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Comparative analysis of radionuclide and potentially toxic element accumulation in sediments from the Northern Bulgarian Black Sea coast

Lyuben Dobrev[1], Tzvetana Nonova[1], Krasimira Slavova[2]

[1] Institute for Nuclear Research and Nuclear Energy

[2] Institute of Oceanology

BULGARIAN ACADEMY OF SCIENCES

Our objectives:

- to provide data for radionuclide and potentially toxic elements accumulation in Black Sea bottom sediments and compare their concentration variations along the whole Bulgarian coast;
- to optimize the well-known in practice and to develop and validate some new fast, reproducible and sensitive analytical methods for radiochemical separation of trace concentrations of radionuclides and for determination of toxic elements in small marine samples;
- to establish the typical values for different sediment types at the Bulgarian Black Sea coast to enable the modeling of radionuclide transfer from the sediments to biota;
- to determine the local and seasonal contaminants concentration variations;
- to obtain a reliable information about the potential hazards of marine ecosystems.

What we do and how we do it?

- During the long-term monitoring, we have selected sampling sites and set up a network of sampling control points along the whole Bulgarian coast. The provided research is based on an ecosystem approach.
- In order to get reliable information, we have determined number of toxic elements and radionuclides:

RADIONUCLIDES (technogenic and natural):	**TOXIC ELEMENTS:**
^{137}Cs, ^{134}Cs, ^{90}Sr, ^{40}K, ^{238}U ^{234}Th, ^{226}Ra, ^{210}Pb, ^{210}Po	Fe, Al, Mn, Ni, Zn, Cu, Pb, As, Cr, Cd, Co



What we do and how we do it?

The determinations are completed in several components of the marine ecosystem – sea water, over 15 macro-algae species, mussels and sediments:

Water
(surface and deep water)

Sediments
(sand, clay and silt)

Green algae
(Chlorophyta)

Brown algae
(Phaeophyta)

Red algae
(Rhodophyta)

Mussels
(Mytilus galloprovincialis)

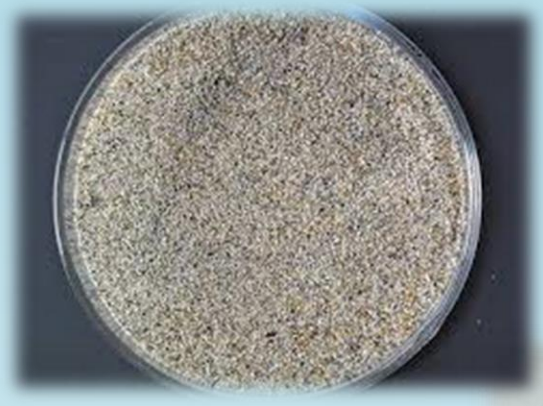
Our sampling:

- Sampling was done with the assistance of colleagues from the diving section of the National Club for Scientific Expeditions of UNESCO (Sofia) and the Institute of Oceanology (Varna).
- Collection of the samples was carried out in spring, summer and autumn seasons since 1991.
- 10 pre-selected sampling posts from Durankulak to Golden sands.
- Samples were collected in the upper layer of sediments from approximately 1 m² of the bottom.
- The depth of the sample layer is about 3 cm to evaluate radionuclide content on the surface of the seabed.

North Black Sea coast

Our samples:

- 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 shoreline.
- There were acquired about 2-3 kg of solid phase mixed with several liters of aqueous phase.
- We also analyzed 7 deep-sea marine sediment samples collected at 150 to 2040 m depth.



