Comparative Assessment of Organic Pollution in the Rivers Influenced Area of the North-Western, Western, and Southern Part of the Black Sea *(Valentina Coatu, Nicoleta Damir, Andra Oros, Hakan Atabay, Ertuğrul Arslan, Leyla Tolun, Yuriy Denga, Yurii Oleinik)*	"Cercetări Marine" Issue no. 50 Pages 26 - 46	2020

COMPARATIVE ASSESSMENT OF ORGANIC POLLUTION IN THE RIVERS IMPACT AREA OF THE NORTH-WESTERN, WESTERN AND SOUTHERN PART OF THE BLACK SEA

Valentina Coatu[1], Nicoleta Damir[1], Andra Oros[1], Hakan Atabay[2], Ertuğrul Arslan[2], Leyla Tolun[2], Yuriy Denga[3], Yurii Oleinik[3]

[1]National Institute for Marine Research and Development "Grigore Antipa", 300 Mamaia Blvd., RO -900591, Constanta, Romania
[2]Scientific and Technological Research Council of Turkey, TUBITAK
[3] Ukrainian Scientific Centre of Ecology of the Sea, UkrSCES
E-mail: vcoatu@alpha.rmri.ro

ABSTRACT

In the context of CBC Project "Assessing the vulnerability of the Black Sea marine ecosystem to human pressures" (ANEMONE), a comparative assessment of rivers impact on the Black Sea ecosystem quality was performed through pilot case studies carried out in the north-western, western and southern marine areas in front of the rivers' mouths.
The evaluation was done using national methods in each area and the HELCOM integrated hazardous substances assessment tool (CHASE) developed by NIVA Denmark. Even though there are many differences between areas regarding indicator substances or threshold values used in assessment, the Black Sea quality is better in the southern part where the status was moderate comparative with the other areas which were in bad status. Therefore, we identified the chemical pressure coming from organic pollutants input. The results can contribute to environmental measures enhancement in the Black Sea region.
Key-Words: Black Sea, organic pollutants, integrated assessment, CHASE

AIMS AND BACKGROUND

The most important European legislation for assessing the ecological status of European coastal aquatic ecosystems is the EU Marine Strategy Framework Directive (MSFD). The MSFD aim at maintaining and improving the aquatic environment status by preventing long term deterioration of coastal and marine ecosystems. A good ecological and environmental status has as a prerequisite condition a good chemical condition. This is one of the most topical challenges facing policymakers, water managers, and scientists (Laane *et al*., 2012).

The recognition of hazardous substances coming from rivers and their distribution and storage in the intermediate layers are of great interest for the goal of preserving the ecological integrity of the Black Sea. Coordinating Black Sea protection measures requires a good understanding of the fate of river flow into the sea (Miladinova *et al*., 2020).

Indicators are generally accepted as tools for evaluating the status of marine environments in relation to management targets or thresholds. Application of the widely used ‘‘one out – all out’’ principle could easily result in a fully negative overall evaluation for all objectives. A drawback of this approach is that a few strongly negative indicator values could shadow the potentially generally positive state of a given ecological objective. This would make any progress towards improving the environmental status invisible, as long as at least one indicator is showing poor performance (Ojaveer and Eero, 2011).

An important aspect in reference-based assessment appears to be selection of an indicator aggregation formula. The assessment results can be highly sensitive to aggregation rules.

The aim of the study is to assess the river impacts on the Black Sea coastal environmental status, by using an integrated hazardous substances assessment tool (CHASE), as a common approach for the Black Sea region.

EXPERIMENTAL

Three pilot case studies were carried out in the north-western, western and southern marine areas in front of the rivers’ mouths in order to assess the river impacts on the Black Sea coastal environmental status in the context of CBC Project “Assessing the vulnerability of the Black Sea marine ecosystem to human pressures” (ANEMONE).

The study area for the Romanian Black Sea coast was the marine area in front of the Danube mouths, bathymetric strip between 20 – 60 m depth, four transects: Sulina, Sf. Gheorghe, Portiţa and Periboina, 19 stations, in spring (11-15 May 2019). Expeditions on the Black Sea coast of Turkey were carried out at the mouths of the Sakarya and Yesilirmak rivers. Water samples were collected from 10 stations in front of each River Mouths in two periods (July 2019 and January 2020) while sediments were collected from 12 and 15 stations of the same river mouths (July 2019). Expedition on the Black Sea coast of Ukraine were carried out at the mouths of the North-Western (Dnieper, Southern Bug and Dniester) and Western (Danube) rivers. Samples were collected from total 6 stations in two periods (June 2019 and September 2019). Location of sampling stations are given in the Fig. 1.

Water samples for organic pollutants were collected from the surface layer (1 m below the surface) from the 5 l Niskin bottles of the Rosette System. About 1 liter seawater was transferred into glass bottles, which were stored at refrigerator temperature until their subsequent analysis in laboratory. Different extraction methods were applied in each area: extraction with hexane using a high-speed mixer followed by organic phase separation in a separating funnel in the Ukraine laboratory, extraction with hexane/dichloromethane (3/1) mixture in separating funnel in the Romanian laboratory or stir bar sorptive method in the Turkey laboratory.

