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RADIONUCLIDES AND POTENTIALLY TOXIC ELEMENTS IN SEDIMENTS FROM THE NORTHERN BULGARIAN BLACK SEA COAST

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Abstract

This paper presents data on the content of toxic elements (Mn, Ni, Zn, Cu, Pb, As, Cr, Cd and Co), technogenic (^{137}Cs, ^{134}Cs) and natural radionuclides of the ^{238}U and ^{232}Th series (^{234}Th, ^{226}Ra, ^{210}Pb, ^{232}Th) and ^{40}K in sediments collected from ten sampling stations along the northern Bulgarian Black Sea coast for a period of more than twenty years. Measurements were made by Gamma Spectrometry and Inductively Coupled Plasma Mass Spectrometry. The results show that the nuclides and toxic elements concentration in sediments strongly depend on the sediments nature. The obtained data create a database on the concentrations of radionuclides and toxic elements in sediments from the Northern Bulgarian Black Sea coast and can be used for assessment of the ecological status of the marine environment along the whole northern coastal zone.

Key words: Black Sea, sediments, radionuclides, toxic elements

Introduction. The potentially toxic pollutants releases due to human activities in the marine ecosystems lead to a change in contamination level and may affect the composition of species in the marine environment [1,2]. Receiving relevant information for radionuclide and toxic element concentrations in coastal sediments is an important stage in realization of monitoring and control of the

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marine ecosystem [3,4]. The accumulation of radionuclides and toxic elements in the sediments in coastal areas makes them a potential hazard for marine ecosystems, as the sea water is constantly in contact with organic and inorganic matter from the sediments.

It is well known that the Black Sea is one of the most isolated sea basins in the world and is characterized by special ecological conditions (low salinity and H_2S accumulation below 150–200 m). Its hydrology and phytobenthos content is different from other seas in the same geographical region [5,6]. The main sources of pollution are local industry, atmospheric fallout and the input of big rivers in the north-west corner of the Black Sea. Anthropogenic toxic elements and nuclides are among the most studied contaminants in the Black Sea ecosystems. Their effect is through direct poisoning as well as by accumulation and transfer along the trophic chain, by which they influence the functioning of biosphere. Metals and radionuclides can settle in sediments in the process of mixing of fresh (from rivers) with saline waters or be sorbed by plankton cells.

It is known that the Black Sea was heavily affected by the Chernobyl accident (1986). Due to its geographical proximity to the reactor, a large amount of direct atmospheric radionuclide sludge enters it [7,8]. Chernobyl nuclides entered the marine environment mostly in the northwest corner of the Black Sea carried by the big rivers Dnieper, Dniester, Danube.

Some authors [9–12] have performed measurements on the Bulgarian Black Sea coast in different coastal locations. However, contemporary data for the ecological status of the whole coast are quite few. There are also no data on the content of radionuclides and toxic elements in sediments obtained from a systematic long-term monitoring of the Bulgarian coast. The lack of information about the current state of the coastal zone and changes in the ecological situation as a result of climate change and anthropogenic factors is the reason to start our systematic studies of the transport and accumulation of radionuclides and toxic elements in sediments from the Bulgarian Black Sea coastal zone. This article reports data on the content of toxic elements Mn, Ni, Zn, Cu, Pb, As, Cr, Cd and Co, technogenic (^{137}Cs, ^{134}Cs), and natural radionuclides of the ^{238}U and ^{232}Th series (^{234}Th, ^{226}Ra, ^{210}Pb, ^{232}Th), and ^{40}K in sediments collected from ten pre-selected sampling stations along the Northern Bulgarian coast for a period of more than twenty years.

