Ph.D. dissertation résumé

ENVIRONMENT GEOCHEMICAL AND RADIOMETRIC STUDY OF BUILDING MATERIAL AND ATTIC DUST SAMPLES AFFECTED BY INDUSTRIAL ACTIVITY IN HUNGARY

submitted to the

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1. Introduction and objectives

In the post-war Hungary many industrial sites were in operation all over the country (e.g. Ajka, Dunaújváros, Komló, Ózd, Miskolc, Salgótarján; Gajzágó, 1962; Kozma, 1996) and produced large amounts of waste and emitted pollutants. Many settlements were built and developed together with the growing local industry; hence, in several cases, the industrial site is identical with the living area. Our urban geochemical (Lyons and Harmon, 2012) knowledge of these industrial sites right up to the present day remains very scant. The emitted and deposited particles and the utilized by-products of the industrial production processes can potentially cause environmental and health problems. This is due to the mobilization of the toxic elements attached to the dust particles (e.g. Duong and Lee, 2009; Gosar et al., 2006), and the possibly elevated radioactivity of by-products used in construction (e.g. Manolopoulou and Papastefanou, 1992; Somlai et al., 2006). My Ph.D. research studies if the industrial activities in the past still influence our indoor living environment, and emphasizes the relevance of urban geochemical studies in Hungary.

The present work has three main aims:

1. to qualify Hungarian building materials containing coal combustion by-products, based on their radioactive material content,
2. to develop a gamma-ray spectrometry measurement system, with which the accurate and fast determination of ^{226}Ra by its peak with the energy of 186 keV can be proven, and
3. to demonstrate the applicability of attic dust to study the relation between potential industrial contamination sources and geochemical behavior of toxic elements (As, Cd, Cu, Hg, Ni, Pb and Zn) in a Hungarian industrial area.

2. Study area and sampling

During the sampling campaigns between 2009 and 2013, 29 building material samples have been collected from eight locations (Budapest, Dunaharaszti, Gödöllő, Kecskemét, Kiskunhalas, Kistarcsa, Sülysáp, Százhalombatta) in the Central Hungarian Region and from Ajka city. The building material samples consisted of brick samples (n=2), concrete (from blocks of flats) samples (n=2), coal slag samples (n=15), coal slag concrete samples (n=3) and gas silicate samples with fly ash as additive (n=6) and without fly ash (n=1). In most cases the owners requested our laboratory to measure the level of indoor radioactivity because they had heard about the harmful effects of coal slag and fly ash-bearing building materials. Most samples were used in bulk amounts, whereas the coal slag samples were only used restrictedly (i.e. used for under-floor filling below the parquet or in the attics above the ceiling).

The city of Ajka in the western part of Hungary was chosen for a detailed urban geochemical study because it is a presumably contaminated settlement with long industrial history. Lignite mining, a lignite-fired power plant, aluminum industry and numerous waste heaps acted as sources of multiple contamination in the area. In Ajka and its vicinity, attic dust sampling was carried out in the summer of 2011 in 27 houses, older than 30 years. Attic dust was chosen because undisturbed attic dusts can act as archives of atmospheric dust by preferentially trapping and preserving airborne particulate matter. Therefore, samples were collected away from the attic entrance and at the highest possible point of the ceiling to minimize possible disturbing effects of resident activities. All sampling data was recorded on a field sheet specially developed for this survey.

3. Methods

1. The radiometric investigations included both in-situ gamma dose rate and laboratory gamma-ray spectrometry measurements of the 29 building material samples. The activity concentrations of ^{226}Ra, ^{232}Th and ^{40}K were measured at the Department of Atomic Physics, Eötvös Loránd University, Budapest. These measurements targeted to qualify the building materials by international hazard indices (Ra_{eq} and I) and perform a comparison to reference data. Where the coal combustion by-products were used in bulk amounts, the absorbed dose rate and annual effective dose estimations were also performed.

2. The demand for the accurate and fast determination of ^{226}Ra by its 186 keV peak was proposed during the gamma-ray spectrometry measurements at Eötvös Loránd University. To prove this method, the necessary experiments and analyses were carried out in collaboration with the Nuclear Analytical and Radiography Laboratory, Centre for Energy Research, Hungarian Academy of Sciences, Budapest. The newly developed system allows the determination of the $^{235}U/^{238}U$ isotopic ratio and the secular equilibrium within the ^{238}U decay chain. In order to achieve this, a low background chamber, a radon tight HDPE (High-density polyethylene) sample holder and an absolute full energy peak efficiency calculation in close, extended sample-detector geometry were needed.

3. In 27 attic dust samples from Ajka the As, Cd, Cu, Hg, Ni, Pb and Zn concentrations were measured by ICP-OES (inductively coupled plazma-optical emission spectrometry) and AAS (atom absorption spectrometry). The results were compared to the reference data and analyzed statistically using the resistant five-letter summary statistics of Tukey (1977), heterogeneity test using the natural brake method in cumulative histograms, spatial and correlation analyses. For the spatial characterization, concentration groups were determined and plotted on maps to visualize the spatial distribution of contaminated attic dust, in order to associate it to industrial sources. Isoline (contour) maps (Triangular Irregular Network interpolation; Guibas and Stolfi, 1985) were also derived. Relationships among measured parameters were studied with the Pearson's correlation coefficient (Pearson, 1896) method.