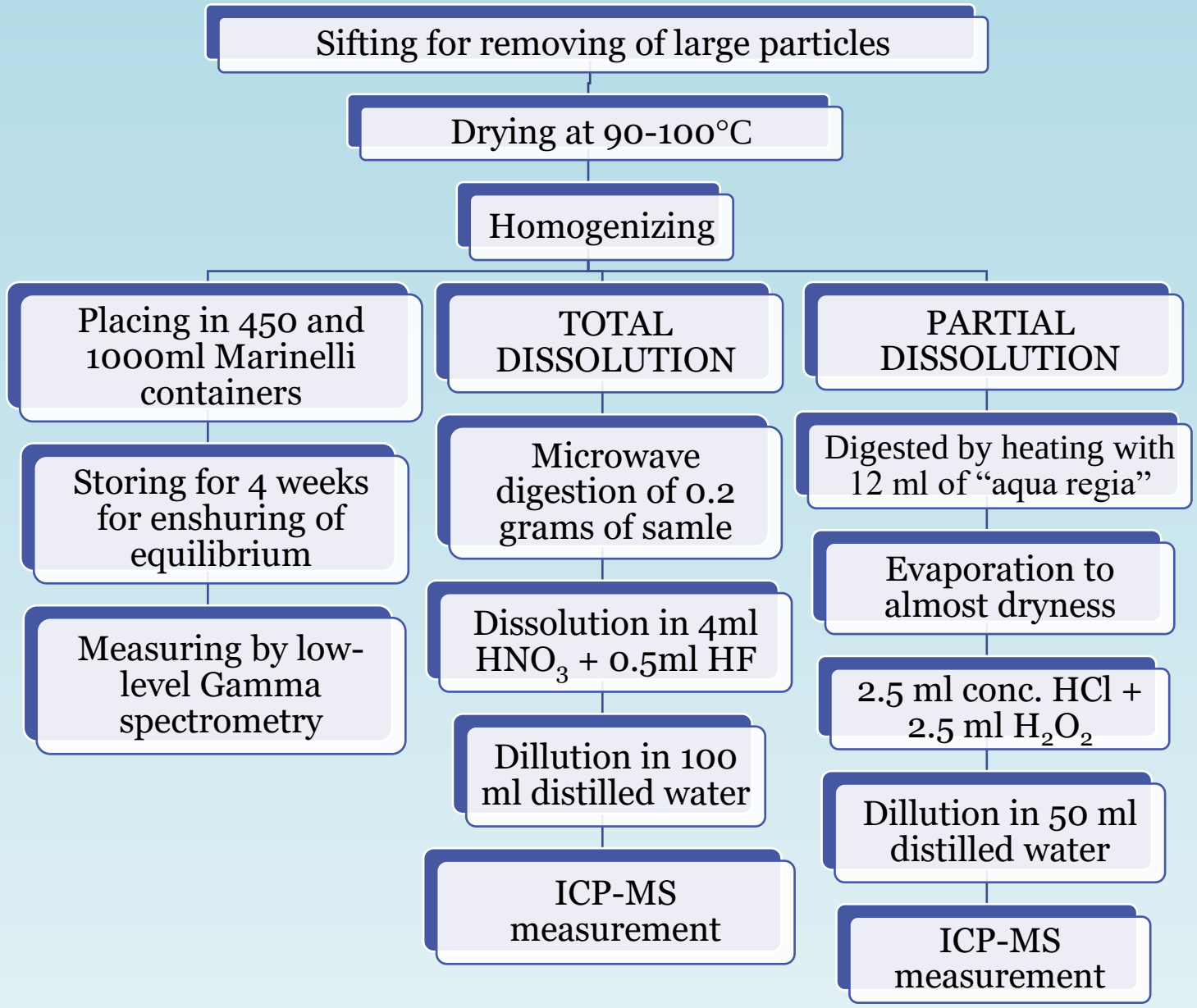
sand

clay

silt

Our sample preparation:

- The determination of gamma radionuclides was performed by Low-level Gamma Spectrometry measurement (High-Purity Germanium (HPGe) – GMX 50P4 detector (Ortec type) with 54.9 % counting efficiency and energy resolution 2.3 KeV at 1332 KeV (^{60}Co).
- The toxic element content was determined by ICP-MS measurement (VARIAN 820-MS ICP-MS spectrometer, with 90 degree reflecting ion optics, 27 MHz RF Generator, quadrupole mass filter and DDEM detector).
- All sediment samples were sieved to remove large particles, dried at about 90-100°C, homogenized and placed in special hermetic containers Marinelli type with volume 450 and 1000 ml for a period of at least four weeks before the measurements. This procedure is applied to ensure the equilibrium within the Uranium decay series for estimation of the natural radioisotopes.