The main objectives of our studies are to provide data for radionuclide and potentially toxic elements accumulation in Black Sea sediments and compare their concentration variations along the whole Northern coastline; to optimize and validate some of the well-known and widely used in practice radiochemical methods and to adapt them for the determination of trace concentrations of radionuclides and toxic elements in small marine samples; to establish the typical values for different sediment types at the Bulgarian Black Sea coast to enable the modelling of radionuclide transfer from the sediments to biota; to determine the local and sea-

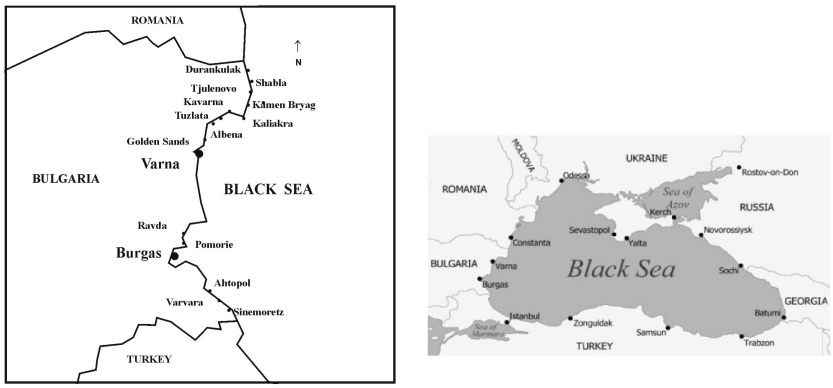

Fig. 1. Black Sea coast – sampling stations

sonal contaminants concentration variations and to obtain a reliable information about the potential hazards of marine ecosystems.

Experimental. In order to assess the contaminants concentration variations, their accumulation and influence on marine ecosystems, sampling was carried out during the spring-summer and autumn periods from 1991 to 2002 (12 years) and in 2005, 2008, 2010, 2012, 2015 and 2018. For the entire observation period, 36 samples were examined in each of the studied locations. The sediments collected at Kaliakra during the period 1991–2002, in 2005 and 2010 were analyzed for determination of Mn, Ni, Zn, Cu, Pb, As, Cr, Cd, and Co concentrations. On the basis of the obtained data, estimates were made of the mean values and the intervals of variation (range: minimum –maximum value) of the studied radionuclides in each location.

Sampling was done with the help of colleagues from the diving section of the National UNESCO Club for Scientific Expeditions (NNEK), Sofia and by the colleagues from the Institute of Oceanology – Varna.

Samples (sand, clay and silt) were taken from the sea shelf at depth 2–20 meters below the sea level and at distance up to 2000 m from the shore line to avoid the direct influence of the surf. Deep-sea marine sediments (150–2040 m depth) were analyzed too.

Samples were collected the upper layer of sediments from approximately 1 m^2 of the bottom acquiring about 2–3 kg of solid phase. The depth of the sample layer is about 3 cm to evaluate radionuclide content on the surface of the sea bed. In this way the potential seasonal variations could be estimated.

Measurements were made by Low-level Gamma Spectrometry and Inductively Coupled Plasma Mass Spectrometry (ICP-MS) for determination of radionuclides and toxic metals, respectively.

The gamma spectrometry measurements were carried out by means of two different gamma spectrometry systems during the years – HPGe detector (Ortec

type, 35% counting efficiency and energy resolution 1.8 keV at 1332 keV) and HPGe – GMX 50P4 detector (Ortec type, 54% counting efficiency and energy resolution 2.3 keV at 1332 keV). The obtained spectra were processed with "ANA" and "WINNER" computer codes, respectively. The spectrometric systems were calibrated by energy and by efficiency with certified calibration sources with wide energy range.

The ^{137}Cs and ^{40}K specific activities were measured by their gamma-lines of 661.6 keV and 1460.7 keV. The ^{134}Cs was measured by gamma-lines of 604 keV and 796 keV. The ^{234}Th was measured by gamma-line at 63.3 keV. The ^{226}Ra content was determined indirectly from the lines of the ^{226}Ra daughters ^{214}Bi and ^{214}Pb. The ^{210}Pb content was obtained using the 46.8 keV peak. In the ^{232}Th series we determined ^{228}Ra by each of the its daughter lines – ^{228}Ac, ^{224}Ra, ^{212}Pb, ^{208}Tl and calculated the mean to obtain the ^{228}Ra content. The obtained values can be ascribed to the parent ^{232}Th, assuming equilibrium with its daughter ^{228}Ra. A more detailed description of the method used is given in our previous studies [13,14].

The ICP-MS measurements were carried out by VARIAN 820-MS ICP-MS spectrometer, with 90 degree reflecting ion optics, 27 MHz RF Generator, quadrupole mass filter and DDEM detector.

