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River Sediment Contamination with Plutonium Isotopes and Heavy Metals in Lublin Agglomeration (Poland)

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Abstract

Plutonium isotopes activity and selected heavy metal concentration in sediment samples from three Lublin rivers are presented. Average values of ^{239,240}Pu radioactivity is equal to 0.050 ± 0.034 Bq/kg dry weight, and ^{238}Pu 0.005 ± 0.005 Bq/kg. These values are about 4-times lower those that found in soils from Lublin region. A close correlations between plutonium and calcium concentrations was observed (r = 0.97), but between plutonium and organic matter this was rather poor (r = 0.63). River sediment contamination with heavy metals: Mn, Zn, Pb, Cu and Ba does not exceed the permissible concentration limit in sewage sludge introduced to soil. Mean values of metal concentrations found are: 242 ppm Mn, 313 ppm Zn, 95 ppm Pb, 72 ppm Cu and 274 ppm Ba. Samples collected from the same points after a 4-year period do not reveal large differences in comparison with old ones.

Keywords: plutonium isotopes, heavy metals, river sediments.

Introduction

Lublin city is situated on Bystrzyca River, a left tributary of the Wieprz River, in the place where two other rivers (Czechowka and Czerniejowka) meet the Bystrzyca. South of Lublin there is an artificial lake - Zemborzycki Zalew - formed on Bystrzyca in 1974. The area of the lake is about 2.8 km^2. The main Lublin river, Bystrzyca (a total length of 74 km) travels 22.5 km inside the city borders. Width of the river ranges from 4 m to 15 m, and in flood-controlled segments equals about 10 m. The two other rivers Czechowka and Czerniejowka, have total lengths of 17.5 km and 32 km, respectively; their lengths within Lublin are 9 km and 7.5 km, respectively.

Water flow in the rivers differs markedly from each other. The average water-flow of Bystrzyca is 3 m^3/s, Czechowka 0.3 m^3/s, and Czerniejowka 0.7 m^3/s [1].

Main sources of river pollutants in Lublin agglomeration are municipal sewage, industrial wastes drained off at 4 points directly into Bystrzyca (or after purification by the Hajdow sewage-treatment plant at a northeastern city border), and 140 points of rain-sewage. Amounts of wastes, drained off annually into Lublin rivers, were about 5.3 •10^7 m^3 (in 1986), 3.5•10^7 m^3 (in 1990), 3.9•10^7 m^3 (in 1991), 3.8•10^7 m^3 (in 1993), and 3.2 •10^7 m^3 (in 1995) [1-3].

Municipal and industrial wastes not purified by the Hajdow sewage-treatment plant (and rain-sewage) introduce into rivers large amount of pollutants in both soluble and suspended forms. The suspended material in the wastes comes up to 200-300 g/m^3. Solid matter content in wastes after purification is about 5 times lower.

During the last several dozen years a continuous water--flow reduction has been observed in Lublin rivers and drainage of river valleys as well. This phenomenon is firstly a result of making of the artificial lake, Zemborzycki Zalew, which cumulates of 6.3 • 10^6 m^3 of water and facilitates water infiltration down the subsoil and evaporation from the surface.

Secondly, continuous introducion of municipal and industrial wastes through the years has contributed to water-flow reduction and formation of a rather thick bottom sediment layer (up to 30 cm). The sediment is composed of