Our results for ^{137}Cs and ^{134}Cs content:

- **Cesium-137 is one of the most studied nuclides in the Black Sea environment after the Chernobyl accident.**

Location	Sediment type	Cs-137, Bq.kg^{-1}		Cs-134, Bq.kg^{-1}	
		mean±SE	range	mean±SE	range
Durankulak	sand	4.75 ± 0.38	1.10 – 9.00	0.23 ± 0.02	0.01 – 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 ± 0.02	0.10 – 0.30
Kaliakra-N	clay	78 ± 6	52 - 82	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

- **Highest values:**

Kaliakra:
^{137}Cs - 78 Bq.kg^{-1}
^{134}Cs - 3.9 Bq.kg^{-1}

Kavarna:
^{137}Cs - 30 Bq.kg^{-1}
^{134}Cs – 1.6 Bq.kg^{-1}

- **Lowest values:**

Durankulak:
^{137}Cs – 4.75 Bq.kg^{-1}
^{134}Cs – 0.23 Bq.kg^{-1}

Albena:
^{137}Cs – 4.7 Bq.kg^{-1}
^{134}Cs – 0.21 Bq.kg^{-1}

Golden Sands:
^{137}Cs – 4.1 Bq.kg^{-1}
^{134}Cs – 0.2 Bq.kg^{-1}

Our results for natural radionuclide content:

- **The observed dependence of radionuclide content on sediment type is valid also for the natural nuclides in sediments.**

Location	Sediment type	K-40, Bq.kg^{-1}		Th-232, Bq.kg^{-1}		Th-234, Bq.kg^{-1}		Ra-226, Bq.kg^{-1}		Pb-210 Bq.kg^{-1},	
		mean±SE	range	mean±SE	range	mean±SE	range	mean±SE	range	mean±SE	range
Durankulak	sand	40.8 ± 2.8	11.0 – 92.0	3.93 ± 0.02	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	14.2 – 22.0	21.9 ± 1.6	15.8 – 26.0	20.2 ± 1.6	17.0 – 23.0
Albena	beach-sand	482 ± 34	320 - 710	6.3 ± 0.5	4.9 – 10.0	14.2 ± 1.1	7.5 – 25.2	12.4 ± 0.9	8.4 – 17.0	14.8 ± 1.2	10.2 – 21.0
Golden Sands	beach-sand	619 ± 43	490 - 740	5.6 ± 0.4	4.5 – 7.3	13 ±1	10.3 – 15.2	6.68 ±0.58	5.6 – 7.5	15.0 ± 1.2	6.0 – 30.0

- The highest concentrations of natural nuclides in sediments from Northern locations were measured in clay sediments from Kaliakra and Kavarna.
- The lowest concentrations of natural nuclides are in the sand sediments from the north locations: Durankulak, Tyulenovo, Kamen Bryag.

Our comparisons:

- The comparison of the mean values obtained for the Northern regions with the data for the Central coastal regions.

Northern locations:

Radionuclide	Mean (Bq.kg^{-1}) ± SE	Range, Bq.kg^{-1}
Th-234	18.4 ± 3	3.0 – 39.0
Th-232	13.5 ± 1.7	1.2 – 35.0
Ra-226	17.3 ± 2	3.2 – 33.0
Pb-210	20.24 ± 3	4.10 – 37.00
K-40	283 ± 28	11 – 740

Central locations:

Nuclide	Mean (Bq.kg^{-1}) ± SE	Range, Bq.kg^{-1}
Th-234	15.5 ± 1.2	3.0 – 50.0
Th-232	9.2 ± 0.8	3.6 – 30.0
Ra-226	11.6 ± 1.1	3.0 – 50.0
Pb-210	13.6 ± 1.2	5.0 – 37.0
K-40	601 ± 48	88 – 1460

Nuclide	Sand sediments		Silt sediments		Clay sediments	
	Mean ± SE Bq.kg^{-1}	Range Bq.kg^{-1}	Mean ± SE Bq.kg^{-1}	Range Bq.kg^{-1}	Mean ± SE Bq.kg^{-1}	Range Bq.kg^{-1}
Th-234	10.7 ± 0.9	3.0 – 42.0	25.5 ± 2.1	3.0 – 77.0	26.2 ± 2.2	5.0 – 50.0
Th-232	7.1 ± 0.6	1.2 – 30.0	14.1 ± 1.2	1.3 – 60.0	17.2 ± 1.5	3.3 – 35.0
Ra-226	8.6 ± 0.7	3.0 – 26.0	23.0 ± 1.9	4.4 – 77.0	24 ± 2	9 – 50
Pb-210	10.8 ±1.1	4.0 – 30.0	27 ± 2	6 – 75	24 ± 2	8 – 37

- The comparison between different sediment types shows significant dependence between nuclide concentrations and nature of the sediment.

