Ph.D. dissertation resume

Distribution and impacts of contamination by natural and artificial radionuclides in attic dust and urban soil samples from two former heavy industrial Hungarian cities: A case study from Salgótarján and Ózd

submitted to the

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I. Introduction and objectives

Radioactivity has become a major concern over the years because of its association with public health (UNSCEAR, 2010). Primordial radionuclides (^{238}U(^{226}Ra), ^{232}Th and ^{40}K) present in various degrees in all environmental spheres as naturally occurring radioactive materials (NORM). Human interventions (e.g. coal mining and coal-fired power plants, and their processes), utilize, recover and dispose of these materials, thereby creating technologically enhanced naturally occurring radioactive materials (TENORM), which can cause extra and enhanced radiation exposures (EPA, 2006). Furthermore, artificial radionuclides (e.g., ^{137}Cs) have been released mostly through nuclear weapon tests (1940s to 1980s) and the major nuclear accidents (Chernobyl, 1986 and Fukushima, 2011) (UNSCEAR, 2010).

Studies about environmental liabilities (such as contaminated areas, waste basins) provide valuable knowledge on radiation risk assessment associated with exposure and dose. From the 1960s, numerous studies all over the world (e.g., Poland, China, Brazil) have been proposed to focus on contamination around coal-fired power plant (CFPP) (e.g., Eisenbud and Petrow, 1964; Bem et al., 2002; Flues et al., 2002). In an industrial Hungarian city, namely Ajka, also several studies of radionuclide impact on urban soils around coal fired power plants were carried out (Papp et al., 2002; 2003; Zacháry et al., 2016) due to usage of local U-rich brown coal (Szabó, 1992). Most of these studies performed radioactivity measurements on surface soils around the local CFPP.

Furthermore, spoil dumps are potentially risk for human since these can increase background of the natural radioactivity levels. Based on this, undisturbed attic dust, having records of long-term pollution, was used for monitoring potentially toxic elements (e.g., Pb, Cd, As) (e.g., Balabanova et al., 2017; Cizdziel and Hodge, 2000; Ilacqua et al., 2003; Völgyesi et al., 2014) and polycyclic aromatic hydrocarbons (e.g., Wheeler et al., 2020) that suspected dominantly emitted from contamination sources to the ambient environment. Radionuclide (e.g., ^{137}Cs and ^{239}Pu) analysis demonstrated (Cizdziel et al.,1999) that attic dust accumulates and preserves valuable information about environment since attic dust went through only slight physical and chemical alteration (Lioy et al., 2002). Additionally, attic dust should be also considered as risky material for human health, particularly in areas with known long-term pollution process (Gabersek et al., 2022). However, natural radionuclide in attic dust has not been studied at all. This fact necessitates to estimate whether attic dust causes radiological concern over decades and provides valuable information compared to urban soils, which is considered as disturbed material comparing to attic dust. The major goal of this study is to identify possible radionuclide contamination impact of former heavy industrial records in attic dust and urban soil in Salgótarján and Ózd. For that purpose, elemental concentration of U, Th, K and Cs and activity concentration of three primordial radionuclides (^{226}Ra, ^{232}Th and ^{40}K) and one artificial radionuclide (i.e., nuclear fission product, ^{137}Cs) were determined in attic dust and urban soil samples. The overall objectives of this research are the following:

1/ To compare the potential U, Th, K and Cs contamination of attic dust and urban soils locally (within cities) and regionally (between cities) in Hungary.

2/ Evaluate the degree of enrichment and contamination of ^{226}Ra, ^{232}Th, ^{40}K and ^{137}Cs in attic dust and urban soils and determine their possible local sources. Determining the presence of radionuclides in attic dust, which provides information about any potential risk of and the pathway for the radionuclide contamination through urban areas. This study also offers a new perspective on and strengthens approaches to radionuclide studies of attic dust in the future.