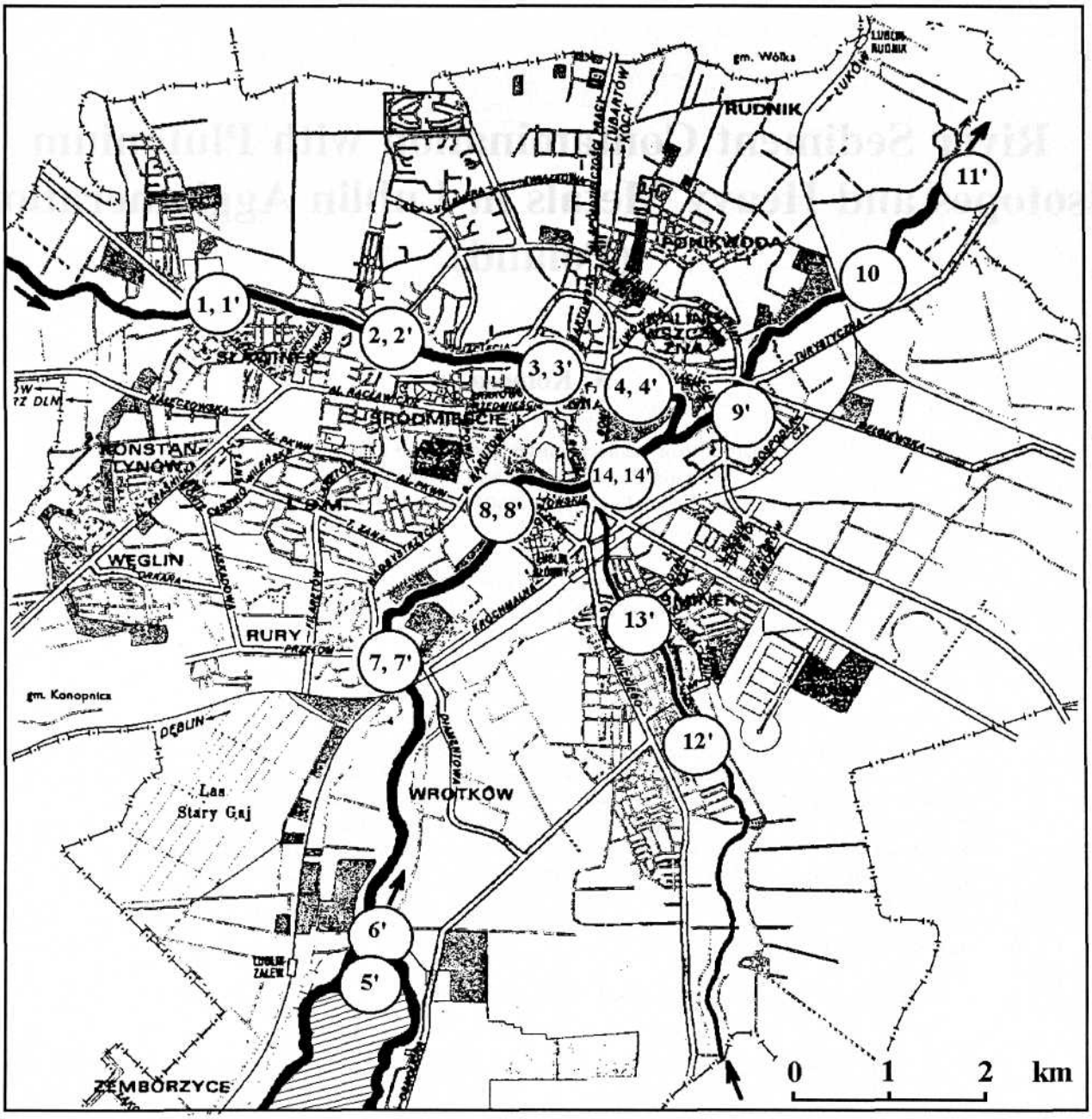

Fig. 1. Map of Lublin showing the location of sediment sample collection points. Arrows show river water-flow direction. Between points 3 and 4 the Czechowka River is covered.

loess clay with an admixture of sand and organic substance. Sediment can be a potential source of secondary water contamination with heavy metals and radionuclides.

Concentration of gamma emitting natural and anthropogenic radionuclides coming from natural uranium series: ^{226}Ra, ^{234}Th, from natural thorium series: ^{224}Ra, ^{228}Ac, and ^{137}Cs and ^{40}K were determined earlier in bottom sediments of Lublin rivers [1].

This paper presents results of determination of heavy metal concentration and highly toxic alpha radiating nuclides - plutonium isotopes in sediments of Lublin agglomeration rivers.

The plutonium isotopes presence in the soil and sediments of the Lublin region is due to global radioactive atmospheric fallout and Chernobyl. Plutonium isotopes presence is a result of nuclear weapons testing from the end of World War II up the '80 s. They reached a maximum intensity in 1954-1963. Until 1980 449 tests were done in the atmosphere, mainly above northern hemisphere [4]. In this way the estimated quantities of alpha emitting plutonium isotopes were introduced into the environment: $1.3 \cdot 10^{16}$ Bq ^{239,240}Pu and $3 \cdot 10^{14}$ Bq ^{238}Pu [5, 6]. Chernobyl fallout occurred in 1986 because of the reactor core burnt up with emission of its constituents into the atmosphere. Among other nuclides plutonium isotopes (about $7.2 \cdot 10^{13}$ Bq ^{239,240}Pu and $3.5 \cdot 10^{13}$ Bq ^{238}Pu) were emitted.