Our results for toxic elements in Black sea sediments:

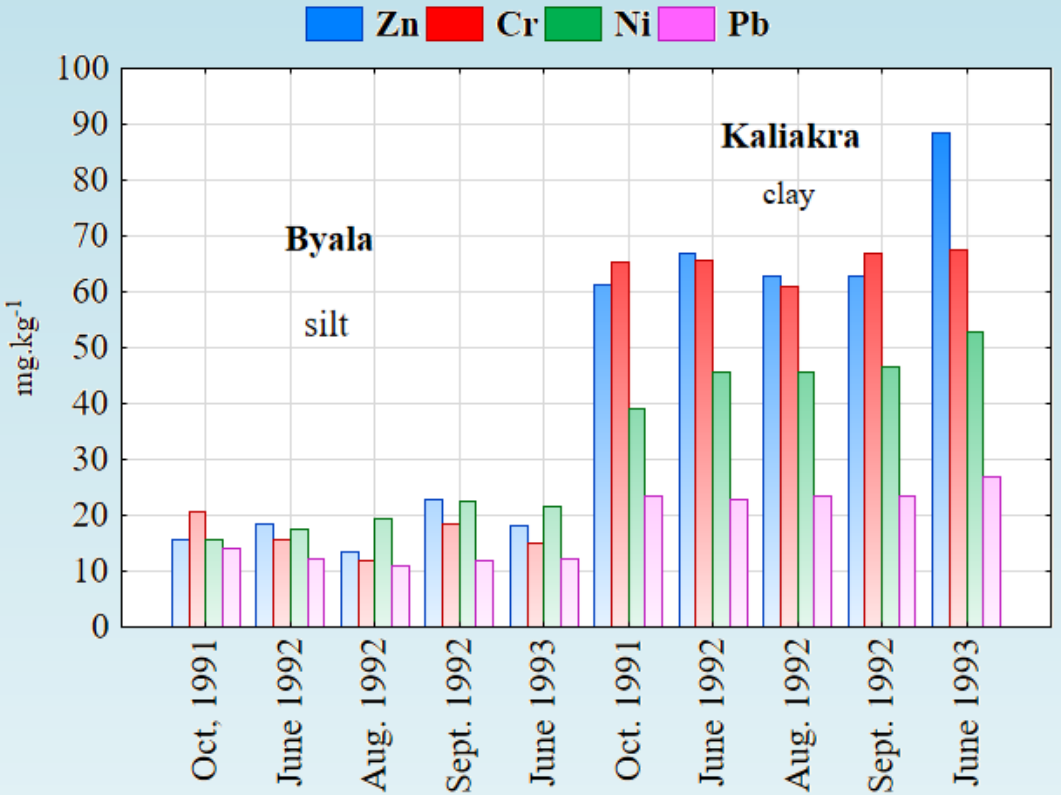
- **The data show that concentrations of all studied elements are higher in sediments from Kaliakra.**

