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Rapid assessment of soil and contaminant variability via portable x-ray fluorescence spectroscopy: Copşa Mică, Romania

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ABSTRACT

Many rural villages in Eastern Europe are severely impacted by aeolian smelter dust/deposits. Commonly, elemental studies in Romania have suffered from limited sampling numbers (n = 5–10) and/or incomplete digestion offering only semi-total quantification of elements using traditional, laboratory-based techniques. These approaches are simply inadequate for evaluating potentially hazardous soils and their spatial extent, particularly at urban/rural interfaces of variable land use. Portable x-ray fluorescence (PXRF) spectroscopy can accurately quantify contamination rapidly, in-situ with a wide dynamic range and little to no sample preparation for analysis of regulated elements (e.g., As, Cd, Cu, Mn, Pb, V, Zn) and other common soil elements such as Ca, Fe, K, Rb, Sr, Ti, and Zr. A contemporary PXRF spectrometer was used to scan 61 soil samples across multiple land use types in urban/rural interfaces on-site. Each site was georeferenced with elemental data inputted into a geographic information system for high resolution kriging interpolation. These models were superimposed over modern aerial imagery to evaluate the extent of pollution for each government-regulated element with simultaneous consideration and quantification of spatial variability in naturally occurring soil elements. Pb exceeded governmental action limits across 100% of the area, while V, Mn, Cu, and Zn were exceeded in 2.2, 2.1, 39.6, and 9.8% of the area. Furthermore, many regulated elements were closely correlated to natural soil elements. In short, georeferenced PXRF data proved a powerful new tool for on-site assessment of contaminated soils; one which has rarely been utilized in Eastern Europe to date.

1. Introduction

Pollution is a worldwide problem that has manifested itself in numerous locations due to anthropogenic activities such as mining, petrochemical refining, and smelting. Previous studies have established the deleterious effects of heavy metals and other elements on human health and environmental quality. In fact, many governments in Eastern Europe and worldwide regulate the limits of elements in soils and sediment, both in industrial and residential areas in an effort to protect the health of its citizens (Brevik, 2013). Other studies in Eastern Europe have reported on heavy metal pollution using traditional lab-based methods, or soil spatial variability as a natural topographic variant. Yet few studies have investigated the two simultaneously, let alone in critical rural/urban interfaces. In Romania, elemental limits in soils were established by the Romanian Ministry of the Forest, Waters, and Environment (1997) establishing normal values, alert limits, and intervention (action) limits; the latter two of which are further defined by sensitive soils and less sensitive soils. To illustrate the similarities and differences between naturally occurring soil elemental concentrations and those artificially imposed by anthropogenic impacts, we will assess elemental levels with comparison to the more sensitive intervention (action) limits, commonly used for agricultural and residential soil quality assessment, along with common soil elements using a proximal sensing system, in-situ. In Romania, government mandated action limits for soil elemental concentrations include the following: Cu (200 mg kg^{-1}), Mn (2500 mg kg^{-1}), Pb (100 mg kg^{-1}), V (200 mg kg^{-1}) and Zn (600 mg kg^{-1}) (Romanian Ministry of the Forest, Waters, and Environment, 1997).

Typical of many rural towns in Eastern Europe impacted by ore processing or smelting operations, Copşa Mică is a town of ~5200 residents located in the central part of Romania (Southern Transylvania) in Sibiu County where only ~278 ha is urbanized (Fig. 1). Copşa Mică is found in the Depression of Transylvania, on the southwest Târnavelor Plateau at the confluence of the Târnava River and the Visa and Vine Valleys. It is generally considered a lowland region, drained by the middle sector of the Târnava Mare River. The city itself has a relatively central position surrounded by hills, with terraces and floodplains well defined with respect to the river. Altitude of the floodplain is ~300 m amsl, with the surrounding hills ranging from 375–472 m to the southwest and northeast and 448–517 m to the east (Szanto et al., 2012).