3/ Of particular interest in the case of ^{137}Cs is that, given its special origin, is the goal of obtaining a better understanding of the pathways of contamination in urban environments by means of attic dust.

4/ To examine the influence of local sources and spatial distribution of the contaminants via the use of widely accepted statistical techniques and geostatistical mapping tools based on kriging.

5/ To assess the risk to the population living in former industrialized areas (i.e., located near coal-fired power plants, iron and steel works, etc.) on the basis of estimating the dose rate and the annual outdoor effective dose in both cities.

II. Study areas and sampling

Sampling was performed in two, former highly industrialized cities, Salgótarján and Ózd, located in a hilly area approx. 40 km distance from each other, where the region was significant brown coal, iron, and steel supplier. The cities were founded centuries ago, and brown coal was discovered in the 1850s nearby both cities. Thereafter, iron and steel manufacturing in both cities, glassworks, mining machine factory, and later ferro alloy factory were established and operated in Salgótarján for more than a century. After the regime change in 1990, economic activity decreased, and heavy industry ceased in both cities. However, in both cities footprint of the significant and long-term anthropogenic industrial activities (coal mining, heavy industry, and road and train transportation) can be recognized even today in both cities due to the presence of potential contamination sources (e.g., ruins of former smelters, coal-fired power plant, slag hill, coal ash cone, closed coal mines, etc.). Sampling was designed to inspect 1×1 km^2 grid cells covering the Salgótarján (STN) and Ózd

(OZD) residential area, where representative targeted urban soil samples (n_{STN}=36; n_{OZD}=42) were selected on the basis of the availability of desired site categories: kindergarten, playground, park and other (i.e., roadsides, cemeteries, and gardens) sites. In the case of attic dust (n_{STN}=40; n_{OZD}=55), from each grid cell one attic dust sample was collected from the available buildings (i.e., family house, blockhouse and kindergarten). A local coal ash sample (CA; n_{STN}=1) was taken from a coal ash cone of the former CFPP in Salgótarján and smelter slag samples (n_{OZD} =2) from the former and the recent smelter dumps in Ózd. Brown forest soils were taken, as the local geochemical background samples, from the nearby forest area, at some considerable distance (~7 km) from all potential contamination sources in both cities. Sampling was carried out in 2016 for Salgótarján and in 2018 for Ózd.

III. Methods

For elemental analysis, all attic dust and urban soil (including brown forest soil) samples were sieved through a 0.180 mm mesh sieve. The coal ash and smelter slag samples were crushed, and then pulverized. All crushing and pulverization were performed at the Bureau Veritas Mineral Laboratories, Vancouver, Canada. For the gamma spectrometry analysis, attic dust samples were sieved through a < 0.125 mm mesh sieve to eliminate agglomerated organic materials (e.g., Völgyesi et al., 2014). Urban soil samples (including brown forest soils and coal ash) were sieved to < 2.0 mm, in line with studies undertaken on similar soils in Spain and Serbia, respectively (e.g., Charro et al., 2013). Sample preparations were done at the Lithosphere Fluid Research Laboratory (Eötvös Loránd University).

Inductively coupled plasma mass spectrometry (ICP-MS) measurements

Inductively coupled plasma mass spectrometry with a quadrupole as a single detector was conducted at the Bureau Veritas Mineral Laboratories, Vancouver, Canada. After homogenization, ~ 1 g (in the case of attic dust) and 15 g (for urban soil) samples were digested in modified aqua regia (1:1:1 HNO_3: HCl: H_2O) at 95°C for 1 hours till soil solution had been completely digested (Reimann et al., 2009) in the Bureau Veritas Minerals Laboratories in Vancouver, Canada.

Gamma spectrometric measurements

Urban soil gamma spectrometry measurement

For urban soils, on average 100 - 150 g of the homogenized samples (urban soil, brown forest soil and coal ash) was placed in a special theoretically radon-leakage-free sample container made of

HDPE because this material has advantageous mechanical and radon-permeability characteristics (Kis et al., 2013). Measurements were taken in a DÖME[1] low background counting chamber at the Nuclear Analysis and Radiography Department at the Centre for Energy Research, Hungary. The n-type HPGe detector (Type: Canberra GR1319) had a relative efficiency of 13 %.