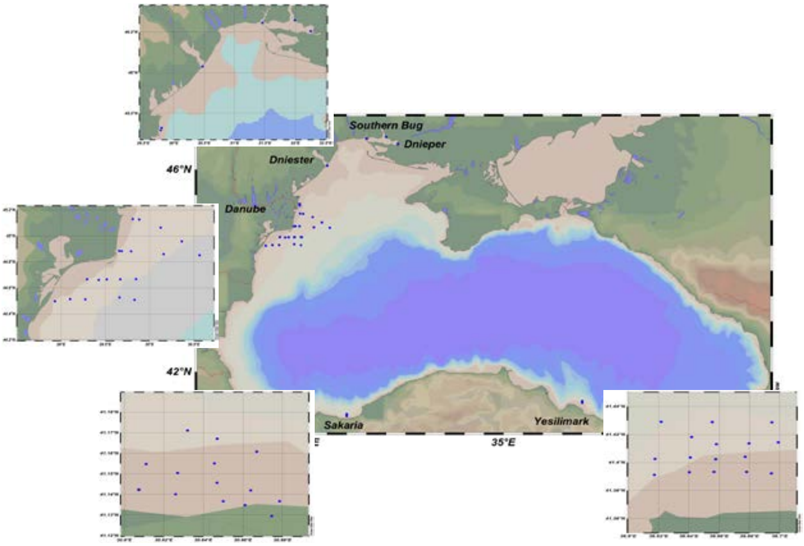

Fig. 1. Map of sampling stations for river – sea interactions study

Sediments samples were collected with a Van Veen bodengreifer. Sediments were freeze-dried and then well homogenized, and the coarse fragments (> 0.5 mm) were removed by sieving. Approximately 5 g portion of each sediment was spiked with internal standards and extracted on an accelerated solvent extraction unit under pressure (PLE) with a hexane/dichloromethane/methanol mixture (60% / 20% / 20%) in the Ukraine laboratory and with hexane: acetone (1:1 v/v) in microwave in the others two laboratory. Sulphur was removed with activated copper. Extraction was followed by purification on florisil column for organochlorine pesticides (OCPs) and polychlorinated biphenyls (PCBs), respectively silica/alumina column for polyaromatic hydrocarbons (PAHs) and concentration using the Kuderna-Denish concentrator or rotary evaporator and nitrogen flow in the Romanian and Turkey laboratories and on a silica gel column and concentration in a turbo evaporator under nitrogen flow in the Ukraine laboratory.

Persistent organic pollutants were analyzed by gas chromatography. GC-ECD method was used for OCPs and PCBs and GC-MS method for PAHs in the Romanian and Ukraine laboratory and GC-MS MS method was used for OCPs, PCBs and PAHs in the Turkey laboratory.

The total petroleum hydrocarbon (TPHs) were analyzed by fluorescence method.

In order to assess the river impacts on the Black Sea coastal environmental status, the organic pollutants concentrations were evaluated against threshold values that define good environmental status in each region using the HELCOM integrated hazardous substances assessment tool (CHASE) developed by NIVA Denmark (Andersen *et al*., 2016). This tool integrates data on hazardous substances in different matrices as well as bio-effect indicators, if available and is based on a substance- or bio-effect-specific calculation of a 'contamination ratio' being the ratio between an observed concentration and a threshold value. Values <1.0 indicate areas potentially 'unaffected', while values >1.0 indicate areas potentially 'affected'. These ratios are combined within matrices, i.e. for water, sediment, and biota and for biological effects. The integrated assessment provides a final status for an assessment unit, placing it in one of five classes: bad, poor, moderate, good and high. Thus, this classification system is essentially binomial (unaffected vs. affected) and is distinguished by a threshold value. The other classes are based on defined deviations from the unaffected/affected boundary. While the threshold between the good and moderate status equals 1.0 (reflecting the use of contamination ratios), the high-good threshold is 0.5, the moderate-poor threshold is 5.0 and the poor-bad threshold is 10.0. The overall assessment uses a "one out, all out principle" with regard to each matrix (Andersen *et al*., 2016). To have a better view of the environmental status in each region the graphic representation was done using the program Ocean Data View, so for each status class it has assigned a value, from 1 – High to 5 – Bad.

Also, the assessment was done using the method in place, in each region, to figure out the benefit of using CHASE tool.

In Romania, the status of Black Sea ecosystem in respect to MSFD is assessed by evaluating the 75% percentile of the data in the assessment unit in a given period of time against threshold values that define good environmental status (MAC-EQS) in accordance with European legislation (EU Directive 2013/39) in water or ERL and EAC values (Effect Range Low and Environmental Assessment Criteria) developed by US EPA and OSPAR for assessing the ecological significance of sediment concentrations (OSPAR, 2008; UNEP MAP, 2011; US EPA, 1998; Long *et al*., 1998) . As a result, a "Good" or "Bad" status for each substance is obtained and the result of each matrix and the overall result is given by the worst case using the "one out, all out principle" (Boicenco *et al*., 2018).

In Ukraine, the national methodology to assess the ecological state is by calculation of a pollution factor, Kz which reflects the concentration of all pollutants of the same type in a certain period in a given area. This factor represents the sum of the ratios of the concentration of each pollutant to its maximum permissible concentration, in accordance with EU Directive

2013/39 (MAC-EQS) for water, even the implementation of MSFD is not obligatory or the maximum permissible concentration according to Ukrainian legislation for sediment, to the number of measurements performed in a given period of time. Similar to CHASE, there are five quality classes (very good, good, satisfactory, bad and very bad) and the overall assessment of the ecological condition of water or bottom sediments in the study area is determined by the worst assessment of the group of pollutants.

In Turkey, implementation of MSFD is not obligatory yet. However, assessment of the contaminant levels in sediment matrix are carried out under the national monitoring program using ERL (Effects Range Low) as threshold value. Some pilot studies are carried out in order to assess contamination in water matrix according to the WFD (EU Directive 2000/60), using Max-EQS (EU Directive 2013/39). In order to decide the chemical status of each station "one out all out principle" are applied for both matrices (except heptachlor which has an EQS below the detection limit) and for overall assessment.

RESULTS AND DISCUSSION

The results obtained in Romanian area influenced by Danube river revealed some exceeding of the threshold values that define good environmental status.

In water, concentration of cyclodiene pesticides (aldrin, dieldrin, endrin) exceeded the threshold values proposed to define good ecological status (according to Directive 2013_39_EU) in 53% of the analyzed sampled and heptachlor in 100% of the samples, as its detection limit is higher than the threshold set up by the European legislation. The others regulated compounds exceeded the threshold values as follow: HCB – 5 %, sum of DDTs (DDT and metabolites) and p,p' DDT - 10% (Fig. 2).

