METALS DETERMINATION IN MILICHOS RIVER WATER AND NATURAL RADIONUCLIDES IN MILICHOS SEDIMENTS (PATRAS, GREECE)

SOUPIONI M., PHILIPPOU A., ILIEVA V. and PAPAEFTHYMIOU H.

Nuclear Chemistry Laboratory, Section of Physical, Inorganic and Nuclear Chemistry, Department of Chemistry, University of Patras, Rio-Patras, GR 26504, GREECE
E-mail: m.soupioni@chemistry.upatras.gr

ABSTRACT

Milichos is a small river near Patras, the capital of Peloponnese, which flows into Patraikos Gulf. It crosses an area near a sanitary landfill, characterized for agricultural, domestic, and traffic activities resulting in pollution of the river.

Heavy metals and radionuclides are considered the most important pollutants, because of their toxicity and accumulation by living organisms, as well as the radiation which contributes to the total dose of the people.

In the present study Ca, Fe, Mg, Pb, Zn and SO_4^{2-} concentrations were measured in water samples of Milichos River and the activity concentration values of the natural radionuclides ^{238}U, ^{232}Th, ^{226}Ra, ^{40}K and of the artificial radionuclide ^{137}Cs were determined in Milichos sediments.

River water and sediment samples were collected from December 2012 until December 2013 three times per month. Metal concentrations were determined by Flame Atomic Absorption Spectrometry, (FAAS) and SO_4^{2-} concentrations by a standard spectroscopic method. The activity concentration measurements were performed by γ-ray spectrometry, using an HPGe detector and the IAEA GANAAS package. The measurements accuracy was estimated against the IAEA-312 and IAEA-375 reference materials.

The results revealed that in river water during the year 2013 the Ca Mg and SO_4^{2-}concentrations were almost the same with those of relative studies, while the Fe, Pb and Zn concentrations were found to be under the detection limits of the spectrometer. Also, in the river sediment samples the activity concentrations of ^{238}U, ^{232}Th, ^{226}Ra, ^{40}K and ^{137}Cs were generally close to the Greek average values for soil.

Keywords: Milichos River (Greece); metals determination; natural radionuclides; activity concentration; γ-ray spectrometry

1. Introduction

The small river Milichos, stems from the north side of Panachaiko Mountain and through Sichena village drains into the northeast side of Patraikos Gulf near Patras, the capital of Peloponnese (Fig. 1). The river crosses an area characterized by its agricultural, domestic, and traffic activities near the Xerolakka sanitary landfill with operational problems. As Milichos carries into the sea large amounts of water and sludge, containing probably urban and agricultural wastes, routine monitoring of contaminants in its water and its estuary sediments is required.

Data for the Gulf of Patras have been already presented (Papaefthymiou *et al.*, 2007; 2010; Kousi *et al.*, 2011), but there is a need for more detailed knowledge obtained through temporal surveys for the water and sludge quality flowing into sea.

Metals and radionuclides can enter the living organisms by the food chain or by the ingestion of polluted water and can cause long-term effects on ecosystems. Specifically, in aquatic environment

heavy metals in high concentrations are considered the most important pollutants, because of their toxicity and accumulation by marine organisms consumed by people. Also, the radiation emitted by radionuclides in river sediments may have a contribution to the collective dose of the population.
In the present work the concentrations of Fe, Ca, Mg, Cu, Pb and SO_4^{2-} were determined in Milichos River water samples, collected near its estuary, in different months. Also, the activity concentration values of the natural ^{238}U, ^{232}Th, ^{226}Ra, ^{40}K and artificial ^{137}Cs radionuclides were measured in sediments of the river at the same area. The ^{137}Cs has a half-life of about 30 years and can be found in the nature as a result of the fallout of atmospheric nuclear bomb tests and in 1986 following the Chernobyl nuclear power plant accident.

Figure 1: Schematic map of the study area
(Milichos River, Patras, Greece)

2. Methodology

In the present study all the used containers and laboratory glassware were made from polyethylene, PTFE or silica. Before use they had been washed with detergent, acid-soaked, and rinsed repeatedly with ultra pure water obtained by a Milli-Q water purifier system (resistivity 18.2 MΩ.cm^{-1})

2.1. Sampling

Three surface river water samples per month were collected from the point of interest (Fig.1) on December 2012 until December 2013, except January 2013, March 2013, August 2013 and September 2013, because of the difficult weather conditions. Also, one sample of sediment per same month was collected from the same point, near the Milichos River estuary in Patraikos Gulf. In winter months the temperature of river water was found about 8-15°C, in spring 17-19°C, in summer 26-31°C and in autumn 12-17°C. The pH value in all seasons was around 8.