Plutonium presence in river sediment is a result of direct radioactive fallout from the atmosphere into the river

and of entering with wastes introducing to the river. Amount of radioisotopes depends on physicochemical conditions in sediment, such as pH of water, redox potential, presence and concentration of organic and inorganic complexing agents, etc., which control the existence of soluble ionic forms of plutonium and dissolution of plutonium being in the form of a precipitate [7, 8].

Studies concerned with plutonium isotope determination in samples of different type of soils collected in the area of the Lublin region in 1993 and 1994 were presented in my earlier paper [9], It was concluded that Pu radioactivity in surface layer (0-2 cm) of a different type of soil does not vary to a large extent. Average value of ^{239,240}Pu was equal to 0.21 ± 0.08 Bq/kg, and of ^{238}Pu 0.02 + 0.02 Bq/kg [9].

Methods and Materials

Sample Collections and Characterization

Sediment samples were collected in June '92 and in November '96 by using an auger of 8.3 cm diameter and 10 cm height, according to EML [10]. The samples were taken near a riverside. A few cores are treated as one sample. The samples were air-dried, ground, sieved (< 1 mm) and stored in plastic containers for further study.

Points of sample collection are shown on the map of Lublin agglomeration presented in Figure 1.

Samples are characterized by determination of contents of a total organic matter, and quantitative chemical composition (by means of X-ray fluorescence spectrometry). Total organic substance contents was calculated as a weight loss, during overnight ashing of a soil sample in 450"C.

Major and trace element contents in samples were determined using an Energy Dispersive XRF spectrometer. A sample preparation method was as follows: 2 g of the sample was accurately pulverized and a pressed pellet was prepared. Measurements were performed with a Canberra XRF System 100 with an Si(Li) detector (an active area of 30 mm^2, a thickness of Be window 0.025 mm and a FWHM resolution at 5.9 keV equals to 156 eV) using ^{109}Cd and ^{24l}Am as excitation sources. Quantitative analysis was performed applying the AXIL software (Canberra-Packard, Belgium) and using calibration curves for all analyzed elements.

Method of Plutonium Isotopes Determination and Counting Equipment

To separate plutonium isotopes for alpha spectrometry measurement a procedure detailed below was used.

Into the dry mineralized sample (50 g dry weight) the tracer ^{242}Pu was added (about 0.1 Bq/kg of sample). Next, leaching with 6M HCl was done by boiling the sample on a sand bath for an hour. After filtration an ammonia was added to the solution to precipitate all slightly soluble hydroxides. In this step alkaline and alkaline earth metals were removed by filtration of the hydroxides. After the dissolution of the precipitate in 6M HC1 a small quantity of calcium ions was added and calcium oxalate precipitated. The next step consists of oxalate destroying by dry ashing, dissolution in 8M HNO_3 and co-precipitation of Pu isotopes with ferric hydroxide.

Further separation of plutonium isotopes was performed on an anion exchange column filled with Dowex 1 x 8 using 8M HNO3 solution, according to Holm and Ballestra [11]. Washing the column with this solution caused removing, among others, iron and uranium ions. Next, thorium was eluted with concentrated HCl, then Pu was stripped by a mixture of concentrated HCl with ammonium iodide. Then a sample was transformed into a form suitable for alpha spectrometry measurement. The Puphal and Olsen electrodeposition procedure was used [12]. Plutonium was plated on a stainless steel plate from ammonium oxalate / hydrochloric acid solution. One minute before the end of electrodeposition ammonia solution was added to prevent a possible dissolution of Pu hydroxide (formed on the cathode) after disconnection of electrodes. Next, after washing the precipitate was fixed on the surface of the electrode by heating in a flame.

Alpha radioactivity of plutonium isotopes was measured (usually 150 + 170 hours) using two Canberra Alpha Spectrometers Model 7401 with a System 100 MCA Master Board for PC. The software SI00 and Alpha Spectroscopy Package (Canberra-Packard) was used. The PIPS detectors: A300-19-AM and A300-17-AM of a counting efficiency of about 35% were used.