TPHs values ranged between 4.25 µg/L and 15.62 µg/L, much lower than maximum admissible value (200 µg/L) stipulated by national legislation (Order no. 161/2006). The PAHs analysis highlighted the presence of four of the sixteen investigated compounds: naphthalene, acenaphthylene, phenanthrene and anthracene. Anthracene was the only regulated compound that exceeded the threshold values proposed for water in order to define good ecological status, according to Directive 2013_39_EU, in 53% of the analyzed sampled (Fig.3).

Except cyclodiene pesticides, heptachlor and anthracene, organic pollutants were in good status in water in Danube influenced area, according to the methodology developed to assess the status of Black Sea ecosystem in respect to MSFD (Boicenco *et al.*, 2018). In sediment, PCB 28 exceeded the threshold values proposed to define good ecological status in 58% of the analyzed sampled (Fig. 4).

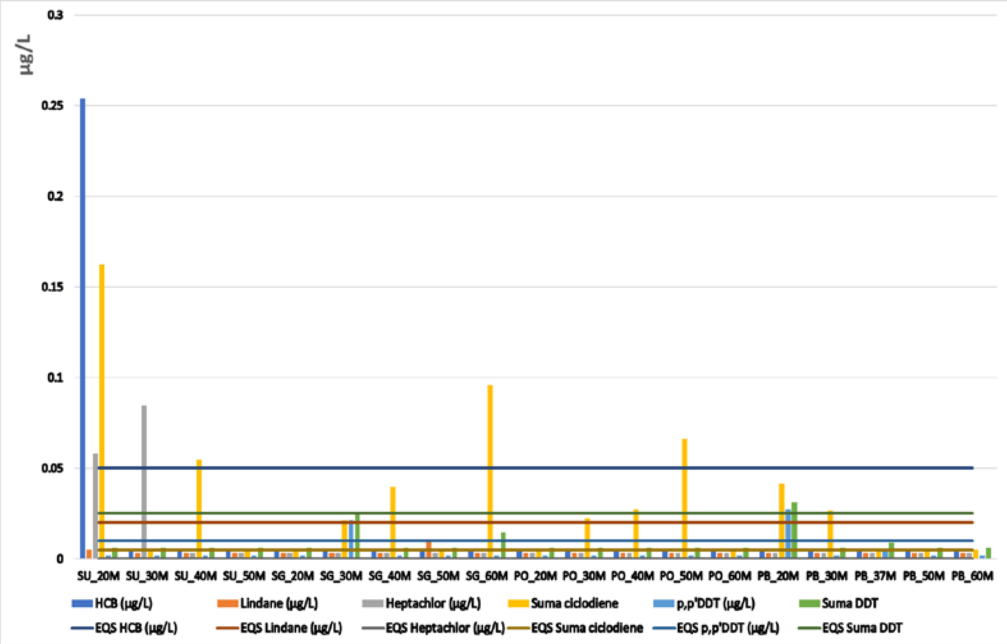

Fig. 2. Concentrations of organochlorinated pesticides in surface waters in marine area under the influence of Danube in relation to the proposed values to define good environmental status, May 2019

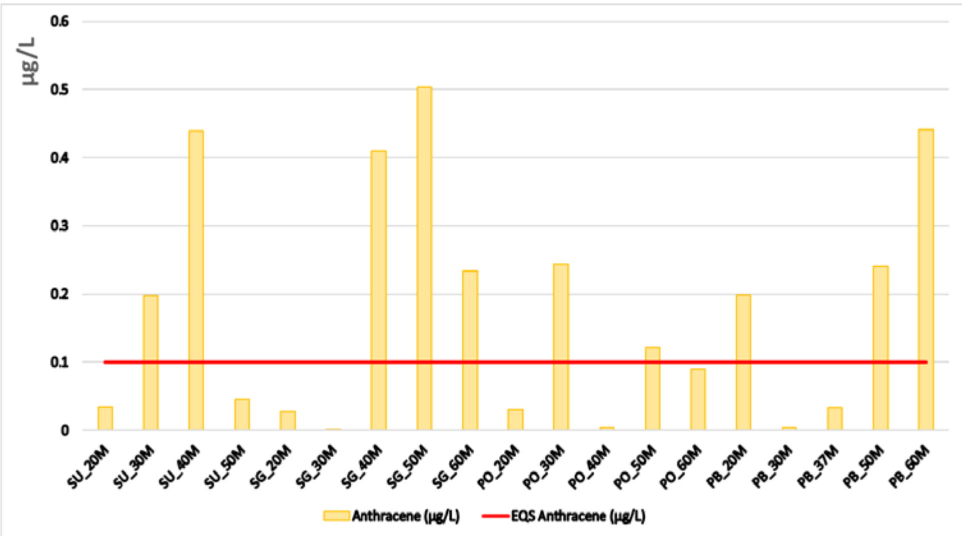

Fig. 3. Concentrations of anthracene in surface waters, in marine area under the influence of Danube, in relation to the proposed value to define good environmental status, May 2019

The others chlorinated compounds exceeded the threshold values in different proportion between 5% and 16%. Total petroleum hydrocarbons exceeded maximum admissible value (100 μg/g) stipulated by national legislation (Order No. 756/1997) in 10% of the analyzed samples and from PAHs group, phenanthrene was the only regulated compound that exceeded the threshold values proposed for sediment in order to define good ecological status in 10% of the analyzed sampled (Fig.5).