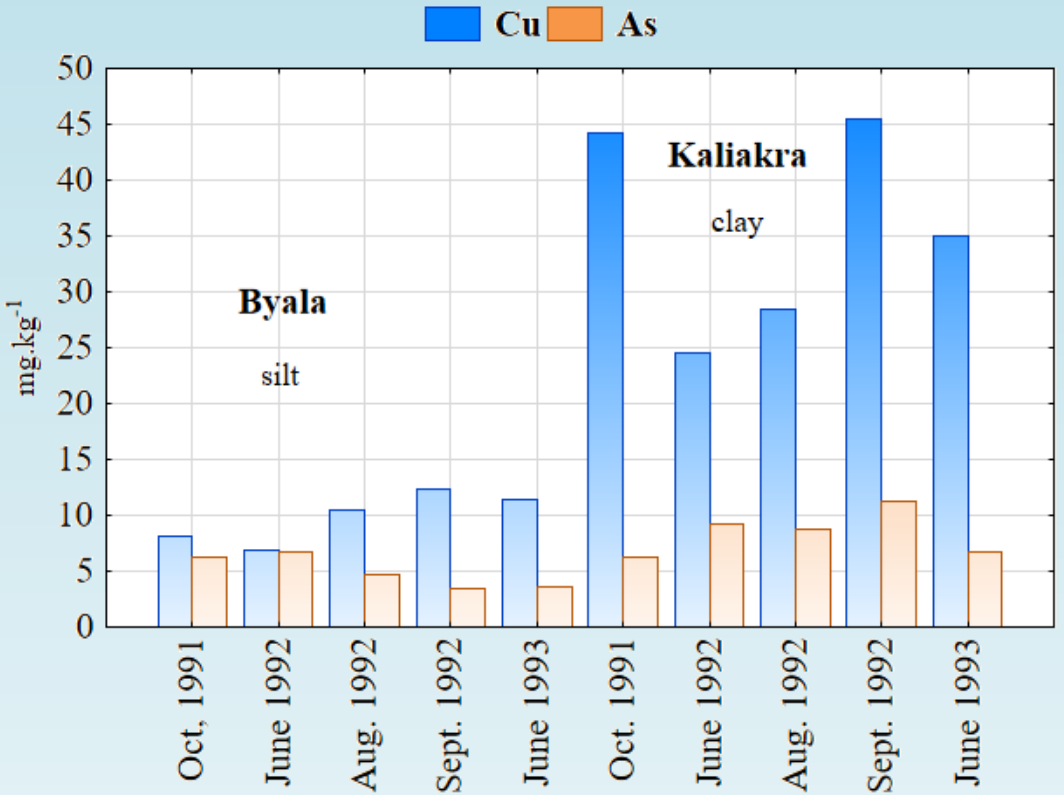
Element	Mean (mg.kg^{-1}) ± SE	Range, mg.kg^{-1}
Mn	323 ± 21	292 – 406
Ni	46 ± 3	39 - 53
Zn	68 ± 5	61 – 88
Cu	36 ± 3	24 – 45
Pb	23.9 ± 0.7	22.7 – 26.8
As	8.4 ± 0.9	6.3 – 11.2
Cr	65 ± 3	61 – 67
Cd	0.28 ± 0.01	0.24 – 0.30
Co	7.18 ± 0.2	6.60 – 7.77

- The sediments with the highest radionuclide content collected at Kaliakra and Byala were analyzed by inductively coupled plasma-mass spectrometry (ICP-MS) in combination with total and partial dissolution of the samples.
- The metal concentrations in sediments decrease in the following order:
  Mn > Zn > Cr > Ni > Cu > Pb > As > Co > Cd
- The lowest concentrations of natural nuclides are in the sand sediments from the north locations: Durankulak, Tyulenovo, Kamen Bryag.

Comparison of the data obtained for potentially toxic elements in the clay sediments from Kaliakra and Byala:

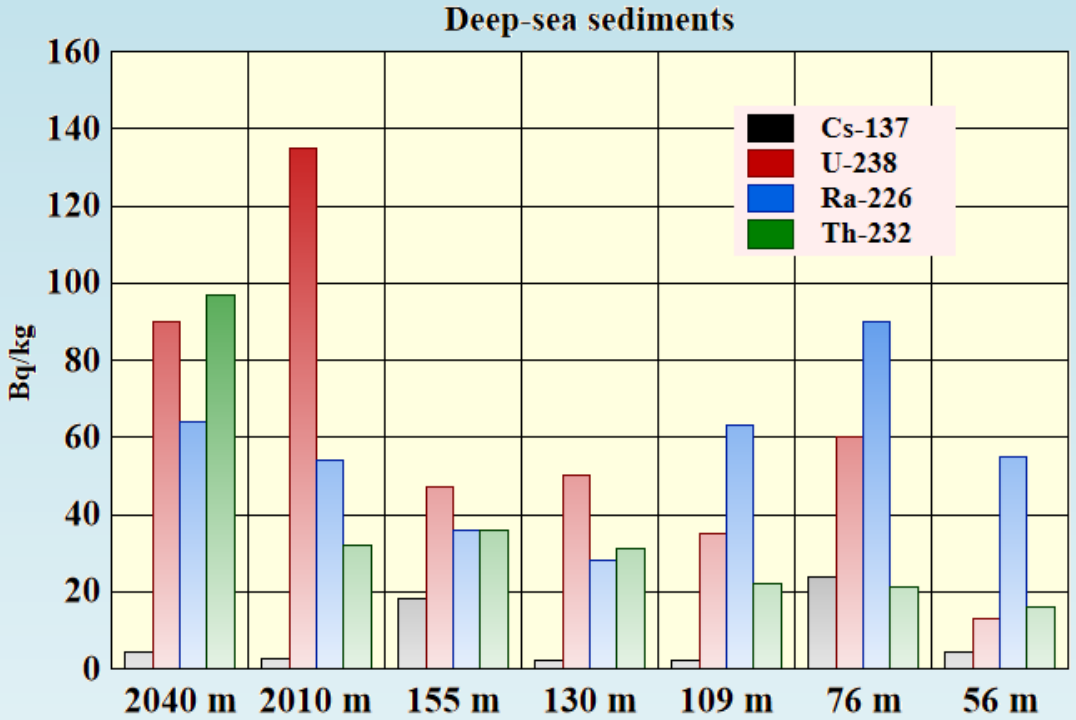
- Clay sediments contain significantly higher amounts of Zn, Ni, Cu, Cr and Co than those in silt sediments. The content of As in both sediments is comparable.