Attic dust gamma spectrometry measurement

The attic dust samples were put in closed cylindrical polyethylene plastic vials, meanwhile keeping the constant sample heights (1.7 mm) and the mass (mean 1.77 ± 0.48 gr) was varied. The prepared samples were placed in a well-type HPGe detector, with hole dimensions of 14 mm in diameter and 40 mm in depth. A well-type HPGe detector (Canberra GCW 6023) with a relative efficiency of 62.8 %. Measurements were carried out at Nuclear Security Department, Centre for Energy Research, Hungary. A well-type detector is ideal for low activity of environmental samples as it combines both low background limit and high detection efficiency due to the 4π solid angle and shorter counting times as well (Laborie et al., 2000; Barbora et al., 20), which has been used in present study.

Statistical methods

To obtain an overview of the data, descriptive statistics were calculated and presented on box and whiskers plots (Kovács et al., 2012). For an in-depth analysis and comparison of the attic dust and urban soil samples, first the data was tested for normal distribution using the Shapiro-Wilk test since the sample size was rather low ($n < 50$) (Reimann et al., 2008). To test the similarity of the median activity concentrations (^{226}Ra, ^{232}Th, ^{40}K and ^{137}Cs Bq kg^{-1}) of measured radionuclides between attic dust and urban soil samples, Mann-Whitney (Wilcoxon) homogeneity was used. The effect of predictors: distance (km) from the coal fired power plant and the measured radionuclides activities was assessed with bivariate least squares regression analysis with the relationship taken as significant at $p < 0.05$. Meteorological data evaluations were based on the ERA5 reanalysis records of the ECMWF[2]. The temporal period ranged from 1 January 1979 to 1 July 2018. The data sets cover the north-eastern (NE) part of Hungary (47.0◦N - 49.0°N, 19.0°E − 21.0°E) with a spatial resolution of about 8 × 8 km (geographic grid 0.125° × 0.125°) and a time resolution of 3 h. To

[1] The Hungarian acronym of "Extremely Heavy Measurement Instrument'

[2] European Centre for Medium-Range Weather Forecasts

obtain a representative interpolated map of the measured radionuclide activities, geostatistical analysis was conducted (Webster and Oliver, 2007).

Radiological assessment

A possible health effect, due to the external exposure to natural gamma radiation, was estimated based on the obtained results for radionuclide activities of ^{226}Ra, ^{232}Th, ^{40}K and ^{137}Cs (Bq kg^{-1}) in the urban soil and attic dust samples.

IV. Thesis points

1/ Salgótarján coal ash has the highest U content among all studied samples from both cities, which suggest that coal ash plays a significant impact on Salgótarján n environment. In contrast, Ózd smelter slags, from the new industrial area, have higher U concentration than the majority of Ózd urban soil and lower than the majority of attic dust samples. This indicates that the new industrial site in Ózd cannot yield elevated U content in the environment. However, Ózd urban soil samples showing noticeable U content, collected at the former industry, suggests that the former industrial activity had a potential influence on elevated U content in the city center.

In both cities urban soils have consistently higher Th content than those of attic dusts, except Salgótarján coal ash and two outlier attic dust samples collected from houses close to coal fired power plant. In contrast, Ózd smelter slags have the lowest Th content. In addition, Th content in Ózd brown forest soil is at least twice higher than that of Salgótarján counterpart. Consequently, urban soil from both cities can be considered as mixtures of local brown forest soil (as geogenic component) and local Salgótarján coal ash/local Ózd smelter slag from the former industrial area (as anthropogenic component). Therefore, certain attic dust samples from Salgótarján and urban soils from Ózd play considerable impact to local contamination sources.