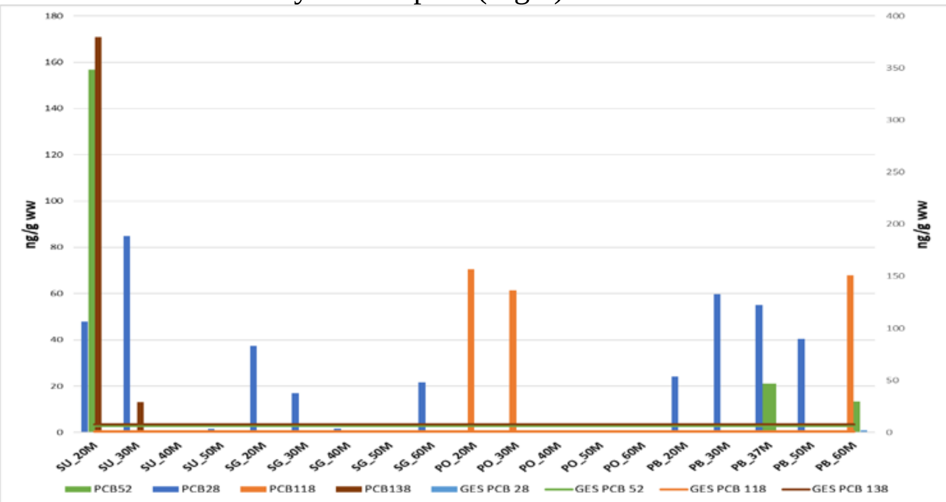

Fig. 4. Concentrations of polychlorinated biphenyls in sediment, in marine area under the influence of Danube, in relation to the proposed value to define good environmental status, May 2019

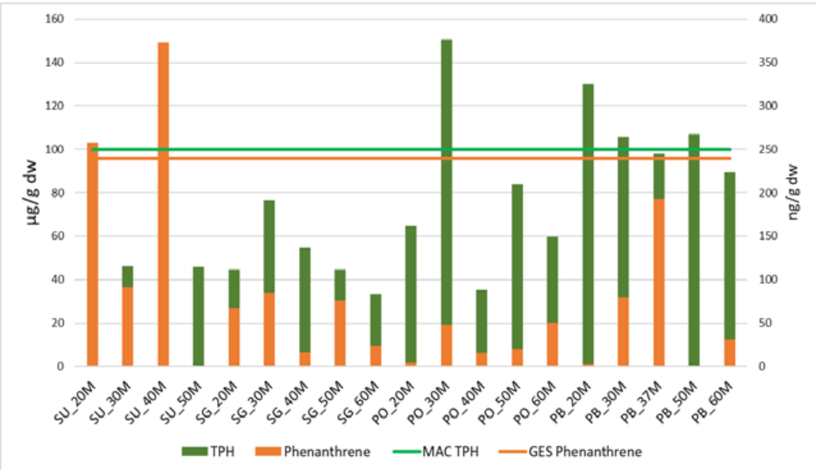

Fig. 5. Concentrations of phenanthrene and TPHs in sediment, in marine area under the influence of Danube, in relation to the proposed value to define good environmental status, May 2019

Except PCB 28, organic pollutants were in good status in sediment in Danube influenced area, according to the methodology developed to assess the status of Black Sea ecosystem in respect to MSFD (Boicenco *et al*., 2018). Based on ‘‘one out – all out’’ principle the sediment status was evaluated as “BAD” in 80% of the stations in sediment (Table 1) and in all station in water (Table 2) and in consequence, the overall status was evaluated as “BAD”.

Based on ‘‘one out – all out’’ principle the sediment status was evaluated as “BAD” in 80% of the stations in sediment (Table 1) and in all station in water (Table 2) and in consequence, the overall status was evaluated as “BAD”.

The evaluation done using the integrated hazardous substances assessment tool (CHASE) in each station, pointed out states of the chemical status from high to bad in sediment, bad in water (Table 1 and 2) and the overall assessment was bad in all stations.

Table 1. Romania sediment status according to CHASE and national methodology assessment

Station	Matrix	CHASE status	National methodology evaluation status
SU_20M	Sediment	5-Bad	Bad
SU_30M	Sediment	5-Bad	Bad
SU_40M	Sediment	2-Good	Bad
SU_50M	Sediment	2-Good	Bad
SG_20M	Sediment	5-Bad	Bad
SG_30M	Sediment	4-Poor	Bad
SG_40M	Sediment	2-Good	Bad
SG_50M	Sediment	2-Good	Good
SG_60M	Sediment	4-Poor	Bad
PO_20M	Sediment	5-Bad	Bad
PO_30M	Sediment	5-Bad	Bad
PO_40M	Sediment	1-High	Good
PO_50M	Sediment	2-Good	Good
PO_60M	Sediment	2-Good	Good
PB_20M	Sediment	4-Poor	Bad
PB_30M	Sediment	5-Bad	Bad
PB_37M	Sediment	5-Bad	Bad
PB_50M	Sediment	5-Bad	Bad
PB_60M	Sediment	5-Bad	Bad

Table 2. Romania water status according to CHASE and national methodology assessment

Station	Matrix	CHASE score/status	National methodology evaluation status
SU_20M	Water	5-Bad	Bad
SU_30M	Water	5-Bad	Bad
SU_40M	Water	5-Bad	Bad
SU_50M	Water	5-Bad	Bad
SG_20M	Water	5-Bad	Bad
SG_30M	Water	5-Bad	Bad
SG_40M	Water	5-Bad	Bad
SG_50M	Water	5-Bad	Bad
SG_60M	Water	5-Bad	Bad
PO_20M	Water	5-Bad	Bad
PO_30M	Water	5-Bad	Bad
PO_40M	Water	5-Bad	Bad
PO_50M	Water	5-Bad	Bad
PO_60M	Water	5-Bad	Bad
PB_20M	Water	5-Bad	Bad
PB_30M	Water	5-Bad	Bad
PB_37M	Water	5-Bad	Bad
PB_50M	Water	5-Bad	Bad
PB_60M	Water	5-Bad	Bad

Based on ‘‘one out – all out’’ principle the sediment status was evaluated as “BAD” in 80% of the stations in sediment (Table 1) and in all station in water (Table 2) and in consequence, the overall status was evaluated as “BAD”. The evaluation done using the integrated hazardous substances assessment tool (CHASE) in each station, pointed out states of the chemical status from high to bad in sediment, bad in water (Table 1 and 2) and the overall assessment was bad in all stations.

The evaluations results are the same for water and some differences are noted for sediment. These differences are the result of the different approach: two quality classes of local methodology and five for the integrated tool. As an overall result, the two assessment concluded the same quality for the area.