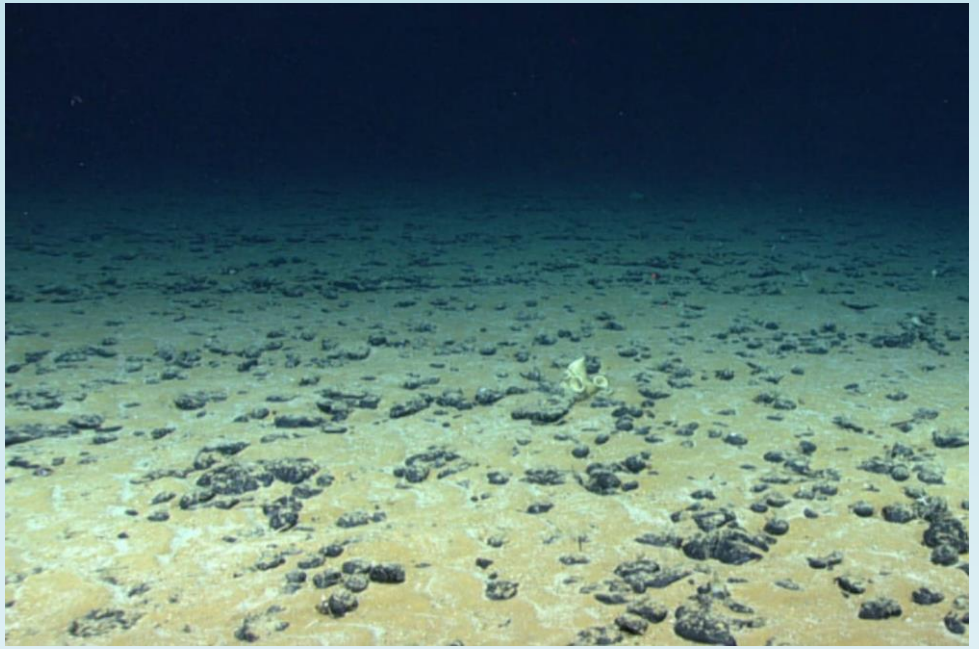




Radionuclide content in deep-sea sediments

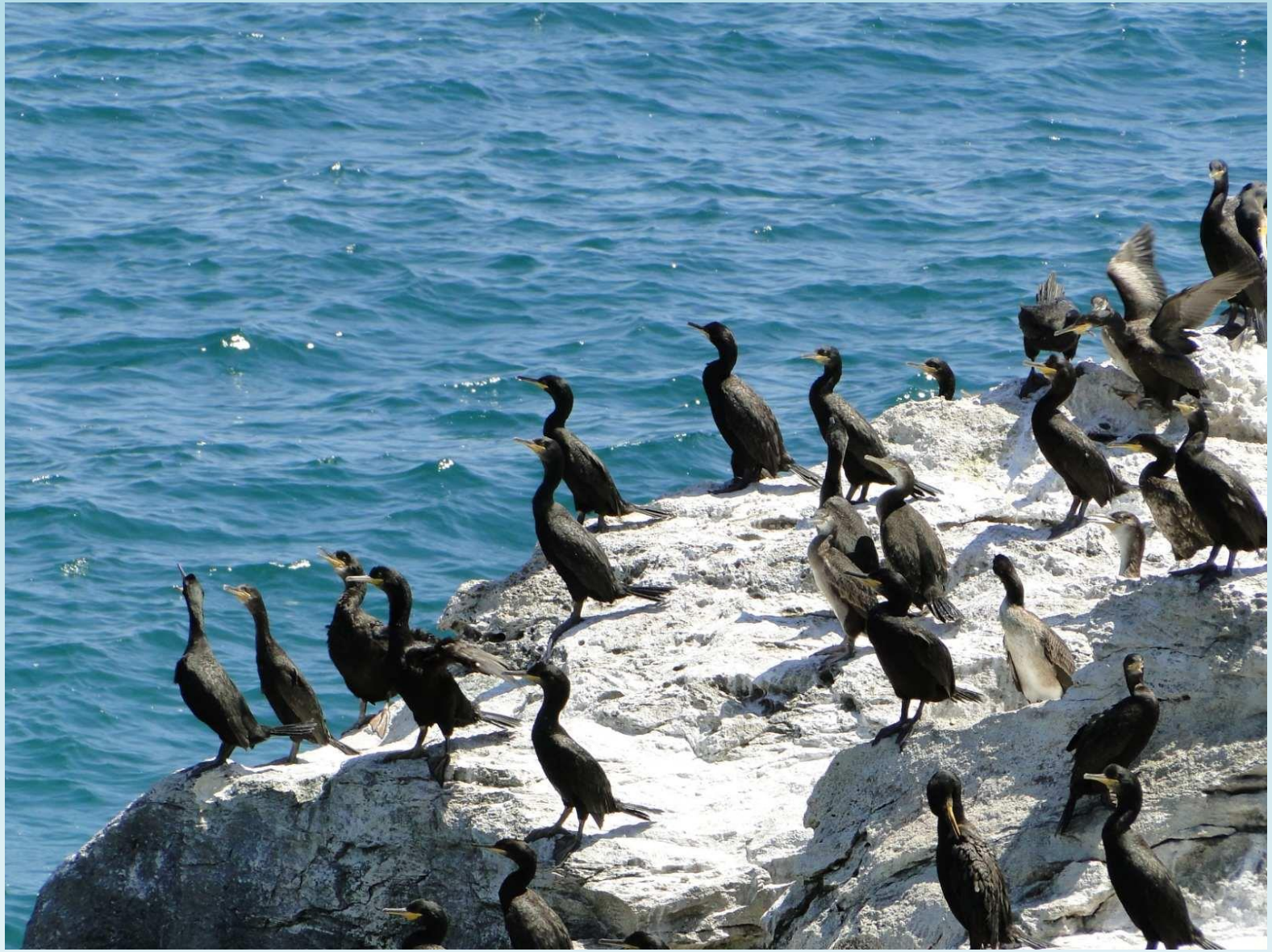
- The obtained results show that Cs content is rather low (compared to the shelf), while natural nuclide concentrations increase with the depth.
- In the sediments collected from 55 to 155 m depth, the highest is the content of ^{226}Ra (55 – 90 $Bq.kg^{-1}$) while at the bottom 2000 m sediments - U (90 – 135 $Bq.kg^{-1}$).





Our conclusions:

- **All the obtained results create a database on the toxic elements and radionuclides concentrations in sediments from the Bulgarian Black Sea coast and can be used for assessment of the ecological status of the marine environment along the Northern coastal zone.**
- **The obtained results were reported in many international scientific forums.**
- **Some data were published in more than 35 articles in international scientific journals, 2 monographs, one PhD and one doctoral dissertations.**



Thank you for your attention!

For questions:

ltdobrev@gmail.com

tz.nonova@gmail.com