RADIONUCLIDE CONTENT IN LAUNDRY DETERGENTS COMMERCIALLY AVAILABLE ON THE SERBIAN MARKET AND ASSESSMENT OF RADIOLOGICAL ENVIRONMENTAL HAZARDS

by

Ivana S. VUKANAC [1], ***Aleksandar B. KANDIĆ*** [1*], ***Mirjana M. DJURAŠEVIĆ*** [1], ***Bojan Ž. ŠEŠLAK*** [2], ***Igor T. ČELIKOVIĆ*** [1], ***Aleksandar M. JEVREMOVIĆ*** [1], ***and Suzana A. BOGOJEVIĆ*** [3]

[1] Laboratory for Nuclear and Plasma Physics, Vinča Institute of Nuclear Sciences, University of Belgrade, Belgrade, Serbia
[2] Terrestrial Environment Laboratory, IAEA Environment Laboratories, Department of Nuclear Sciences and Applications, International Atomic Energy Agency, Vienna, Austria
[3] Serbian Institute of Occupational Health "Dr Dragomir Karajović", Belgrade, Serbia

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Laundry detergents are chemicals widely used in everyday life, and in numerous industry branches. In order to perceive the radiological aspect of environmental pollution by wastewater, the analysis of laundry detergents available on the Serbian market was undertaken. Laundry detergent samples were measured by means of gamma spectrometry and the results are presented in this paper. Analysis of the obtained activity concentrations showed that laundry detergents in Serbia mostly fulfill the international recommendation and requirements regarding the phosphate content. Besides that, the content of the detected radionuclides in laundry detergent samples indicates the minor radiological risk to the environment via wastewaters.

Key words: laundry detergent, gamma spectrometry, external radiation hazard index, radium equivalent activity

INTRODUCTION

The increasing pollution of the environment has been one of the greatest concerns for science and the general public in the last decades. The extensive use of fertilizers in agriculture and expansion of the chemical industry has caused the continuous release of man-made chemicals into natural ecosystems [1]. Consequently, the atmospheres, bodies of water and soil, have become polluted by a large variety of toxic materials. Some of these materials are resistant to physical, chemical, or biological degradation and thus, represent a considerable environmental burden.

There are some materials extracted for industrial use that contain radioactive substances at concentrations which cannot be disregarded. In some cases, industrial processing can lead to further enhancement of the concentrations in the product, by-product or in the waste materials.

Phosphate rock is used as a source of phosphorous for fertilizers, for making phosphoric acid and gypsum, and also for production of some laundry detergent ingredients. Ores typically contain a significant amount of uranium, thorium and radium [2] so, phosphate processing industry, usually as a result, has products and wastes containing radionuclides whose concentrations cannot be disregarded [3, 4]. In general, phosphate ores of sedimentary origin have higher concentrations of the uranium family nuclides. Eventually, products of the phosphate ore industry become somewhat enriched in uranium relative to the ore (up to 150 %), while approximately 80 % of ^{226}Ra, 30 % of ^{232}Th and 5 % of uranium are left in the phosphogypsum.

A study published by the UK Ministry of Agriculture, Food, and Fisheries [5] showed that the wastes from detergent manufacturing factory contained significant inventories of ^{226}Ra and thorium isotopes [6]. Similar environmental enhancements of natural decay series nuclides have been observed quite regularly in the vicinity of phosphate processing plants. The fertilizer and detergent industries are the main sources of the release of enhanced natural radioactivity in phos-

* Corresponding author; e-mail: akandic@vinca.rs

phatic wastes. Generally, releases of phosphate processing industry are directed mainly to air and water.

Environmental pollution with phosphates

Three main ingredients of laundry detergent, or washing powder, are builders (50 % by weight, approximately), the surfactant (8 %-18 %), bleaches and other miscellaneous ingredients (15 %-30 %). Phosphates (compounds with phosphorus, oxygen and sometimes hydrogen) are excellent builders [7], which are often used as either sodium tripolyphosphate (dry detergents) or sodium/potassium phosphates (liquid detergents) [8]. Phosphate detergents are generally safe to use with minimal toxicity problems. The major drawback is that secondary wastewater treatment removes only a small percentage of phosphorus from the influent. Thus, a considerable amount of polyphosphates may be introduced into the streams, rivers, lakes, and estuaries through wastewater effluent.