4. Theses

1. I have made a contribution to the development of a gamma-ray spectrometry measurement system for the accurate and fast determination of ^{226}Ra. The applied HDPE sample holder tests showed with >95% probability that radon leakage was negligible, i.e. less than 2% of the decay constant. The difference between the result of the efficiency transfer method and the control measurement was less than 5% (Kis et al., 2013). With the system I confirmed the existence of natural uranium activity ratio (weighted average: 0.0466 ± 0.0030) and secular equilibrium between uranium and radium (determined from the comparison of the peak of the ^{234m}Pa and that of radon decay products, ^{214}Pb and ^{214}Bi) in coal slag samples. I concluded that the 186 keV gamma-peak can be used for efficient radium measurement without a radon-tight sample holder and without a ~30 days waiting period (Völgyesi et al., 2014a).

2. I have qualified 29 artificial building material samples from the central Hungarian Region and the city of Ajka, among which I identified seven hazardous samples (six coal slags and one coal slag concrete) with an elevated Ra_{eq}, I index, and annual effective dose values. The ^{226}Ra activity concentration in most of the coal slag samples was much higher (780 ± 975 Bq kg^{-1}) than that in the other samples, and the world references. Samples from Ajka represent a group with extremely high activity concentrations (1571 ± 1092 Bq kg^{-1}). Th-232 and ^{40}K activity concentration results were comparable to the international values with few outlying values (e.g. high ^{40}K content of bricks) (Szabó et al., 2013; Völgyesi et al., 2014a). These statements were confirmed by in situ gamma dose rate measurements. All of these shed light on necessity of the examination of houses in the Central Hungarian Region where coal slag was used.

3. I have applied attic dust as a new sample medium to study the relation between potential industrial contamination sources and spatial distribution and behaviour of the toxic elements in a Hungarian industrial area. The enrichment calculations (Pb>>Zn>Hg>>Cu>=Cd>As>Ni) showed that the studied dust is mostly contaminated with Hg, Pb and Zn compared to the regional geochemical background values. Considering the pollution limit, the highest contamination exists for As, Cd, Hg and Pb, in addition to Zn, with occasional extremely high concentrations. There was no remarkable contamination with Ni and Cu, their concentrations lie very close to the limit values (Völgyesi et al., 2014b).

4. I have demonstrated that the spatial distribution analysis of the toxic elements revealed the impact of lignite mining (As and Zn distributions), the lignite-fired power plant (Hg distribution), the power plant waste dumps (As distribution) and traffic (Pb and Cu distributions) in attic dust samples from Ajka. Arsenic, Hg, Pb and Cu dust showed multi-modal distributions and delineated areas impacted by airborne dust from the anthropogenic sources. Cadmium and Zn showed uni-modal distributions with extreme outliers, suggesting that the anthropogenic (point) source(s) determine(s) their geochemical distribution. Nickel has low overall variability with one outlier and its spatial distribution is not driven by prominent point sources. By means of As, Pb and Cu distributions the advantage of using statistical and spatial analysis was verified (Völgyesi et al., 2014b).

5. I have studied the relationship between soil and attic dust samples and established that attic dust is a sensitive sample medium, and is therefore highly suitable for the demonstration of anthropogenic industrial impacts. However, there were no significant correlations between concentrations of toxic elements and the age of the houses, indicating the applicability of attic dust in Ajka rather for spatial than temporal analysis. Even though average toxic element concentration range was smaller in soils than in attic dust, As, Hg and Pb showed similar spatial patterns. Our study on soils supports that soil is a highly complex environmental medium with a lot of natural and anthropogenic impacts difficult to identify separately (Zacháry, et al., submitted; Völgyesi et al., 2014b).

6. I have concluded that the mutual correlations (r=0.53–0.88) between the toxic elements of the Pb-Zn-Cd-Ni-Cu group in attic dust samples confirm their common industry related source which was even stronger among Pb-Cd-Zn elements (r>0.75). The partial correlations of Ni and Cu with Fe pointed out that the correlation of these two elements (Ni-Cu) is mainly due to their connection to iron-oxy-hydroxide compounds, hence Fe keeps these elements appearing together. Neither Hg nor As displayed any notable correlation with the other elements indicating clearly that their origin and geochemistry is different from the other potential contaminants. The correspondence between the correlation of As and Fe in soil and attic dust indicated the wind-blown origin of As in attic dust and corroborated the common As distributions in both sample medium. The weak correlation between Pb and Fe in attic dust confirmed the traffic related Pb source (Zacháry, et al., submitted; Völgyesi et al., 2014b).

5. Selected publications

Szabó, Zs., **Völgyesi, P.,** Nagy, H. É., Szabó, Cs., Kis, Z. Csorba, O. (2013) Radioactivity of natural and artificial building materials – a comparative study. ***Journal of Environmental Radioactivity***, 118, 64-74.
IF: 3.571

Kis, Z., **Völgyesi, P.,** Szabó, Zs. (2013) DÖME – revitalizing a low-background counting chamber and developing a radon-tight sample holder for gamma-ray spectroscopy measurements. ***Journal of Radioanalytical and Nuclear Chemistry***, 298, 2029-2035.
IF: 1.415

Völgyesi, P., Kis, Z., Szabó, Zs., Szabó, Cs. (2014a) Using the 186 keV peak for ^{226}Ra activity concentration determination in Hungarian coal slag samples by gamma-ray spectroscopy. ***Journal of Radioanalytical and Nuclear Chemistry***, 302, 375-383.
IF: 1. 034

Völgyesi, P., Jordan, G., Zacháry, D., Szabó, Cs., Bartha, A., Matschullat, J. (2014b) Attic dust reflects long-term airborne contamination of an industrial area: A case study from Ajka, Hungary. ***Applied Geochemistry***, 46, 19-29.
IF: 2.268

Zacháry, D., Jordan, G., *Völgyesi, P.*, Bartha, A., Szabó, Cs. (*submitted*) Urban geochemical mapping for spatial risk assessment of multisource potentially toxic elements - a case study in city of Ajka, Hungary. *Journal of Geochemical Exploration*
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