In Ukraine area, influenced by Danube, Dniester, Dnieper and Southern Bug rivers, the overall assessment conducted to a similar result.

In water, high levels of individual PCBs were observed, especially in

June, in the bottom layer of water at station 1 in the Danube Delta area (exit from the Kiliya arm) and at station 4 (Dnieper region) (Fig. 6). In September, extreme pollution with organochlorine pesticides, particularly with heptachlor (Fig. 7), was recorded in the surface layer of sea waters at station 3 (Dniester region) and at stations 1, 2 (Danube region). Also, in September, an increased content of benzo (g,h,i)perylene was recorded at all stations with a maximum in the Danube and Dnieper-Bug regions (Fig. 8). As follows, the ecological status of sea waters corresponded to the quality class - very bad (Table 3).

In sediment, an increased content of organochlorine pesticides was noted. In June, were measured high levels of lindane at station 6 in the Ochakov area (exit from the Dnieper-Bug estuary), DDT at station 2, in Danube region and dieldrin at station 3, at the outlet of the Dniester waters.

In September, the concentrations of these pesticides were even higher: lindane and dieldrin - at station 3 and the sum of DDT and its metabolites - at station 6 (Fig. 9). Also, naphthalene was in bad status at station 6, in September (Fig. 10). As a result, in these stations, the overall quality class was assessed as bad (Table 4).

Table 3. Ukraine water status according to CHASE and national methodology assessment

Station	Matrix	CHASE status	National methodology evaluation status
ST 1	Water	5-Bad	Very bad
ST 2	Water	5-Bad	Very bad
ST 3	Water	5-Bad	Very bad
ST 4	Water	5-Bad	Very bad
ST 5	Water	5-Bad	Very bad
ST 6	Water	5-Bad	Very bad

Table 4. Ukraine sediment status according to CHASE and national methodology assessment

Station	Matrix	CHASE status	National methodology evaluation status
ST 1	Sediment	3-Moderate	Satisfactory
ST 2	Sediment	3-Moderate	Satisfactory
ST 3	Sediment	5-Bad	Bad

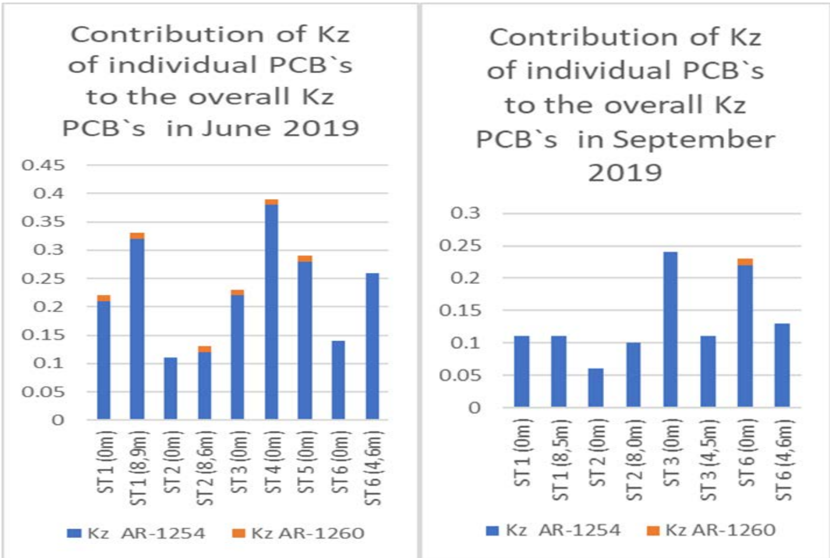

Fig. 6. Contribution of Kz of individual pollutants in seawater to the pollution of the PCBs group at monitoring stations in 2019

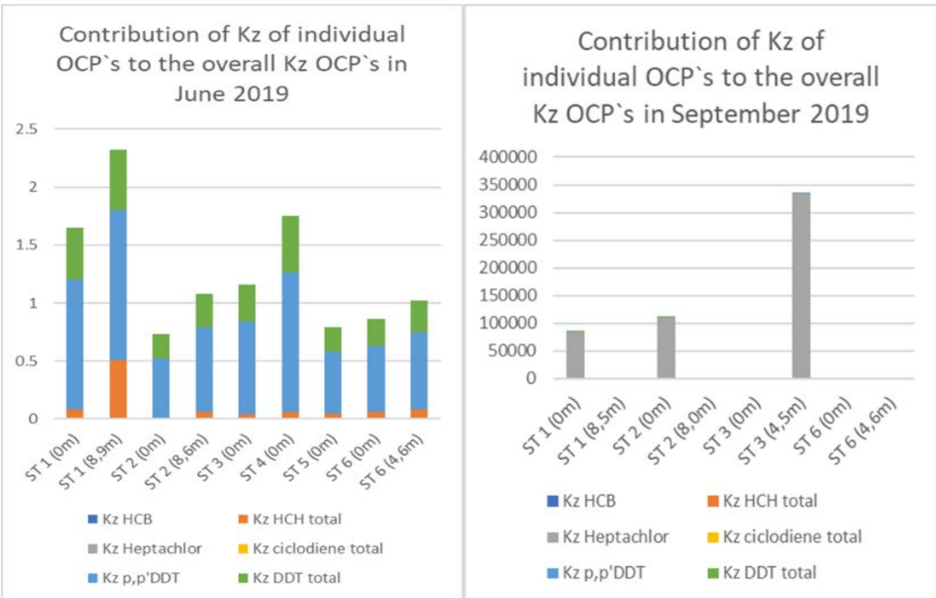

Fig. 7. Contribution of Kz of individual pollutants in seawater to the pollution of the OCPs group at monitoring stations in 2019

The evaluation done using the integrated hazardous substances assessment tool (CHASE) in each station pointed out states of the chemical status “Moderate” and “Bad” in sediment and “Bad” in water (Table 3 and 4) and the overall assessment was “Bad” in all stations.

The evaluations results are the same both in water and sediment. The two approaches are the same using five quality classes, even if their definition is slightly different. As an overall result, the two assessment concluded the same quality for the area.