The purity of the standard ^{242}Pu solution (AEA Fuel Services, U.K.) used as a radiochemical yield monitor, was < 0.1% of ^{238}Pu and ^{24l}Am, and < 0.01% of ^{239,240}Pu (as certified by the producer). Measured purity of the tracer solution was: 0.05% of ^{238}Pu and ^{241}Am, and 0.02% of ^{239,240}Pu Background values measured with a blank source in the ^{239,240}Pu peak region was about 0.012 cpm and 0.004 cpm (of the first and the second detector, respectively). In the ^{238}Pu peak region background was 0.002 cpm and 0.0005 cpm, respectively. Considering these background values the minimum detectable amount (MDA) of plutonium isotopes was calculated according to Boecker et al. [13]. The average MDA values for determination of ^{238}Pu and ^{239,240}Pu were equal to 0.004 and 0.010 Bq/kg, respectively.

To ensure proper quality of the results of Pu activity measurements a Soil-6 an IAEA Reference Material, was used. The method of separation and validity of alpha spectrometry measurement was checked by determining ^{239,240}Pu concentration in the Soil-6 sample (which is certified by IAEA). A difference between obtained result (1.09 ± 0.09 Bq/kg) and certified value (1.04 ± 0.07 Bq/kg) was treated as statistically insignificant (based on Student's t-test). Details of plutonium separation procedure and alpha spectrometry measurements are presented in earlier papers [9, 14].

Results and Discussion

Results of Heavy Metal Determination

Results of major and trace elements determination in sediment samples of Lublin agglomeration rivers are presented in Table 1. The samples were collected twice at the same place in 4-year interval (first collection in 1992, second in 1996). There is shown a percentage concentration of major element and organic matter entering into the composition of sediment, also selected trace element concent-

Table 1. Characterization of Lublin river sediment samples: organic matter contents (OM), major element (in percent of dry weight), and trace (in ppm) concentration. Number with an apostrophe denotes sample collected in 1996, all others were collected in 1992. Samples 1 —4': Czechowka river, samples 5' - 11': Bystrzyca river, samples 12' - 14': Czerniejowka river.

Sample No.	OM %	K %	Ca %	Fe %	Ti %	Mn ppm	Zn ppm	Pb ppm	Cu ppm	Ba ppm
1	9.2	1.5	4.1	1.7	0.26	310	250	120	60	n.d.
1'	7.3	1.2	2.3	2.2	0.26	470	190	60	40	350
2	1.0	1.0	1.7	0.5	0.11	160	40	30	20	n.d.
2'	7.5	1.5	3.8	1.8	0.39	580	470	110	110	410
3	1.2	0.8	2.3	0.6	0.08	130	200	70	40	n.d.
3'	3.9	1.1	2.1	0.9	0.12	240	230	40	60	210
4	0.5	0.8	1.6	0.5	0.05	110	190	30	30	n.d.
4'	4.4	0.8	1.8	0.7	0.13	< 90	280	60	80	280
5'	19.5	0.9	19.5	1.1	0.18	330	70	50	30	n.d.
6'	1.5	0.8	0.5	0.2	0.09	< 90	20	15	30	120
7	17.0	1.3	4.1	1.4	0.27	200	760	120	1300	n.d.
7'	2.8	0.7	1.3	0.4	0.11	< 90	80	60	60	150
8	7.2	1.5	3.9	1.1	0.27	210	120	40	30	n.d.
8'	0.8	1.0	1.0	0.5	0.12	< 90	50	20	30	160
9'	12.1	1.2	4.8	1.8	0.32	290	500	110	110	350
10	11.1	1.3	4.0	1.7	0.29	370	550	120	110	n.d.
11'	10.2	0.9	3.3	1.5	0.27	320	600	140	130	350
12'	14.0	1.5	4.9	1.9	0.37	280	830	360	150	370
13'	10.0	0.9	3.3	1.2	0.21	210	430	130	130	290
14	7.9	1.5	4.5	1.4	0.29	210	280	100	80	n.d.
14'	7.9	0.9	4.3	1.9	0.29	300	450	220	110	250

n.d. – not determined

ration (in ppm). Table 1 was divided in 3 parts: the upper one (samples No. 1-4) presents samples from Czechowka river; the middle one, from Bystrzyca river (samples No. 5-11); and the bottom one, from Czerniejowka river (samples No. 12-14). As can be seen in Table 1 a concentration of major elements does not reveal a significant variability between old and new samples (latters marked by an apostrophe). The largest changes are observed in organic matter contents (in two cases even 6 and 9 times: samples 7 and 8). The differences are a result of flood-control work performed between sampling periods, which caused a change in sediment thickness.