For determination of gamma radionuclides by Low-level Gamma Spectrometry all sediment samples were sieved to remove large particles and debris, dried at about 90–100 °C, homogenized and placed in special hermetic containers Marinelli type with volume 450 ml for a period of at least four weeks before the measurements. This procedure was applied to ensure the equilibrium within the Uranium decay series for estimation of the natural radioisotopes.

In order to determine the toxic elements, both partial and total dissolution have been performed prior to analysis.

Total dissolution: The samples were dried at 105 °C for 3 h. About 0.2 g of sample was accurately placed in a microwave pressure vessel and after addition of 4 ml of concentrated nitric acid and 0.5 ml of concentrated hydrofluoric acid was digested by using a progressively increasing microwave power. After cooling, the solutions were accurately diluted to 100 ml with water.

Partial dissolution: About 0.5 g of sample was digested by heating with 12 ml of aqua regia for 45 min, followed by evaporation almost to dryness. To the hot residue, 2.5 ml of concentrated hydrochloric acid and 2.5 ml of hydrogen peroxide were added, followed by accurate dilution to 50 ml with water.

Results and discussion. Cesium-137 is one of the most studied nuclides in the Black Sea environment after the Chernobyl accident. The increase of ^{137}Cs concentration in clay sediments and sorption on fine particles leads to cesium scavenging and occurrence at greater depths, which can be explained by physicochemical interaction processes of the soluble Cs forms with the surrounding media. In sand sediments Cs content does not change greatly while the process of Cs

accumulation is observed in clay and slit sediments. The results obtained for Cs isotopes (Table 1) show that the highest measured values are in the locations with clay type of sediments Kaliakra and Kavarna.

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^{137}Cs and ^{134}Cs content in sediments from Northern locations (Bq.kg^{-1})

Location/ sediment type	^{137}Cs		^{134}Cs	
	Mean±SE	Range	Mean±SE	Range
Durankulak/sand	4.75±0.38	1.10–9.00	023±0.02	0.10–0.40
Shabla/silt	7.6±0.62	2.8–13.0	0.35±0.03	0.10–0.60
Tyulenovo/sand	5.04±0.40	4.00–7.10	0.21±0.02	0.10–0.30
Kamen Bryag/sand	5.18±0.41	4.42–6.52	0.21±0.002	0.10–0.30
Kaliakra N/clay	78±6	52–92	3.9±0.3	1.5–5.9
Kavarna/clay	30±2	14–41	1.6±0.1	0.2–4.4
Tuzlata/silt	9.4±0.7	1.6–14.6	1.2±0.1	0.10–5.80
Balchik/sand	6.2±0.5	4.6–7.8	0.26±0.02	0.10–0.61
Albena/sand	4.7±0.4	3.4–7.3	0.21±0.02	0.10–0.50
Golden Sands/sand	4.10±0.33	2.50–6.90	0.20±0.02	0.11–0.32

The measured mean values in sediments from the other northern locations range from 1.1 to 14.6 Bq.kg^{-1} for ^{137}Cs and between 0.1 and 5.8 Bq.kg^{-1} for ^{134}Cs.

The lowest measured mean values are in the locations with sand type of sediments – Durankulak (4.75 Bq.kg^{-1} for ^{137}Cs and 0.23 Bq.kg^{-1} for ^{134}Cs) and the main Bulgarian Black Sea resorts Albena (4.7 Bq.kg^{-1} for ^{137}Cs and 0.21 Bq.kg^{-1} for ^{134}Cs) and Golden Sands (4.1 Bq.kg^{-1} for ^{137}Cs and 0.2 Bq.kg^{-1} for ^{134}Cs).

The comparison of the obtained results with our data for the central and southern part of the Bulgarian coast (unpublished data) shows that the highest content of cesium (^{137}Cs and ^{134}Cs) was measured in sediments collected from the northern Bulgarian Black Sea places.

All measured activities of Cs isotopes in the Northern part of the coast vary between 1.1 and 92.0 Bq.kg^{-1} for ^{137}Cs and from 0.1 to 5.9 Bq.kg^{-1} for ^{134}Cs. The total mean value for ^{137}Cs is 15.50 Bq.kg^{-1}and 0.84 Bq.kg^{-1}.