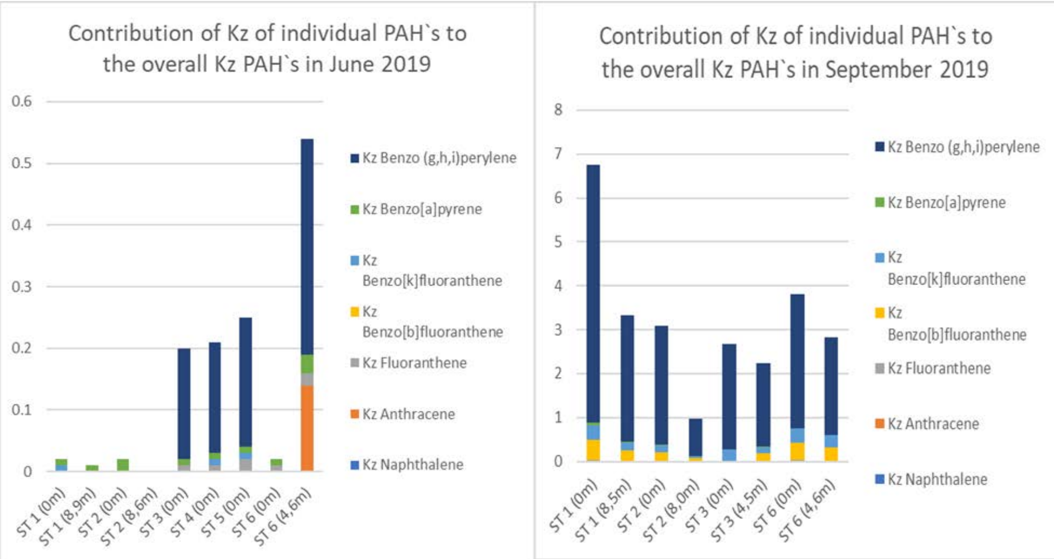

Fig. 8. Contribution of Kz of individual pollutants in seawater to the pollution of the PAHs group at monitoring stations in 2019

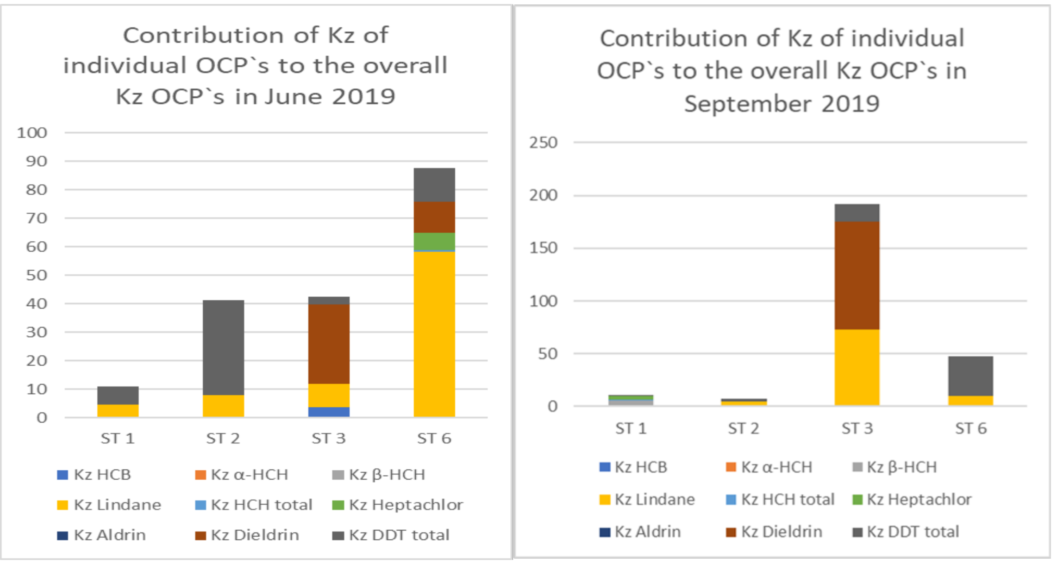

Fig. 9. Contribution of Kz of individual pollutants in bottom sediments to the pollution of the OCPs group at monitoring stations in 2019

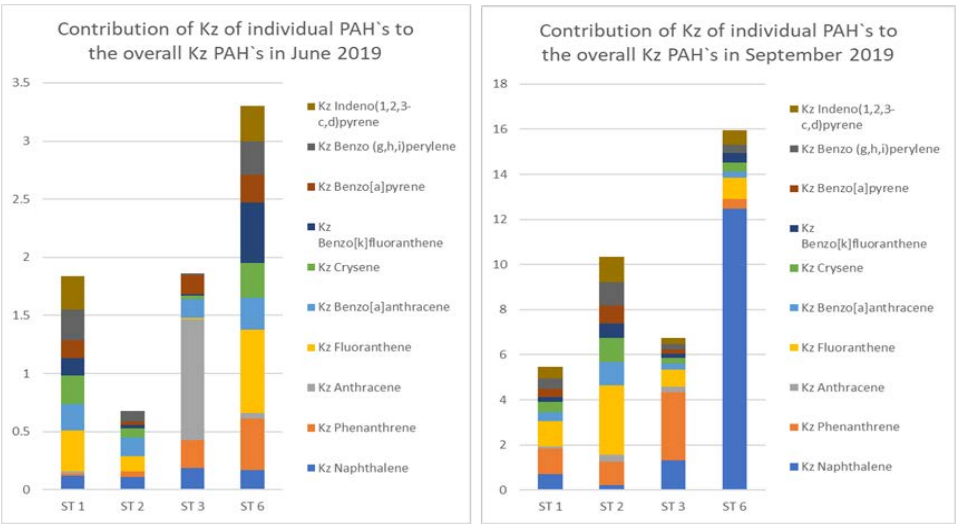

Fig. 10. Contribution of Kz of individual pollutants in bottom sediments to the pollution of the PAHs group at monitoring stations in 2019