By its nature, laundry detergent usage is both widespread and diffuse, because these types of consumer products are typically used in homes, restaurants, hotels, hospitals, *etc*. and then disposed of in wastewater. Due to this diffuse distribution in the environment, the goal of related studies is to ensure that side effects to the environment are as low as possible. This is generally accomplished by limiting the ingredients volume to quantities that do not pose unacceptable risks to the environment [8, 9].

In order to provide a high level of environmental protection, the European Union introduced regulations to require biodegradability in all detergents in 2004 [5], with the intention to ban phosphates in household products. The EU took further steps in 2010 to prohibit the use of phosphates and restrict the amount of phosphorus-containing compounds in all laundry detergents sold in the European Union.

The aim of this study was to assess the potential radiation risk that can result from the presence of naturally occurring radioactive materials (originated from the raw materials that are usually considered as not radioactive) in laundry detergents available on the Serbian market and widely used as consumer products.

MATERIAL AND METHODS

Thirty one samples of different brands of laundry detergents were purchased at different stores in Serbia and were taken to the laboratory for analysis. Countries of detergent origin were Czech Republic, Croatia, Moldavia, Romania, and Serbia. The samples were placed in Marinelli bakers, sealed for six weeks and measured after reaching the radioactive equilibrium.

All the samples were measured with a coaxial, high purity germanium (HPGe) semiconductor detector (AMETEK-ORTEC GEM 30-70, with 37 % relative efficiency and 1.8 keV resolution for ^{60}Co at the 1332 keV line) and multichannel analyzer Canberra Multiport II. Measurements were performed in accordance with international recommendation [10]. The obtained spectra were recorded and analyzed using Canberra's Genie 2000 software, net areas of the peaks were corrected for the background, dead time and coincidence summing effects.

All the calculations were performed with the Mathematica 5.2 software (Wolfram Research, Inc.). In order to achieve acceptable statistics, the samples were measured from 65 000 s to 255 000 s. Reliable and accurate analysis of the recorded spectra requires good energy and adequate efficiency calibration. A Marinelli standard (silicone resin matrix – $\rho = 0.985$ 0.01 gcm^{-3}, spiked with common mixture of gamma ray emitters – ^{241}Am, ^{109}Cd, ^{139}Ce, ^{57}Co, ^{60}Co, ^{137}Cs, ^{113}Sn, ^{85}Sr, and ^{88}Y) certified by CMI was used for the HPGe detector efficiency calibration traceable to the Czech Metrological Institute [11]. Net peak areas of ^{60}Co and ^{88}Y were corrected for the coincidence summing effect applying the calculation method of Debertin and Schötzig [12]. The analytical expression of obtained efficiency curves was

$$\varepsilon \quad e^{P(\ln E)} \tag{1}$$

where ε is the detection efficiency, E – the energy, and $P(\ln E)$ – the polynomial function of the fifth order. The uncertainty of the efficiency calibration includes uncertainty of radionuclide activities in the standard, statistical uncertainty and fitting uncertainty of the efficiency curve.

RESULTS AND DISCUSSION

The activity concentrations of natural radionuclides ^{40}K and ^{226}Ra in laundry detergent samples were determined directly by analyzing full-energy peaks of their principal energies at 1460.83 keV and 186.21 keV, respectively. The activity of ^{40}K was corrected for the contribution of ^{228}Ac (1459.14 keV), which could not be resolved in the recorded spectra. For the same reason, the activity of ^{226}Ra was corrected for the contribution of ^{235}U (185.72 keV) evaluated by measuring the ^{235}U photopeak at 143.77 keV, and additionally approved by analyzing activity concentrations of its descendants ^{214}Bi (609.31 keV, 1120.29 keV, and 1764.49 keV), as well as ^{214}Pb (295.21 keV and 351.92 keV). The activity concentration of ^{238}U was determined via its descendant ^{234m}Pa (1001.01 keV and 766.42 keV resolved from photopeak of ^{214}Bi at 768.36 keV), and approved by measuring the ^{234}Th photopeak at 63.3 keV. Furthermore, the activity concentration of ^{232}Th was determined by using the evaluated activity of its descendants ^{228}Ac (338.42 keV, 911.16 keV, and

968.97 keV), ^{212}Bi (727.25 keV), ^{212}Pb (238.58 keV), and ^{208}Tl (583.19 keV). The specific activity of ^{210}Pb was recorded at 46.5 keV (in the range of 2.6 Bqkg^{-1} to 19 Bqkg^{-1}) but, since the efficiency curve can only be extrapolated at this energy, which makes uncertainty very large, the results could not be taken into consideration.