The measured activities in sediment from central coast vary between 1.6 and 19.8 Bq.kg^{-1} for ^{137}Cs and from 0.1 to 1.0 Bq.kg^{-1}for ^{134}Cs. The total mean values are lower – 7.82 Bq.kg^{-1}for ^{137}Cs and 0.33 Bq.kg^{-1}for ^{134}Cs.

The observed dependence of radionuclide content on sediment type is valid also for the natural nuclides in sediments. Data obtained for natural radionuclides content in sediments from all studied locations are presented in Table 2.

The data in Table 2 show that the highest mean concentrations of natural nuclides ^{232}Th, ^{234}Th, ^{226}Ra, and ^{210}Pb were determined in clay sediments from

Table 2

Natural nuclide content in sediments from Northern locations (Bq.kg^{-1})

Location sediment type	^{40}K	^{232}Th	^{234}Th	^{226}Ra	^{210}Pb
	Mean ± SE (Range)	Mean ± SE (Range)	Mean ± SE (Range)	Mean ± SE (Range)	Mean ± SE (Range)
Durankulak sand	41±3 (11–92)	3.9±0.1 (1.2–7.8)	5.3±0.4 (3.0–9.0)	5.25±0.48 (3.20–8.80)	6.75±0.54 (5.00–9.00)
Shabla silt	122±9 (37–210)	7.1±0.6 (2.4–11.5)	9.0±0.7 (3.0–16.0)	7.5±0.6 (4.4–11.5)	9.3±0.74 (6.0–14.0)
Tyulenovo sand	82±6 (26–124)	4.2±0.3 (2.8–5.5)	5.5±0.4 (4.0–8.0)	4.67±0.37 (3.62–5.90)	5.6±0.4 (4.0–7.0)
Kamen Bryag sand	72±5 (40–110)	3.9±0.3 (2.7–5.4)	5.1±0.4 (3.0–6.6)	4.36±0.35 (3.52–6.00)	5.7±0.3 (4.1–7.0)
Kaliakra N clay	532±37 (440–580)	27.3±2.2 (3.3–35.0)	29.6±2.1 (6.2–39.0)	26.2±2.2 (12.2–33.0)	30±2 (16–37)
Kavarna clay	132±9 (71–225)	10.8±0.9 (7.2–17.7)	28.7±2.3 (25–33.0)	28±3 (24–31)	28±2 (25–32)
Tuzlata silt	115±8 (40–370)	10.1±0.8 (1.3–25.0)	19.2±1.5 (3.7–36.0)	23.6±1.9 (7.9–38.0)	25±2 (17–32)
Balchik sand	236±17 (170–290)	7.2±0.6 (6.1–9.7)	17.5±1.4 (14–22)	21.9±1.6 (15.8–26.0)	20.2±1.6 (17.0–23.0)
Albena sand	482±34 (320–710)	6.3±0.5 (4.9–10.0)	14±1 (7.5–25.2)	12.4±0.9 (8.4–17.0)	14.8±1.2 (10.2–21.0)
Golden Sands sand	619±43 (490–740)	5.6±0.4 (4.5–7.3)	13±1 (10–15)	6.68±0.58 (5.6–7.5)	15.0±1.2 (6.0–30.0)

Kaliakra and Kavarna. Higher average values were also registered in silt sediments fromTuzlata and sand sediments from Balchik. The highest mean values for ^{40}K were obtained in the sand sediments from Golden Sands and Albena, as well as in the clays from Kaliakra. The lowest mean values for all studied natural radionuclides were measured in sand sediments from Kamen bryag, Durankulak and Tyulenovo. The total mean values for all studied northern locations are 8.64 Bq.kg^{-1} for ^{232}Th (range: 1.2–35.0 Bq.kg^{-1}), 14.7 Bq.kg^{-1} for ^{234}Th (range: 3.0–39.0 Bq.kg^{-1}), 14.1 Bq.kg^{-1} for ^{226}Ra (range: 3.2–38.0 Bq.kg^{-1}), 16 Bq.kg^{-1} for ^{210}Pb (range: 4–37 Bq.kg^{-1}) and 243 Bq.kg^{-1} for ^{40}K (range: 11–740 Bq.kg^{-1}).