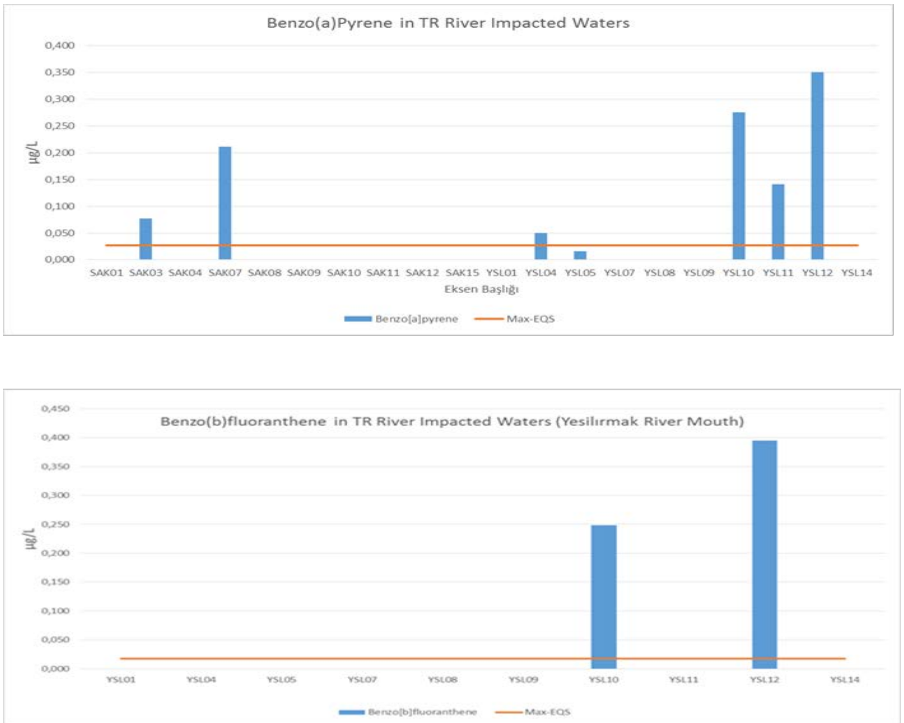

Fig.11. Concentrations of benzo(a)pyrene and benzo(b)fluoranthene in surface waters, in marine area under the influence of Sakarya and Yesilırmak in relation to the proposed value to define good environmental status, January 2020

Measurement results of the organic compounds such as petroleum hydrocarbons, PAHs, PCBs and OCPs in water and sediment matrices indicate relatively less contamination of the Turkish coastal areas under the influence of rivers.

In the water matrix, TPH values ranged between 0.019-0.960 µg/L and 0.055-1.014 µg/L in Sakarya and Yesilirmak river impact areas, respectively. These values are lower than the Max-EQS value (100 µg/L) stated in the National Surface Water Management Regulation from 2016. Concentrations of most of the priority organic substances were found below the Max-EQS (Directive 2013/39/EU) except Benzo(a)Pyrene(BaP), one of the 16 polyaromatic hydrocarbons. The BaP levels were found higher than the Max-EQS (0.027 µg/L) in the winter season at two stations of Sakarya (SAK07 and SAK03: 0.211 µg/L and 0.078 µg/L) and four stations of Yesilirmak river mouths (YSL4, YSL10, YSL11 and YSL 12: 0.050 µg/L, 0.276 µg/L, 0.141 µg/L and 0.351 µg/L respectively). Benzo(b)fluoranthene concentrations were also higher in the two stations of Yesilırmak (0.248 µg/L and 0.395 µg/L at YSK10 and YSK12) than the threshold value (Max-EQS 0.017 µg/L) (Directive 2013/39/EU) (Fig.11.).

Pesticide derivatives (a-BHC, b-BHC, heptachlor, aldrin, dieldrin and endrin) were measured at trace quantity or below the detection limit.

In sediment, sum of the DDT's including metabolites (DDE+DDD+DDT) exceeded the threshold values (1.58 ng/g) in approximately 18% of the Sakarya and 73% of Yesilirmak samples (Fig.12). Concentrations of organochlorinated pesticides and polychlorinated biphenyls were below the threshold values in all stations of both study sites.

The average values of DDT and its metabolites detected in Sakarya River sediment samples (p'p- DDT 8.5 % > p'p- DDE 48.9 % > p'p- DDD 42.6 %) and Yeşilırmak River sediment samples (p'p- DDT 4.9 % > p'p- DDE 39.6 % > p'p- DDD 55.6 %) indicated that DDT metabolites, p'p- DDE and p,';DDD were dominant. Distribution of DDT and its metabolites (%) in sediment are shown in Figure 13. This means that DDTs are caused by historical degradation. DDT can biodegradable to DDE under aerobic conditions and to DDD under anaerobic conditions (Da *et al.*, 2013).

Integration of all organic parameters was carried out using the CHASE program (https://niva.shinyapps.io/ANEMONE_CHASE/) and the method used in national monitoring program based on "one out all out" principle of WFD. According to the CHASE results, the assessment made for the water matrix shows that all stations are of medium quality, while the national assessment shows that six stations are bad, and the others have good water quality (Table 5). Organic contaminant levels in sediment matrix were aggregated using similar methods (Table 6). Based on these assessments, it can be said that the use of the CHASE tool makes a better separation in the chemical status. National classification based on "one out all out" principle can only create two categories that may not be useful for the coastal managers. DDT and its derivatives were found above the limit values in the sediments in front of Sakarya and Yeşilırmak rivers. Although the use of DDT as a pesticide was completely banned in 1985 in Turkey, it is still above the measurement limits in the sediments in some coastal regions. However, the previous monitoring studies in that area showed that these higher DDT contents are originated from old usage (MoEU and TUBITAK-MRC, 2020). Hence, the stations in the "bad" class are due to the presence of legacy usage DDTs similarly.