Obtained results are presented in tab. 1. Reported specific activities are given with uncertainties (coverage factor $k = 2$) that included the statistical uncertainties and uncertainty of efficiency calibration. Total count rates in recorded spectra ranged from 0.02 s^{-1}kg^{-1} to 2.18 s^{-1}kg^{-1}. Specific activities were within the ranges (0.9-20.7) Bqkg^{-1} for ^{40}K, (0.05-8.6) Bqkg^{-1} for ^{226}Ra, specific activity concentrations of ^{238}U, ^{235}U, and ^{232}Th were up to 43.0 Bqkg^{-1}, 2.2 Bqkg^{-1}, and 1.5 Bqkg^{-1}, respectively. In all the measured samples, the content of the artificial radionuclide ^{137}Cs (661.62 keV) was below 0.04 Bqkg^{-1} (MDA ranged 0.02 Bqkg^{-1}-0.09 Bqkg^{-1}).

Considering the country of production, the highest content of ^{226}Ra, ^{238}U, and ^{235}U was measured in laundry detergents produced in Serbia, for ^{40}K the highest value was measured in the sample produced in Romania, and for ^{232}Th, the highest value was measured in the sample produced in Croatia (tab. 2). Analysis of the obtained results showed that laundry detergents mostly used in Serbia have a low content of radionuclides but still, considering the quantities used annually (our estimation ~ 10^7 kg), this aspect of environmental pollution through wastewaters cannot be neglected. Also, it should be mentioned that in facilities for wastewater treatment, during the technological

Table 1. Specific activity concentrations of loundary detergent samples, available on the Serbian market, with uncertainties given for coverage factor $k = 2$

Sample	Country of origin	^{226}Ra	^{238}U	^{232}Th	^{235}U	^{40}K
		Specific activity [Bqkg^{-1}]				
MERIX – white rose	Serbia	<0.1	5.0 1.0	0.14 0.08	0.23 0.10	9.1 1.0
ARIEL – mountain spring	Romania	0.94 0.12	<3	0.24 0.10	0.17 0.10	2.4 0.4
ARIEL – color & style	Romania	0.60 0.08	<2.23	0.42 0.16	0.04 0.02	1.25 0.16
Persil gold, business line, cold active	Moldavia	0.05 0.08	1.6 0.4	0.31 0.16	0.006 0.004	6.0 0.8
DUEL baby sensitive	Serbia	8.6 1.0	6 2	1.1 0.4	0.4 0.2	14.3 1.8
Persil gold brilliance	Serbia	1.63 0.2	<2.1	0.13 0.06	0.08 0.04	5.9 0.8
BONUX magnolia & spring flowers	Romania	3.3 0.4	2.8 1.0	0.11 0.08	<0.2	20.7 2.4
Axal, touch of nature	Serbia	3.9 0.6	<5	0.5 0.2	<0.3	14 2
Deus pure glow	Serbia	2.9 0.4	26 6	1.2 0.4	1.3 0.6	8.2 1.2
Rubel action fresh	Croatia	1.5 1.6	<3	1.5 0.4	0.13 0.10	1.7 0.2
Persil gold active	Moldavia	1.2 1.2	<2	<0.14	<0.11	5.4 0.6
Rubel total care active fresh	Croatia	0.7 0.4	3.8 1.6	1.0 0.2	0.22 0.26	2.3 0.4
ARO	Serbia	0.98 0.2	43 6	<0.2	2.0 0.4	5.4 0.6
Fax exotic dream	Croatia	1.35 0.16	0.37 0.10	<0.3	0.28 0.14	2.02 0.26
Merix crystal white	Serbia	2.2 0.3	<4	<0.4	<0.2	6.6 1.0
Merix baby soap	Serbia	1.06 0.16	<2	<0.2	<0.11	5.7 0.6
Tide alpine fresh	Romania	<1.2	<3	<0.2	0.07 0.04	2.7 0.4
DEUS infinity sense	Serbia	0.5 0.1	40 8	1.2 0.4	2.2 1.2	9.2 1.2
Tide absolute lemon fresh	Romania	<1	<2.3	<0.2	0.06 0.04	2.3 0.2
Ariel 3-D actives touch of lemon fresh	Czech Republic	<1.4	0.7 0.2	<0.3	0.13 0.06	5.2 0.6
Ariel 3-D actives with flowers	Romania	<1.2	<2.7	<0.3	<0.15	2.3 0.2
Ariel 3-D actives	Czech Republic	1.3 0.2	4.8 1.0	0.4 0.2	0.14 0.06	5.9 0.6
Ariel Color and style 3-D actives 3 kg	Romania	<0.7	6.2 1.4	0.5 0.2	0.24 0.02	5.3 0.6
Duel mountain fresh	Serbia	1.2 0.2	3.9 1.6	0.4 0.2	0.16 0.04	10.3 1.4
Rubel power fresh	Croatia	0.7 0.1	6.2 1.4	1.1 0.2	0.22 0.06	6.1 0.6
Fax super aktiv	Croatia	0.26 0.04	<1.6	0.5 0.1	<0.1	3.1 0.4
Faks with aloe vera	Croatia	0.16 0.04	1.4 0.4	<0.3	<0.2	0.9 0.1
Persil expert	Serbia	0.07 0.02	2.8 1.2	0.4 0.2	<0.2	5.5 0.8
Persil expert	Serbia	<0.5	6.0 2.4	0.7 0.4	0.2 0.2	3.5 0.6
Ariel mounting spring	Romania	0.43 0.04	1.5 0.4	0.4 0.2	0.1 0.1	6.7 1.0
Duel lily of the valley	Serbia	<0.3	1.7 0.4	0.3 0.2	<0.2	5.7 0.8