Concentration of heavy metals such as Mn, Zn, Pb, Cu and Ba were determined. The measured values are rather typical for this kind of material [16].

Manganese concentrations determined in sediment samples range from < 90 ppm to 580 ppm (mean value 242 ± 130 ppm). This is much below the limit recommended for plowing soils by the European Community, which is 3000 ppm [15, 16].

Zinc concentrations range from 40 ppm to 830 ppm (arithmetic mean 313 ± 248 ppm, geometric mean 214 ppm). The EC recommended level of 300 ppm is exceeded by 40% of the samples. These samples were taken from the Czerniejowka and Bystrzyca Rivers. However, zinc concentrations in all samples are smaller than permissible concentrations in municipal sewage sludge allowed to be introduced to soil (2000 ppm) [15].

Concentrations of lead vary from 15 ppm to 360 ppm (arithmetic mean 95 ± 79 ppm, geometric mean 72 ppm), and about 60% of samples do not exceed 100 ppm. As the EC recommended value is 250 ppm for soils, only one sample (No. 12') from the Czerniejowka River lies above this limit. All results are below the level of 1000 ppm, a permissible Pb concentration limit in the sludge [15].

Copper content in sediment samples ranges from 20 ppm to 1300 ppm. Almost all of the samples do not exceed the EC limit of 135 ppm for soils. Only one sample reveals a little higher value (No. 12' from Czerniej6wka River). Also, in one sample from Bystrzyca River an extremely high Cu concentration is observed (1300 ppm), supposedly caused by accidental contamination. Average value of Cu concentration (without sample 12') is equal to 72 ± 41 ppm, which does not exceed a limit of permissible concentration of 1000 ppm [15].

Values of barium concentration were determined only in samples collected in 1996. They show a small range of variability, a mean value of 274 ± 96 ppm.

Results of Plutonium Isotope Determination

The results of plutonium isotope (^{238}Pu and ^{239,240}Pu) determination are presented in Table 2. In the last column a calculated Chernobyl fraction of total ^{239,240}Pu radioactivity is shown. This fraction was calculated according to the Hirose formula [17] based on the ^{238}Pu to ^{239,240}Pu activity ratio, determined in the sample. It was assumed that the ratio for global fallout is 0.04 [18], and for Chernobyl 0.5 [17]. Average value of the Chernobyl fraction presented in Table 2 is equal to 13%. However, a value of ^{238}Pu /^{239,240}Pu ratio is sensitive on the accuracy of plutonium activity determination. This is especially important with the ^{238}Pu isotope because its concentration sometimes

Table 2. Results of plutonium isotope concentrations in Lublin river sediment samples. Number with an apostrophe denotes sample collected in 1996; all others were collected in 1992.

River name	Sample No.	^{239,240}Pu ± 1σ [Bq/kg]	^{238}Pu ± 1σ [Bq/kg]	Yield [%]	Chernobyl fraction of ^{239,240}Pu [%]
Czechówka	1	0.100 ± 0.003	0.009 ± 0.001	35	11
	1'	0.038 ± 0.007	0.005 ± 0.002	35	20
	2	0.043 ± 0.003	0.007 ± 0.001	43	27
	2'	0.087 ± 0.004	0.002 ± 0.001	69	0
	3	0.013 ± 0.001	0.001 ± 0.001	61	8
	3'	0.009 ± 0.003	0.001 ± 0.001	85	11
	4	0.010 ± 0.001	0.002 ± 0.001	37	35
	4'	0.012 ± 0.002	0.001 ± 0.001	53	9
Bystrzyca	5'	0.650 ± 0.060	0.017 ± 0.016	38	0
	6'	0.028 ± 0.003	0.003 ± 0.001	50	15
	7	0.021 ± 0.003	0.004 ± 0.002	63	33
	7'	0.030 ± 0.003	0.003 ± 0.001	59	13
	8	0.025 ± 0.001	0.002 ± 0.001	43	9
	8'	0.048 ± 0.004	0.048 ± 0.005	63	
	9'	0.071 ± 0.006	0.005 ± 0.002	46	7
	10	0.083 ± 0.007	0.016 ± 0.005	25	34
	11'	0.031 ± 0.003	0.004 ± 0.002	34	19
Czerniejówka	12'	0.101 ± 0.005	0.001 ± 0.001	42	0
	13'	0.062 ± 0.004	0.001 ± 0.001	41	0
	14	0.062 ± 0.002	0.002 ± 0.001	42	0
	14'	0.135 ± 0.007	0.010 ± 0.002	95	7

