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TECHNICAL NOTE

Evaluation of the coal combustion input to the ^{226}Ra ground-level air concentration in the Lodz city, Poland

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Abstract The network of high volume aerosol samplers type ASS-500 in Poland, established mainly for monitoring radionuclides of artificial origin, offers also a unique opportunity for measuring natural radionuclide concentrations in ground-level air. Recounting of the closed (sealed) filters after a one month period, necessary for establishing radioactive equilibrium between ^{226}Ra and ^{222}Rn, as well as its short-lived decay products, remarkably improves the accuracy of ^{226}Ra determination. The Currie's average detection and determination limits (with 10% relative accuracy) calculated for ^{226}Ra for 160,000 s counting time and combined with the average filtered air volume of 60,000 m^3 were 0.3 and 1.2 μBq/m^3, respectively. The observed ^{226}Ra concentrations in air in Lodz during the half year collection period, including parts of winter and summer seasons, were always above the detection limit and ranged from 0.76 to 2.75 μBq/m^3. ^{226}Ra, present in the ground level air mainly as a result of resuspension from the top layer of soil and fly ash emissions from coal burning, was used for rough estimation of the contribution of the coal combustion to the total suspended particulate matter. On the basis of available data for ^{226}Ra content in the soil and fly ashes for the Lodz region of Poland, the calculated coal combustion input to the total air suspended particulate matter ranged from 8 to 39%.

Key words ^{226}Ra concentration in air • γ-spectrometry • fly ash

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Introduction

Primordial radionuclides present in the ambient air are useful tracers for studying physical processes of the formation and transport of aerosol particles [7]. However, they are very seldom used to evaluate the source apportionment of urban dust. It is generally accepted that the main source of ^{232}Th, ^{238}U and ^{226}Ra in surface air is soil erosion and resuspension of solid particles by wind [8, 12]. The so-called reference values for these radionuclides, equal to 1 μBq/m^3 [16], are calculated on the basis of their world average concentrations in surface soils (33 Bq/kg) and typical suspended solid particle concentration in ground level air (30 μg/m^3). On the other hand, in some areas another source of natural radionuclides in air is coal combustion. Natural radionuclides from the uranium and thorium series present in coal in activities ranging from tens to hundreds Bq/kg are concentrated a few times in fly ashes escaping from the stacks [1, 2]. Although the problem of technologically enhanced natural radiation (TENR) in the vicinity of coal-fired power plants is still discussed (see for example: [1, 3, 14]), there are only computer simulated calculations of uranium and thorium decay product concentrations [13]. Direct measurements of their concentrations in air in the vicinity of such emitters are still lacking. As the activity concentrations of these radionuclides in air are usually very low, a large quantity of air should be filtered,

especially for radium nuclide determinations. For this reason, the experimental data for radium concentrations in air are scarce. Measured ^{226}Ra concentrations in the air over Germany ranged, from 1.2 μBq/m^3 to 3.3 μBq/m^3 [9], while the reported value for the USA is even lower – 0.6 μBq/m^3 [16]. Slightly higher concentrations, from 2.9 to 9.31 μBq/m^3, were measured during 10-year observations in a rural area of Japan [17]. ^{226}Ra radionuclide concentrations in different levels: from the ground to the stratosphere were also measured in Poland and they ranged from 3.28 μBq/m^3 in surface air to 12.3 μBq/m^3 in the tropopause (11 km) [10].

The existing aerosol sampling network in Poland based on high-volume air samplers of type ASS-500 (about 500 m^3/h) gives a unique opportunity for the determination of both natural and anthropogenic radionuclides in the ambient air. According to the routine procedure, the Petrianov type air filter is exchanged after a one week sampling time, sufficient for filtering up to 100,000 m^3 of air [11]. For monitoring of artificial radionuclides concentrations in normal radiological situations, γ-spectrometry measurements are done twice: immediately after sampling and after a two-day delay time necessary for decaying of the short-lived natural radionuclides. This short delay enables ^{226}Ra determination only via the 186 keV line. However, this line is situated in the region of high Compton background, additionally, strongly influenced by ^{235}U present in the lead shield of spectrometer as well as in the dust sample. For these reasons, the majority of the reported ^{226}Ra results from this network was close to the detection limits of the γ-spectrometric measurements [4]. Particularly, for the station in Lodz the lower detection limits were in the range of 3.7–13.3 μBq/m^3.