Table 2. Minimal and maximal values of specific activities of naturally occurring radionuclides measured in detergent samples of different origin*, available on the Serbian market, with uncertainties given for coverage factor $k = 2$

Country of origin		Serbia		Romania		Croatia	
		Specific activity [Bqkg^{-1}]					
^{238}U	Min	1.7	0.4	1.5	0.4	0.37	0.1
	Max	43	6	6.2	1.4	6.2	1.4
^{226}Ra	Min	0.07	0.2	0.43	0.04	0.16	0.04
	Max	8.6	1.0	3.3	0.4	1.5	1.6
^{235}U	Min	0.08	0.04	0.04	0.02	<0.1	
	Max	2.2	1.2	0.24	0.02	0.28	0.14
^{232}Th	Min	0.13	0.06	0.11	0.08	<0.3	
	Max	1.2	0.4	0.5	0.2	1.5	0.4
^{40}K	Min	3.5	0.6	1.25	0.16	0.9	0.2
	Max	14.3	1.8	20.7	2.4	6.1	0.6

*Since there were only two samples from Moldavia and also, from Czech Republic, it was insignificant to show min-max values for those samples

processes involved in water purification, precipitation and accumulation, some radioactivity can occur, although the content of radionuclides is not expected to be high.

In order to acquire an indication of the value of doses that are due to the content of radionuclides in the samples of laundry detergents, radium equivalent activity (Ra_{eq} [Bqkg^{-1}]) and the external hazard index (H_{ex} [Bqkg^{-1}]) were calculated based on the obtained results. Calculated values of these indicators are presented in tab. 3.

The radium equivalent activity (Ra_{eq}) is used to assess the hazards associated with materials that contain ^{226}Ra, ^{232}Th, and ^{40}K. The definition of Ra_{eq} is based on the assumption that 370 Bqkg^{-1} of ^{226}Ra produce the same gamma dose rate as 259 Bqkg^{-1} of ^{232}Th or 4810 Bqkg^{-1} of ^{40}K. Thus, Ra_{eq}, besides the specific activity of Ra, includes also the specific activities of Th and K.

The external radiation hazard index (H_{ex}) is used to estimate the external radiation hazard due to the emitted gamma radiation.

Radium equivalent activity (Ra_{eq}) and external radiation hazard index (H_{ex}) were calculated according to the following equations

$$Ra_{eq} \quad A(Ra) \quad 1.43A(Th) \quad 0.077A(K) \qquad (2)$$

$$H_{ex} \quad \frac{A(Ra)}{370} \quad \frac{A(Th)}{259} \quad \frac{A(K)}{4810} \qquad (3)$$

Table 3. Ranges and average values of calculated radium equivalent (Ra_{eq}) and external hazard index (H_{ex}) for laundry detergent samples available on the Serbian market

	Minimum	Maximum	Average
Ra_{eq} [Bqkg^{-1}]	0.7	11.3	2.5
H_{ex} [Bqkg^{-1}]	0.002	0.03	0.007

where A(Ra) [Bqkg^{-1}] is the specific activity of ^{226}Ra, A(Th) [Bqkg^{-1}] – the specific activity of ^{232}Th, and A(K) [Bqkg^{-1}] – the specific activity of ^{40}K.