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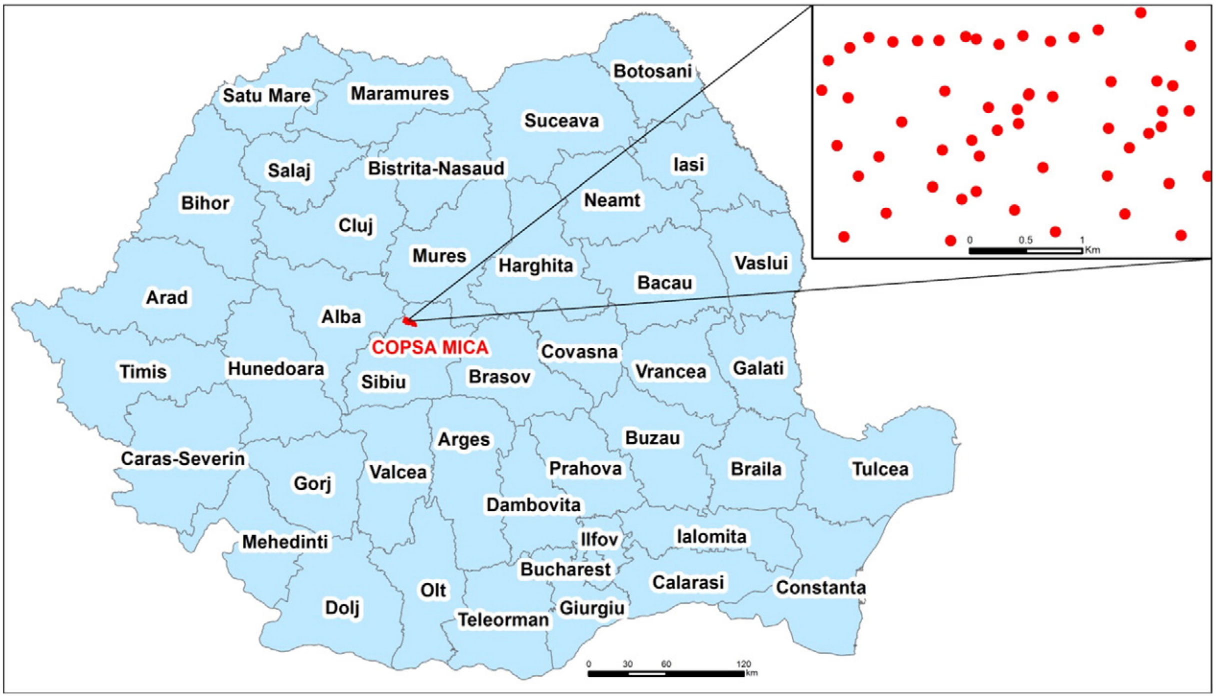

Fig. 1. Location of Copşa Mică, in Sibiu County Romania, with spatial rendering of sampling points.

Pollution in Copşa Mică is mainly due to the activity of two industrial plants: SC SOMETRA SA, which specialized in non-ferrous metallurgy and SC CARBOSIN SA, a chemical plant. The former was founded in 1939 to produce metallurgical Zn. In 1955, a sulfuric acid production plant was built (required for the extraction of heavy metals) and operated until 1966, along with a sinter plant for Zn–Pb concentrates. In 1983, a new plant was commissioned for Sb recovery. In 1988 a dispersion stack some 250 m tall was constructed in an effort to dissipate the smoke produced. In 1998, SC SOMETRA SA was privatized, with a majority stake-hold coming from the Greek company *Mytilineos*. After privatization, a compliance program was mandated to operate the plant in accordance with the Environmental Protection Act no.137/1995 which included 14 measures for reducing the impact of pollutants on the environment by reducing gas fumes and toxic dust. Among the measures implemented were dalamatic filter elements installed in 2006. As a result, pollution emission was dramatically curbed by 2007.

The other main production plant in Copşa Mică, SC CARBOSIN SA, operated from 1935 until 1993 producing carbon black by methane chemical treatment. From 1950–1970, additional carbon black production lines were brought online, as well as facilities for the production of formic acid (methanoic acid, CH_2O_2), oxalic acid (ethanedioic acid, $C_2H_2O_4$), and methacrylate (methyl-2-methyl-2-propenoate, $C_5H_8O_2$). The resulting products were used as raw materials to manufacture various rubber goods in the chemical industry and for medical and agricultural products. Production of various types of carbon black in 1989 was 24,400 t (compared to an estimated 63,000 t yr^{-1} in optimal production years). Subsequently, pollution of carbon black powder affected a 20 km long strip of land with a width of 5–6 km (Directia Silvica Sibiu, 2008).

Today, the spoil bank (Fig. 2) is located west-northwest of the town, along the banks of the Târnava Mare River, upstream from the junction with the Visa River. The spoil bank is estimated to cover an area of 192,308 m^2 with a storage volume of 2,000,000 m^3 consisting of 3,150,000 t of wastes including pyrite ashes, clinker, building materials, and furnace slag (Comănescu et al., 2010); materials which can clearly act as a point source for contaminant leaching. Furthermore, the chemical compounds of the industrial spoil can be dissolved and/or removed by surface waters (e.g., rainfall and runoff) (Fig. 2). Heavy metal pollution clearly extends to the Târnava Mare River. Chicea et al. (2008) reported high Zn concentrations exceeding maximum allowable limits, with elevated levels of Cd and Pb as well. This confirms earlier results of Mosneanu (2004) who also found high levels of Pb, Zn, and Cd. In a

Fig. 2. Carbon black spoil piles (above) and associated runoff (below) in Copşa Mică, Romania.