2.2. Metal analysis

The collected river water samples were acidified with Suprapur 65% HNO_3 and were stored in polyethylene bottles until their analysis. Before measuring, all samples were filtered using cellulose membrane filters (0.45 μm). Finally, the concentration of Ca, Fe, Mg, Pb and Zn were measured by Flame Atomic Absorption Spectrometry (FAAS) using a Shimadzu (AA-6500) spectrophotometer equipped with SR hollow cathode lamps for good background correction and corrosion resistant nebulizer. Analytical precision was better than 10% on the basis of replicate analyses.

2.3. Sulphate analysis

In collected river water samples the concentrations of SO_4^{2-} were determined using the spectrophotometer DR4000 PROCEDURE and the SoulfaVer 4 mixture.

2.4. Natural radionuclides and ^{137}Cs analysis

The collected sediment samples were first air dried, crushed to fine powder, homogenized and were finally dried at 105°C to constant weight. Then, samples were packed into cylindrical containers, weighted, sealed hermetically and stored for a minimum period of 3 week prior counting, in order to establish secular radioactive equilibrium between ^{226}Ra and its short-lived daughter products. Both energy and efficiency calibration procedures and activity concentration measurements are described in detail elsewhere (Papaefthymiou *et al.*, 2010). Briefly, all countings were performed using Canberra HPGe detector and minimum counting time of 24h. The spectra were analyzed using the GAMANAL routine, included in the GANAAS package, distributed by IAEA, while peak areas were determined using the Ganaas 3.1 computer program of IAEA. The accuracy was estimated against the IAEA-312 and IAEA-375 reference materials.

2.5. Statistical analysis

The statistical treatment of the data, including summary statistics and one-way analysis of variance (ANOVA) was performed using the SPSS v.15 software package.

3. Results and discussion

In Table 1 only the concentrations of Ca and Mg in Milichos River water samples are shown, because the concentrations of Fe, Pb and Cu were found to be under the detection limit of the spectrophotometer (0.003, 0.001 and 0.01 ppm, respectively). The results illustrated that the Ca concentrations were higher during winter and autumn compared with those during summer and spring. But, the statistical treatment showed that the differences in Ca concentrations in relation with the months were not statistically significant ($p<0.001$). Also, the Mg concentrations were almost the same except on December 2012 and October 2013, where the highest and the lowest value were appeared respectively. Instead, Mg concentrations in relation with the months were statistically significant ($p=0.293$).

Table 1: Average monthly (n=3) concentrations (in ppm ± SD) of metals in Milichos River water (Patras, Greece).

Month	Fe	Ca	Mg	Cu	Pb
December 2012	UDL	95.8 ± 6.0	0.46 ± 0.10	UDL	UDL
February 2013	UDL	91.9 ± 5.6	0.41 ± 0.10	UDL	UDL
April 2013	UDL	87.4 ± 2.7	0.37 ± 0.05	UDL	UDL
May 2013	UDL	77.8 ± 5.9	0.33 ± 0.22	UDL	UDL
June 2013	UDL	63.2 ± 4.4	0.33 ± 0.07	UDL	UDL
July 2013	UDL	63.2 ± 11.3	0.36 ± 0.02	UDL	UDL
October 2013	UDL	84.8 ± 12.5	0.28 ± 0.07	UDL	UDL
November 2013	UDL	121.9 ± 7.0	0.39 ± 0.01	UDL	UDL
December 2013	UDL	98.6 ± 15.9	0.31 ± 0.15	UDL	UDL

UDL: Under detection limit, SD: Standard deviation

It is remarkable that the measured metal concentrations for Milichos River water samples were found to be about 50% reduced, compared to those of Glafkos water at estuary in Patraikos Gulf (Kousi *et al.*, 2011). Also, from Table 2 is obvious that the sulphate concentrations for Milichos are lower compared with those of Glafkos River, located near Patras too (Mandilaras 2005). Sulphates are present in the river water, as constituents in minerals. They also can be found in agricultural wastes or acid rain (H_2SO_4).

Table 2: Average monthly (n=3) concentrations (in mg/L ± SD) of sulphate anions in Milichos River water samples (Patras, Greece).

Month	**SO_4^{2-}**	**Month**	**SO_4^{2-}**
December 2012	52.73 ± 3.35	July 2013	53.53 ± 1,46
February 2013	51.60	October 2013	27.33 ± 22.06
April 2013	47.58 ± 1.82	November 2013	61.30 ± 7.53
May 2013	43.00 ± 4.70	December 2013	42.00 ± 0.70
June 2013	33.83 ± 13.60		

The average activity concentrations of the natural radionuclides ^{238}U, ^{232}Th, ^{226}Ra, ^{40}K in nearshore sediments of Milichos River are shown in Table 3. Also, Table 3 presents the average activity concentrations of the natural radionuclides of different Greek areas, as well as the world and Greek average values for soil (UNSCEAR 2000). Generally speaking, all the natural radionuclides concentrations in Milichos River sediments are lower than those measured in other coastal areas of Greece.