Furthermore, Ózd and Salgótarján attic dust samples showed higher variability in their K-content compared to urban soils, local brown forest soils, coal ash and smelters slag samples. The elevated K concentration of attic dust is characteristic for agriculturally active areas, far from industrial districts, where the K fertilizer is commonly used *(Tserendorj et al., 2023)*

2/ Activity concentrations of ^{226}Ra, ^{232}Th and ^{40}K in Salgótarján majority attic dust are higher than Salgótarján urban soils and Ózd attic dust. The elevated activity concentrations of ^{226}Ra, and ^{232}Th in Salgótarján attic dust and urban soil correspond to the close distance of sampling sites to the local coal fired power plant. Furthermore, attic dust and urban soil pairs shed light on their similar features in the change of activity concentration. It is supporting that these Salgótarján environmental samples are indeed considerable as mixtures of local brown forest soil (as geogenic component) with local coal ash as by-production of the coal fired power plant, which also contributed to in long-term accumulation of attic dust materials. Low activity concentrations in Ózd attic dust samples suggest that anthropogenic components from the former and recent industrial sites were not high enough to elevate the amount of radionuclides in attic dust, hence it was regarded as insignificant.

The highest activity concentration of ^{40}K in attic dust samples is related to samples with highly elevated K content in both cities. Also, this reveals that a high ^{40}K value is possibly significant input from the surrounding agricultural areas in both cities *(Tserendorj et al., 2023)*

3/ Activity concentration of ^{137}Cs in attic dust from Salgótarján and Ózd values are greater than those found in present urban soils and soils from Hungary and other countries. Study of layered attic dust samples in Ózd from the former steel factory highlights on the significance of ^{137}Cs investigation in residential area: the older attic dust layer, accumulated during operation of the former steel factory, shows one order higher activity concentration compared to the younger one, accumulated during the past ~25 years after steel factory was shut down and source of ^{137}Cs was not available in the local environment. This finding indicates that attic dust, accumulating in closed and safe area, can more efficiently preserve fingerprints of the past atmospheric ^{137}Cs pollution compared to any soil occurring in open environments, which remain still detectable (*Tserendorj et al., 2022)*.

4/ The variation of ^{137}Cs activity concentration as a function of year of building gradually decreases towards older buildings, from the three extremely high values (223.4; 238.6 and 272.8 Bq kg^{-1}) measured in Ózd houses built between 1954 and 1978. This trend indicates that ^{137}Cs activity concentration reaches back to a background value of 0 if there is no unknown sources to create an overprint on it. Thus, meteorological simulations on the studied cities back during Chernobyl NPP accident showed that Ózd had earlier been contaminated by rain precipitation containing material the radioactive plume of the Chernobyl NPP accident than Salgótarján which can explain the appearance of outlier values of ^{137}Cs activity concentrations in mentioned three Ózd houses. Also, in both cities, houses built on the westerly orientated slopes were found to be the most loaded with ^{137}Cs, displaying elevated activity concentrations according to terrain aspect modelling. (*Tserendorj et al., 2022)*.

5/ The radiological dose assessments (absorbed gamma dose rate and annual effective dose rate) on Salgótarján urban soil indicate that the 82 years long operation of the coal-fired power plant in Salgótarján and different slag dumps do not cause increased levels of background radiation in city. However, our findings outlined that elevated radioactive levels at the surrounding area of the coal-fired power plant, especially on two family houses (STN18AD and STN35AD) where the attic dust have high enough coal ash component, to produces potential risk. Therefore, potential concern not only the in the vicinity where industrial activities took place but also disperse the contaminants all around the cities and pose the health treat over decade, particularly, risk assessment performed on kindergarten, family houses, church, and playgrounds.

It was concluded that attic dust provides an indirect evaluation and serves as a highly adequate historical record of local airborne dust deposition when compared to soil, and it is also an excellent environmental media for monitoring long-term, particularly in industrial urban environments (*Tserendorj et al., 2022, 2023; Abbaszade et al., 2022)*

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