From tab. 3 it can be seen that the Ra_{eq} values for the detergent samples are very low and that none of them exceeds the suggested maximal admissible value of 370 Bqkg^{-1}. Also, all the obtained values for H_{ex} are much lower than unity.

CONCLUDING REMARKS

The aim of this paper is to bring attention to the possible radiological pollution of the environment caused by ingredients from laundry detergents and other household products. Such products are typically manufactured in large quantities, used by many people, and disposed of, after usage, into the environment via the sewer. The vast majority of this waste stream is treated via wastewater treatment plants.

Concern for the environment, in some countries, has resulted in the existence of strict legislation which is referred to wastewater treatment and whose application is leading to a significantly reduced entry of chemical substances in the surface waters and so, has become an intrinsic part of exposure and risk assessment of household chemicals [13].

The experimentally obtained activity concentrations showed that laundry detergents used in Serbia represent a minor radiological risk to the environment via wastewaters. It would be interesting to compare our results with investigations from other European countries unfortunately, the authors could not find any data on radionuclide content of detergents produced and sold in Europe.

Results given in this paper could be of great importance in terms of providing input data into mathematical models used in theoretical calculations and predictions related to the presence of radionuclides in the aquatic environment, their distribution and concentrations, as well as their applicability to predict the transfer of radioactivity in the environment. The obtained results can also be useful in assessing radiation risk in the working environment in chemical industries, and also in the evaluation of accumulation of radioactivity in sewage wastewater treatment facilities. In addition, the observations presented in this paper emphasize the radiological aspect of environmental pollution by wastewater, which has been mainly neglected in research related to the subject.

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AUTHORS' CONTRIBUTIONS

The idea for the study was put forward by I. S. Vukanac and A. B. Kandić. The measurements were carried out by M. M. Djurašević, I. S. Vukanac, B. Ž. Šešlak, and A. B. Kandić. The theoretical calculations were carried out by M. M. Djurašević, I. S. Vukanac, A. S. Kandić, and S. A. Bogojević. The samples were obtained and prepared by M. M. Djurašević, I. S. Vukanac, B. Šešlak, I. T. Čeliković, A. M. Jevremović, and A. B. Kandić. The paper was written by I. S. Vukanac and S. A. Bogojević. All the authors were engaged in interpretation and evaluation of the results.

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Ивана С. ВУКАНАЦ, Александар Б. КАНДИЋ, Мирјана М. ЂУРАШЕВИЋ, Бојан Ж. ШЕШЛАК, Игор Т. ЧЕЛИКОВИЋ, Александар М. ЈЕВРЕМОВИЋ, Сузана А. БОГОЈЕВИЋ

САДРЖАЈ РАДИОНУКЛИДА У ДЕТЕРЏЕНТИМА ЗА ПРАЊЕ ВЕША КОМЕРЦИЈАЛНО ДОСТУПНИМ НА СРПСКОМ ТРЖИШТУ И ПРОЦЕНА РАДИОЛОШКЕ ОПАСНОСТИ ПО ЖИВОТНУ СРЕДИНУ

Детерџенти за веш су хемикалије које се широко користе у свакодневном животу као и у бројним гранама индустрије. Да би се сагледао радиолошки аспект загађења животне средине од отпадних вода, предузета је анализа детерџената за веш доступних на српском тржишту. Узорци детерџента мерени су гамаспектрометријски и резултати су приказани у овом раду. Анализа концентрације добијених активности радионуклида показала је да већина детерџената за прање рубља комерцијално доступних у Србији испуњава међународне препоруке и захтеве у вези са садржајем фосфата, тако да садржај детектованих радионуклида у узорцима детерџената за рубље представља мали радиолошки ризик по животну средину преко отпадних вода.

Кључне речи: детерџенти за прање рубља, гамаспектрометрија, индекс радијационог ризика, радијум еквивалентни индекс