Finally, the ^{137}Cs average activity concentration in Milichos River sediments was (1.10 ± 0.21) $Bq.kg^{-1}$ and in some samples it was under the minimum detectable activity, MDA (MDA: 0.35 $Bq.kg^{-1}$). The lowest value of ^{137}Cs activity concentration was (0.43 ± 0.10) $Bq.kg^{-1}$ and the highest one was (2.1± 0.90) $Bq.kg^{-1}$

4. Conclusions

The determined Ca and Mg and sulphate concentrations in Milichos River water on December 2012 until December 2013 (except January 2013, March 2013, August 2013 and September 2013) could be considered as normal in rivers.

Table 3: The average activity concentrations (lower-highest value) of ^{238}U, ^{232}Th, ^{226}Ra and ^{40}K ($Bq.kg^{-1}$) in nearshore sediments of different Greek areas.

Greek Area	**^{238}U**	**^{226}Ra**	**^{232}Th**	**^{40}K**	**Sample type**	**Reference**
Cyclades islands	67(29-110)	26(7-159)	31(4-106)	666(189-1214)	Nearshore sediments	Florou *et al.* (1988)
Milos island		70(16-119)	75(19-152)	890(158-3893)	Nearshore sediments	Florou and Kritidis (1991)
Gulf of Corinth	79.5(13,1-399.8)	48.7(12.9-185.2)	85.5(15.1-412)	318,8(28.3-539.9)	Nearshore sediments	Papatheodorou *et al.* (2005)
Patras Harbour	21.8(13,6-33,3)	24.5(16.6-34.1)	24.5(16.6-34.1)	497(327-763)	Nearshore sediments	Papaefthymiou *et al.* (2007)
Greek Average	25(1-240)	25(1-240)	21(1-190)	360(12-1570)	soil	UNSCEAR 2000
World Average	35(16-110)	35(17-60)	30(11-64)	1700(140-850)		UNSCEAR 2000
Glafkos River	27	18	21	327	sediments	K.Kousi *et al.* 2011
Glafkos estuary	37	30	37	578	sediments	K.Kousi *et al.* 2011
Milichos River	7.9(4-10.5)	9.02(7-15)	7.5(5.5-12)	178.3(118-265)	sediments	This study

Unlike the Ca concentrations, the Mg ones in river water samples were statistically significant in relation with the months. Also, the activity concentrations of ^{238}U, ^{232}Th, ^{226}Ra and ^{40}K in Milichos River sediments were lower than the Greek average for soil, while the ^{137}Cs activity concentration was relatively low.

REFERENCES

1. Florou H., Kritidis P. (1991), Natural radioactivity in environmental samples from an island of volcanic origin (Milos, Aegean Sea), Marine Pollution Bulletin, 22 (8), 417-419
2. Florou H., Kritidis, P., Pavlakis P., Veldeki K. (1988), Enhanced natural radioactivity in some areas of the Aegean Archipelagos. In: Proceedings of the International Conference on Environmental Radioactivity in the Mediterranean Area, Barcelona, 10-13 May
3. Kousi K., Soupioni M., Papaefthymiou H. (2011), A preliminary study for metal determinations in Seawater and Natural Radionuclides in Sediments of Glafkos estuary in Patraikos Gulf (Greece), In: Advances in the Research of Aquatic Environment, Volume 2, Editors: Nicolaos Lambrakis, George Stournaras, Konstantina Katsanou., Published by Springer-Verlag, Berlin Heidelberg, (ISBN: 978-3-642-24075-1, eISBN: 978-3-642-24076-8, DOI:10.1007/978-3-642-24076-8)
4. Mandilaras, D. (2005), Environmental-Hydrogeological study of Glafkos River. PhD thesis, University of Patras.
5. Papaefthymiou H., Papatheodorou G., Moustakli A., Christodoulou D, Geraga M (2007), Natural radionuclides abd 137Cs distributions and their relationship with sedimentological processes in Patras Harbour, Greece. J. Environ. Radioactivity, 94, 55-74
6. Papaefthymiou H., Papatheodorou G., Christodoulou D., Geraga M., Moustakli A., Kapolos J. (2010), Elemental concentrations in sediments of the Patras Harbour, Greece, using INAA, ICP-MS and AAS. Microchemical Journal, 96, 269–276
7. Papatheodorou G., Papaefthymiou H., Maratou A., Ferentinos G. (2005), Natural Radionuclides in bauxitic tailings (red-mud) in the Gulf of Corinth, Greece. Radioprotection, 40, 549-555
8. UNSCEAR (2000), Sources and Effects of Ionizing Radiation. United Nations Scientific Committee on the effects of atomic radiation. Report to General Assembly with Scientific Annexes. United Nations, New York