The main aim of this work was to attempt to improve the detection limit of ^{226}Ra in the dust samples by sealing and measuring them after a one-month period, necessary for establishing transient equilibrium between ^{226}Ra present in the sample and the γ-emitting ^{222}Rn short-lived daughters, ^{214}Pb and ^{214}Bi.

The lowering of the detection and determination limits allows not only for more precise ^{226}Ra measurements of the usually observed concentrations, but also allows use them in evaluations of the fly ash influence on the ^{226}Ra levels in surface air. Comparison of the ^{226}Ra levels in the dust with those for surface soil and fly ash escaping from chimneys enables the calculation of the coal combustion input into the total dust in the vicinity of the sampling stations. It is important for the Lodz city area, where inside the city there are three big coal-fired power plants which emitted 1070 Mg of fly ash in 2002 [15]. Furthermore, several smaller plants with insufficient fly ash removal systems are the basic sources of the dust in some parts of the city and in about 40% of houses coal is burnt without any fly ash removal systems [15].

Experimental

Sampling

The standard procedure for aerosol sampling system by the ASS-500 station has been described elsewhere [4]. After routine γ-spectrometry counting for monitoring purposes, the samples were hermetically sealed in polypropylene Petri dishes and kept for at least 1 month, to reach ^{226}Ra – ^{222}Rn and its daughters equilibrium.

Fly ash samples, supplied from the Power Station EC II, Lodz, were preliminarily fractionated by sieving to get the fraction with particle diameters below 40 μm, and finally the fractions below 10 μm were separated by the Anderson type Cascade Impactor.

γ-Spectrometry

The activities of the γ-emitting ^{214}Pb and ^{214}Bi were determined by the Canberra spectrometric system with a 15% REGe detector. Sealed samples were put directly on the detector and counted for 160,000 s. Calibration of the system was completed by adding a known amount of the standard ^{226}Ra solution (Isotope Product Laboratory, USA) to a clean pressed filter. This filter, with the ^{226}Ra standard, was then treated in the same way as the measured samples to get absolute detection efficiencies for the γ-lines: 295.1 keV and 351.9 keV of ^{214}Pb and 609.3 keV of ^{214}Bi. The activity of the standard ^{226}Ra solution was confirmed by α-particle counting in a Betascout (Perkin-Elmer) liquid scintillation counter.

The calculated detection and determination limits according to Currie criterion [6] for 160,000 s counting time were equal to 0.02 Bq and 0.07 Bq, respectively. Taking into account the average volume of the filtered air equal to 60,000 m^3, the corresponding average limits for ^{226}Ra in air were 0.3 and 1.2 μBq/m^3, respectively.

Quality assurance

The accuracy of the analytical procedure was determined in an independent experiment by checking the activity of ^{226}Ra in 5 g of the standard reference materials: IAEA-327 "Radionuclides in Soil" and IAEA-Soil-6. These materials were added to a clean filter sheet and pressed, sealed and counted after a one-month waiting period. The obtained values of 35.4 ± 1.6 (1 SD) Bq/kg for IAEA-327 and 80.1 ± 6.1 (1 SD) Bq/kg for Soil-6 were very close to the recommended reference values of 34.1 Bq/kg and 79.9 Bq/kg, respectively.

Results and discussion

The results of ^{226}Ra determination for two sampling periods: summer (No: 1÷14) and autumn + winter (No: 15÷28) heating periods are presented in Table 1. The combined counting and calibration uncertainties for the results were in the range of 6.9–18.2%.