The comparison of the mean values obtained for the Northern regions with the data for the Central coastal regions (unpublished data) shows that the activities of ^{226}Ra and ^{210}Pb are higher in the Northern locations. Data obtained data for ^{232}Th and ^{234}Th are comparable. The ^{40}K content is higher in sediments collected from the Central Bulgarian coastline. The total mean values for sediments at central locations are 15.5 Bq.kg^{-1} for ^{234}Th, 9.2 Bq.kg^{-1} for ^{232}Th, 11.6 Bq.kg^{-1}

for ^{226}Ra, 13.6 Bq.kg^{-1} for ^{210}Pb and 601 Bq.kg^{-1} for ^{40}K.

The obtained results for natural radionuclide content in sediments show that radionuclide concentrations strongly depend on the nature of the sea bed sediments, because the data obtained for sand sediments are within a close range while those for silt and clay ones are higher and vary to a much greater extent (Table 3).

T a b l e 3

Natural nuclide content in different sediment types (Bq.kg^{-1})

Nuclide	Sand	Silt	Clay
	Mean ± SE (Range)	Mean ± SE (Range)	Mean ± SE (Range)
^{234}Th	10.7 ± 0.9 (3.0–42.0)	25.5 ± 2.1 (3.0–77.0)	26.2 ± 2.2 (5.0–50.0)
^{232}Th	7.1 ± 0.6 (1.2–30.0)	14.1 ± 1.2 (1.3–60.0)	17.2 ± 1.5 (3.3–35.0)
^{226}Ra	8.6 ± 0.7 (3.0–26.0)	23.0 ± 1.9 (4.4–77.0)	24 ± 2 (9–50)
^{210}Pb	10.8 ± 1.1 (4.0–30.0)	27 ± 2 (6–75)	24 ± 2 (8–37)

Samples taken from 56–155 m depth from the Bulgarian territorial waters plus two samples at maximal depth 2010 m and 2040 m also were measured for radionuclide content. The character of sediment samples is clay except at 2010 m where the matrix is very hard in structure and black in colour. The obtained data show that Cs content is rather low (compared to the shelf), while natural nuclide concentrations increase with the depth. ^{226}Ra concentration is higher in the middle depths (55–90 Bq.kg^{-1}). At the bottom 2000 m U isotopes are the highest (90–135 Bq.kg^{-1}).

Sediments with the highest content of radionuclides collected on Kaliakra (clays) during the period 1991–2002, in 2005 and 2010 were analyzed to determine the concentrations of Mn, Ni, Zn, Cu, Pb, As, Cr, Cd and Co. Mean values and intervals of variation of the concentration of the content of toxic elements for 12 samples of clay sediments were obtained. The samples were prepared by partial dissolution method. This method was chosen after applying both studied procedures (total and partial dissolution) and comparing the results obtained for the accuracy and reproducibility. A detailed description of the sample preparation procedures, validation and adaptation to our sediment samples will be described in detail in a separate publication.

The obtained total mean values and concentration variation intervals for toxic elements content in 12 clay sediment samples from Kaliakra vary as follows: 323 ± 21 mg.kg^{-1} (between 292 and 406 mg.kg^{-1}) for Mn; 46 ± 3 mg.kg^{-1} (39–53

mg.kg^{-1}) for Ni; 68 ± 5 mg.kg^{-1} (61–88 mg.kg^{-1}) for Zn; 36 ± 3 mg.kg^{-1} (24–45 mg.kg^{-1}) for Cu; 23.9 ± 0.7 mg.kg^{-1} (22.7–26.8 mg.kg^{-1}) for Pb; 8.4 ± 0.9 mg.kg^{-1} (6.3–11.2 mg.kg^{-1}) for As; 65 ± 3 mg.kg^{-1} (61–67 mg.kg^{-1}) for Cr; 0.28 ± 0.01 mg.kg^{-1} (0.24–0.30 mg.kg^{-1}) for Cd and 7.18 ± 0.2 mg.kg^{-1} (6.60–7.77 mg.kg^{-1}) for Co. Data show that the toxic elements concentrations decrease in the order: Mn > Zn > Cr > Ni > Cu > Pb > As > Co > Cd.

The established fluctuations in the concentrations of the studied radionuclides and toxic elements in the sediments collected from a certain sampling site are most likely due to the composition and structure of the sediment. The surface layers of the sediments change continuously as a result of tidal processes, sedimentation processes, under the influence of marine biota and other abiotic and biotic factors of the marine environment.

