) to the peat mixtures decreased the coefficient to 1.1-1.4. Among studied PTM, copper and lead had the most stable conversion factors, while other elements had different factors in different intervals of concentrations. However, for all studied elements, the pXRF-readings were unreliable at concentrations less than 5-10 ppm. The pollution indices calculated based on pXRF and ICP-OES data differed but in most cases corresponded to an equal level of contamination. Overall, the Olympus Vanta C portable XRF-analyzer is a promising device for the assessing and mapping of PTM pollution in highly heterogenic urban soils, but pXRF readings of samples with low PTM concentrations and high organic matter content require correction.

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