As is evident, almost all determined activities were above the determination limit with 10% accuracy (0.07 Bq/sample). But in seven cases the measured total activities of ^{226}Ra were below 0.07 Bq. For the lowest of these concentrations, the measured activity exceeded twice the detection limit – 0.02 Bq and the calculated relative error was equal to 18%.

However, the relatively high weekly fluctuations, both in the total dust and ^{226}Ra concentrations make the diffe-

Table 1. ^{226}Ra concentration activity in surface air in the Lodz city, Poland.

No.	Sampling period	Dust concentration	^{226}Ra concentration activity	
		[μg/m^3]	[Bq/sample]	[μBq/m^3]
1	30.06.2003 – 07.07.2003	31.5	0.100 ± 0.009	1.15 ± 0.10
2	07.07.2003 – 14.07.2003	32.6	0.091 ± 0.009	0.99 ± 0.10
3	14.07.2003 – 21.07.2003	33.0	0.106 ± 0.009	1.27 ± 0.10
4	21.07.2003 – 28.07.2003	47.2	0.120 ± 0.011	1.40 ± 0.13
5	28.07.2003 – 04.08.2003	33.2	0.089 ± 0.009	1.10 ± 0.11
6	04.08.2003 – 11.08.2003	45.1	0.120 ± 0.009	1.55 ± 0.12
7	11.08.2003 – 18.08.2003	59.3	0.163 ± 0.011	2.18 ± 0.15
8	18.08.2003 – 25.08.2003	48.6	0.095 ± 0.009	1.17 ± 0.11
9	25.08.2003 – 01.09.2003	48.8	0.162 ± 0.011	2.07 ± 0.14
10	01.09.2003 – 08.09.2003	31.5	0.073 ± 0.009	0.89 ± 0.11
11	08.09.2003 – 15.09.2003	53.9	0.118 ± 0.009	1.46 ± 0.11
12	15.09.2003 – 22.09.2003	98.9	0.135 ± 0.010	2.75 ± 0.20
13	22.09.2003 – 29.09.2003	85.2	0.140 ± 0.010	2.23 ± 0.16
14	29.09.2003 – 06.10.2003	42.7	0.059 ± 0.008	0.76 ± 0.10
	average	49.4	0.112	1.50 ± 0.59
15	20.10.2003 – 27.10.2003	50.0	0.092 ± 0.008	1.55 ± 0.13
16	27.10.2003 – 03.11.2003	57.9	0.097 ± 0.009	2.20 ± 0.20
17	03.11.2003 – 10.11.2003	46.0	0.144 ± 0.010	2.54 ± 0.18
18	10.11.2003 – 17.11.2003	60.8	0.089 ± 0.008	1.84 ± 0.17
19	17.11.2003 – 24.11.2003	36.3	0.064 ± 0.008	0.98 ± 0.12
20	24.11.2003 – 01.12.2003	72.3	0.084 ± 0.008	2.21 ± 0.21
21	01.12.2003 – 08.12.2003	47.5	0.082 ± 0.008	1.76 ± 0.17
22	08.12.2003 – 15.12.2003	50.3	0.078 ± 0.009	1.71 ± 0.20
23	15.12.2003 – 22.12.2003	27.8	0.074 ± 0.008	1.40 ± 0.15
24	29.12.2003 – 05.01.2004	49.1	0.052 ± 0.007	1.29 ± 0.18
25	05.01.2004 – 12.01.2004	90.2	0.044 ± 0.007	1.68 ± 0.28
26	12.01.2004 – 19.01.2004	37.2	0.049 ± 0.007	1.12 ± 0.17
27	19.01.2004 – 26.01.2004	42.2	0.040 ± 0.007	0.84 ± 0.15
28	26.01.2004 – 02.02.2004	76.2	0.057 ± 0.007	1.54 ± 0.20
	average	53.1	0.075	1.62 ± 0.48

rence in the average values statistically insignificant for these two periods. The observed arithmetic mean value of 1.56 μBq/m^3 of ^{226}Ra activity concentration in the ground level air in the vicinity of ASS-500 location in Lodz city is close to values determined for Germany [16], but somewhat lower than values given for 12 sites in Poland in 2003 (mean value of ~5 μBq/m^3, range <1.7–17.8) [5]. However, it must be taken into account that the latter value, as well as the values presented for 1999 [4], were obtained for concentrations, which in more than 50%, were lower than the detection limits of the nine γ-spectrometric laboratories of the network, and that such concentrations were in the statistical calculations taken as equal to the detection limits. In the second half of 2003, these detection limits were in the range of 1.8–17.2 μBq/m^3. Among them three laboratories reported detection limits higher than 10 μBq/m^3.