Conclusions. The obtained results create a database on the concentrations of radionuclides and toxic elements in sediments from the Northern Bulgarian Black Sea coast and can be used for assessment of the ecological status of the marine environment along the whole northern coastal zone.

As a result of the conducted analyses some well-known in radiochemical practice methods for sediment analysis have been optimized and validated and successfully applied in our laboratories.

The obtained results fill the lack of sufficient data on the accumulation of radionuclides and toxic elements in Bulgarian Black Sea sediments and are of interest to the databases of the IAEA Marine Radioactivity Information System (MARiS).

REFERENCES

[1] Dassenakis M., H. Andrianos, G. Depiazi, A. Konstantas, M. Karabela et al. (2003) The use of various methods for the study of metal pollution in marine sediments, the case of Euvoikos Gulf, Greece, Appl. Geochem., **18**, 781–794.

[2] Yi L., B. Gao, H. Liu, Y. Zhang, C. Du et al. (2020) Characteristics and assessment of toxic metal contamination in surface water and sediments near a uranium mining area, Int. J. Environ. Res. Public. Health., **17**, 548.

[3] Saçan S., A. Uğur, U. Sunlu, B. Büyükışık, M. Aksu et al. (2010) The ^{210}Po and ^{210}Pb levels in surface sediment samples in the Izmir Bay (Aegean Sea-Turkey), Environ. Monit. Assess., **161**, 575–582.

[4] Bezhenar R., K. Tae Jung, V. Maderich, S. Willemsen, G. De With et al. (2016) Transfer of radiocaesium from contaminated bottom sediments to marine organisms through benthic food chains in post-Fukushima and post-Chernobyl periods, Biogeosciences, **13**, 3021–3034.

[5] Jorgensen B. B., H. Fossing, C. O. Wirsen, H. W. Jannasch (1991) Sulfide oxidation in the anoxic Black Sea chemocline, Deep-Sea Res., **38**, 1083–1103.

[6] Sorokin Y. I. (2002) The Black Sea – Ecology and Oceanography, Backhuys Publishers, UNESCO Venice Office, Leiden.
[7] Vakulovsky S. M., A. I. Nikitin, V. B. Chumichev, I. Katrich, O. V. Voitsekhovich et al. (1994) ^{137}Cs and ^{90}Sr contamination of water bodies in the area affected by releases from the Chernobyl NPP accident: an overview, J. Environ. Radioac., **23**, 103–122.
[8] Eremeev V. N., L. M. Ivanov, A. D. Kirwan, T. M. Margolina (1995) Amount of ^{137}Cs and ^{134}Cs radionuclides in the Black Sea produced by the Chernobyl accident, J. Environ. Radioac., **27**, 49–63.
[9] Kolarova M., T. Dimtchev (1980) Gamma-spectrometric investigations of marine sediments, water and algae at the Black Sea Side. https://inis.iaea.org/collection/NCLCollectionStore/_Public/13/712/13712621.pdf
[10] Minev L., S. Teophilov, P. Kritidis, I. Uzunov, V. Konstantinov (1986) On Environmental Radioactivity of Bulgarian Black Sea coast, CIESM, **30**, 211.
[11] Strezov A., Tz. Nonova (2006) Anthropogenic contamination in marine ecosystems at Northern Bulgarian Black Sea sector, Ovid. Univ. Ann. Chem., **17**, 13–16.
[12] Strezov A. (2012) Sustainable Environment – Monitoring of Radionuclide and Heavy Metal Accumulation in Sediments, Algae and Biota in Black Sea Marine Ecosystems. In: Sustainable Environment. Environmental contamination (ed. J. Srivastava), IntechOpen, 51–78.
[13] Strezov A., M. Milanov, P. Mishev, T. Stoilova (1999) Radionuclide accumulation in near-shore sediments along the Bulgarian Black Sea coast, Appl. Radiat. Isotopes, **49**(12), 1721–1728.
[14] Strezov A., T. Stoilova, A. Jordanova, M. Ayranov, N. Petkov (1999) Heavy metal assessment in algae, sediments and water from the Bulgarian Black Sea coast, Wat. Sci. Technol., **39**(8), 207–212.

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