only slightly exceeds a minimum detectable amount. Thus, the calculated Chernobyl fraction can be treated as an information value only because of rather high uncertainty. Plutonium isotope concentration in sediment samples from three Lublin rivers does not differ considerably. Only in the Czerniejowka river a slightly higher average value is observed. Arithmetic mean values calculated (without sample 5' with especially high Pu concentration) is equal to 0.050 ± 0.036 Bq/kg ^{239,240}Pu and 0.005 ± 0.005 Bq/kg ^{238}Pu.

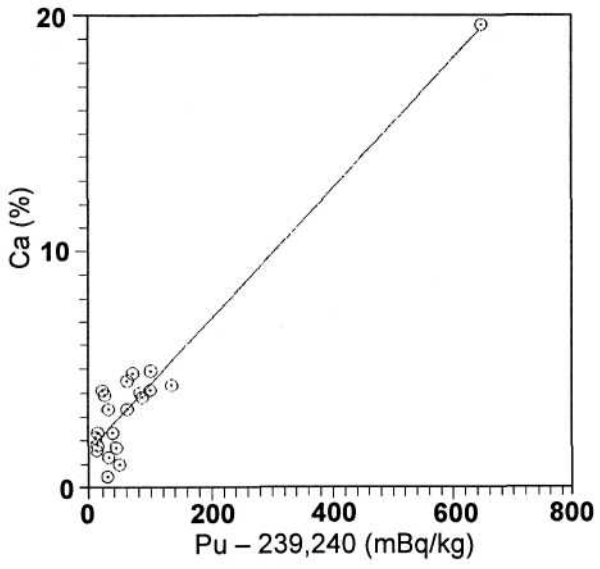

Fig. 2. Relationship between Ca concentration (in percent of dry weight) and ^{239240}Pu radioactivity in sediment samples of Lublin rivers. Linear correlation coefficient r = 0.97.

It is interesting to compare the amount of plutonium in sediment and in soil, collected simultaneously in the Lublin region [9]. Soil samples reveal a very close average Chernobyl fraction value (12%) to that of river sediments. However, mean concentrations of ^{239,240}Pu in soil is about four times higher than in sediment. Plutonium present in soil and sediment is of the same origin (global and Chernobyl fallout). Then the 75% of plutonium activity is supposed to be converted in a water soluble form, as an effect of different chemical reactions going on in soil and during treatment of sewage sludge.

Comparison of plutonium radioactivity (Table 2) with the concentration of major elements and organic matter (Table 1) enables us to search for a correlation between these values. An unexpected correlation between plutonium and calcium concentration in sediments was found (correlation coefficient r = 0.97). This relationship is drawn in Figure 2. On the other hand a rather poor correlation between Pu activity and organic substance contents was noted (r = 0.63). This is also an unexpected observation because, in common opinion, plutonium concentration in soil should correlate to the amount of organic substances. Organic substances bind plutonium ions in stable complexes [19-21]. A close correlation between plutonium and calcium provides evidence of the presence in sediment of the species, which can bind both elements simultaneously. It was recently discovered, that a major part of soil plutonium is incorporated into the compounds of humic acid with calcium, iron and aluminium ions and also into ferric and aluminium hydroxides [22].

Conclusions

The average radioactivity value of plutonium isotopes in sediments of Lublin agglomeration rivers is about four times smaller than their average concentration in soils. Plutonium concentration correlates closely with calcium content, but poorly with the quantity of organic substance. Contamination of sediments with heavy metals such as Mn, Zn, Pb, Cu and Ba does not exceed the EC permissible concentration limits in sewage and sludge introduced to soil. A regularity in plutonium and metal concentration variation between early and late sample collection was not discovered.

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