The calculated specific activities of ^{226}Ra in the captured dust in Bq/kg (Table 2) were remarkably higher than its concentrations in surface soil in the Lodz area (mean value of 16.6 Bq/kg) [3].

It is known that besides the surface soil resuspension, the combustion of coal and emissions from gasoline-fuelled road vehicles (transport) and other industrial activities make a large contribution to the urban air particulate matter. But the enhanced levels of ^{226}Ra in the air particulate matter in the Lodz area can be caused mainly by fly ashes. It has been well documented that during coal combustion the mineral components, including natural radionuclides of the coal, are partitioned between the bottom ash and fly ash and their concentrations in the particles captured by electrostatic precipitators are significantly higher than in crude coal or surface soil layer [1]. Moreover,

Table 2. Calculation of the fly ash contribution (u_f) to the total urban dust.

No.	Sampling period	Specific activity in urban dust (A_d) [Bq/kg]	u_{f_1}	u_{f_2}	$\bar{u}_f$	$1 - \bar{u}_f = u_t + u_r$
1	30.06.2003 – 07.07.2003	36.3	0.18	0.28	0.23	0.77
2	07.07.2003 – 14.07.2003	30.4	0.12	0.24	0.18	0.82
3	14.07.2003 – 21.07.2003	38.5	0.20	0.30	0.25	0.75
4	21.07.2003 – 28.07.2003	29.6	0.12	0.23	0.18	0.82
5	28.07.2003 – 04.08.2003	33.0	0.15	0.26	0.21	0.79
6	04.08.2003 – 11.08.2003	34.3	0.16	0.27	0.22	0.78
7	11.08.2003 – 18.08.2003	36.8	0.18	0.29	0.24	0.76
8	18.08.2003 – 25.08.2003	24.1	0.07	0.19	0.13	0.87
9	25.08.2003 – 01.09.2003	42.4	0.23	0.33	0.28	0.72
10	01.09.2003 – 08.09.2003	28.3	0.10	0.22	0.16	0.84
11	08.09.2003 – 15.09.2003	27.2	0.09	0.21	0.15	0.85
12	15.09.2003 – 22.09.2003	27.7	0.10	0.22	0.16	0.84
13	22.09.2003 – 29.09.2003	26.1	0.09	0.20	0.15	0.85
14	29.09.2003 – 06.10.2003	17.8	0.01	0.14	0.08	0.92
15	20.10.2003 – 27.10.2003	30.9	0.13	0.24	0.19	0.81
16	27.10.2003 – 03.11.2003	38.0	0.19	0.30	0.25	0.75
17	03.11.2003 – 10.11.2003	55.1	0.34	0.43	0.39	0.61
18	10.11.2003 – 17.11.2003	30.2	0.12	0.24	0.18	0.82
19	17.11.2003 – 24.11.2003	27.0	0.09	0.21	0.15	0.85
20	24.11.2003 – 01.12.2003	30.7	0.13	0.24	0.19	0.81
21	01.12.2003 – 08.12.2003	36.9	0.18	0.29	0.24	0.76
22	08.12.2003 – 15.12.2003	34.0	0.16	0.26	0.21	0.79
23	15.12.2003 – 22.12.2003	49.4	0.29	0.38	0.34	0.66
24	29.12.2003 – 05.01.2004	26.3	0.09	0.20	0.15	0.85
25	05.01.2004 – 12.01.2004	18.5	0.02	0.14	0.08	0.92
26	12.01.2004 – 19.01.2004	30.4	0.12	0.24	0.18	0.82
27	19.01.2004 – 26.01.2004	20.1	0.03	0.16	0.10	0.90
28	26.01.2004 – 02.02.2004	20.3	0.03	0.16	0.10	0.90

it was observed that some more volatile elements show a tendency for enrichment in the submicron size fraction of fly ash. As it was previously observed, the escaping fly ashes from the Power Station EC II, close to the air sampling site, have aerodynamic diameters lying in the range of 0 to 10 μm [2]. Separation of the fly ash samples according to particle diameters revealed that the specific activity of ^{226}Ra in the fraction with particle diameters below 10 μm (A_f) was equal to 128.3 Bq/kg.

Therefore, the resultant radium activity concentration in the urban dust can be described by the following equations:

$$A_d = A_s u_s + A_t u_t + A_f u_f \tag{1}$$

$$u_s + u_t + u_f = 1 \tag{2}$$

where: A_d – ^{226}Ra specific activity in urban dust (Bq/kg); A_s – ^{226}Ra specific activity in surface soil (Bq/kg); A_t – ^{226}Ra specific activity in vehicle emission particles (Bq/kg); A_f – ^{226}Ra specific activity in fly ash (Bq/kg); u_s – contribution of soil resuspension to the total dust concentration; u_t – contribution of motor vehicle emission; u_f – contribution of the escaping fly ash.

The range of the fly ash contribution u_f to the total urban dust can be evaluated for two border conditions:

a) Assuming that the contribution of the motor vehicle emission is negligible (for example in suburban or rural areas) $u_t = 0$, and the ^{226}Ra specific activity in particles from the vehicle emission is generally also negligible in comparison to that in fly ashes or even in surface soil – $A_t = 0$. From the combinations of eqs. (1) and (2), one gets:

$$A_d = A_s(1 - u_{f_1}) + A_f u_{f_1} \tag{3}$$

and finally

(4) $$u_{f_1} = \frac{A_d - A_s}{A_f - A_s}.$$

From this equation one can calculate the lower range of the fly ash contribution to the total dust.

b) Assuming that the soil resuspension contribution is negligible – $u_s = 0$ (for instance in winter period), one can get simply:

(5) $$u_{f_2} = \frac{A_d}{A_f}.$$

From equation (5), the upper range of fly ash contribution can be calculated, respectively.

In Table 2, the calculated values of dust-specific activities – A_d and the range of possible u_f values for each ^{226}Ra determination are given.

In practice both of the remaining dust sources (motor vehicles and soil resuspension) have some influence impossible for direct evaluation form ^{226}Ra data only. For estimation of the average fly ash input, we assumed their equal contribution. Therefore, the average values of $\bar{u}_f$ can be calculated from the following formula:

(6) $$\bar{u}_f = \frac{u_{f_1} + u_{f_2}}{2}.$$

Such calculated values of $\bar{u}_f$ are given in the last but one column, while the sum of the soil resuspension and motor vehicle emission contributions are reported in the last column.

As it was expected, the calculated average values for fly ash contributions ranged from 0.08 to 0.39 and they are generally consistent with the data given in the annual reports of the local environmental protection authority [15]. However, one has to take into account that the proposed method for calculation of the coal combustion input to the total urban dust is valid, if there is only one kind of emission source, for example, a coal-fired power station (A_f = constant). In reality, when during the winter season the so-called low emission from domestic heating is prevailing in some areas, the ^{226}Ra specific activity of the escaping fly ash may differ from the values determined for escaping fly ash from power station chimneys.

Conclusions

Recounting hermetically closed filter discs from the ASS-500 station after a one-month waiting period enables almost 10-fold lowering of the ^{226}Ra determination limit. The average ^{226}Ra activity concentration in ground level air during a 28-week monitoring period was equal to 1.56 μBq/m^3 and close to values reported for Germany [16].

Comparison of the specific activities of filter-captured dust with those for surface soil and fly ash escaping from power stations allows the evaluation of the coal combustion input for the total ground-level air particulate matter concentrations.

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