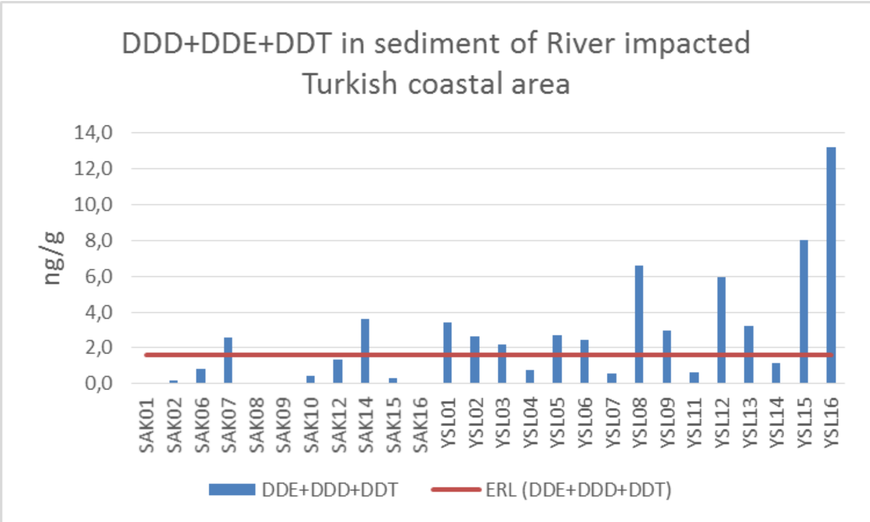

Fig. 12. Concentrations of DDD+DDE+DDT in surface sediments of marine area under the influence of Sakarya and Yesilırmak Rivers, in relation to the proposed value to define good environmental status January 2020

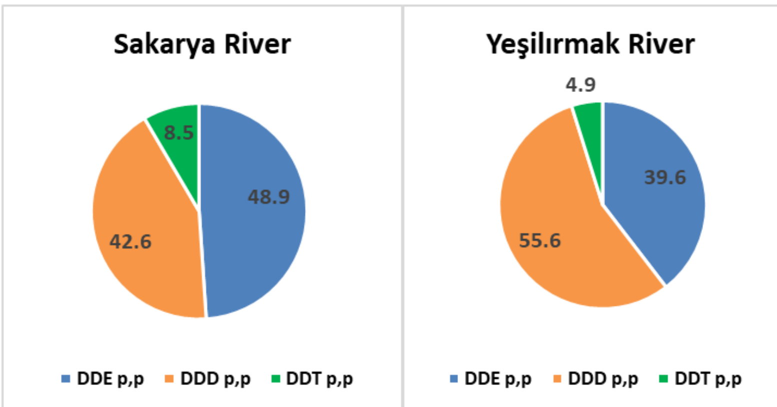

Fig. 13. Distribution of DDT and its metabolites (%) in sediment

Table 5. Turkey status according to CHASE and national methodology assessment

Station	Matrix	CHASE status	National methodology evaluation status
SAK01	Water	3-Moderate	Good
SAK02	Water	3-Moderate	Good
SAK03	Water	3-Moderate	Bad
SAK04	Water	3-Moderate	Good
SAK07	Water	3-Moderate	Bad
SAK08	Water	3-Moderate	Good
SAK09	Water	3-Moderate	Good
SAK10	Water	3-Moderate	Good
SAK11	Water	3-Moderate	Good
SAK12	Water	3-Moderate	Good
SAK15	Water	3-Moderate	Good
YSL01	Water	3-Moderate	Good
YSL04	Water	3-Moderate	Bad
YSL05	Water	3-Moderate	Good
YSL07	Water	3-Moderate	Good
YSL08	Water	3-Moderate	Good
YSL09	Water	3-Moderate	Good
YSL10	Water	3-Moderate	Bad
YSL11	Water	3-Moderate	Bad
YSL12	Water	3-Moderate	Bad
YSL14	Water	3-Moderate	Good
YSL16	Water	3-Moderate	Good

As the overall assessment, CHASE use the ‘one out, all out principle’, so the global status was evaluated to “Bad” for the north-western and western part of the Black Sea, whereas the southern area was evaluated to “Moderate” (Fig.14), even if in sediment the evaluation concluded a better quality than in the water (Fig. 15 and Fig.16).

The CHASE results give a warning about the general status in the assessment area: if a chemical is in bad status, it must take measures to protect the ecosystem against its effects. Still, the five quality classes allow for prioritization between different areas as some of them are more affected than others (even if we are talking about the levels of pollutants or the number of pollutants exceeding the thresholds). Any classification below good status requires adequate measures to reduce the pollution

Table 6. Turkey sediment status according to CHASE and national methodology assessment

Station	Matrix	CHASE status	National methodology evaluation status
SAK01	Sediment	2-Good	Good
SAK02	Sediment	2-Good	Good
SAK03	Sediment	1-High	Good
SAK04	Sediment	1-High	Good
SAK06	Sediment	2-Good	Good
SAK07	Sediment	3-Moderate	Bad
SAK08	Sediment	2-Good	Good
SAK09	Sediment	2-Good	Good
SAK10	Sediment	2-Good	Good
SAK11	Sediment	3-Moderate	Good
SAK12	Sediment	2-Good	Good
SAK14	Sediment	3-Moderate	Bad
SAK15	Sediment	2-Good	Good
SAK16	Sediment	2-Good	Good
YSL01	Sediment	3-Moderate	Bad
YSL02	Sediment	3-Moderate	Bad
YSL03	Sediment	3-Moderate	Bad
YSL04	Sediment	2-Good	Good
YSL05	Sediment	3-Moderate	Bad
YSL06	Sediment	2-Good	Bad
YSL07	Sediment	2-Good	Good
YSL08	Sediment	3-Moderate	Bad
YSL09	Sediment	3-Moderate	Bad
YSL11	Sediment	2-Good	Good
YSL12	Sediment	3-Moderate	Bad
YSL13	Sediment	3-Moderate	Bad
YSL14	Sediment	2-Good	Good
YSL15	Sediment	3-Moderate	Bad
YSL16	Sediment	3-Moderate	Bad

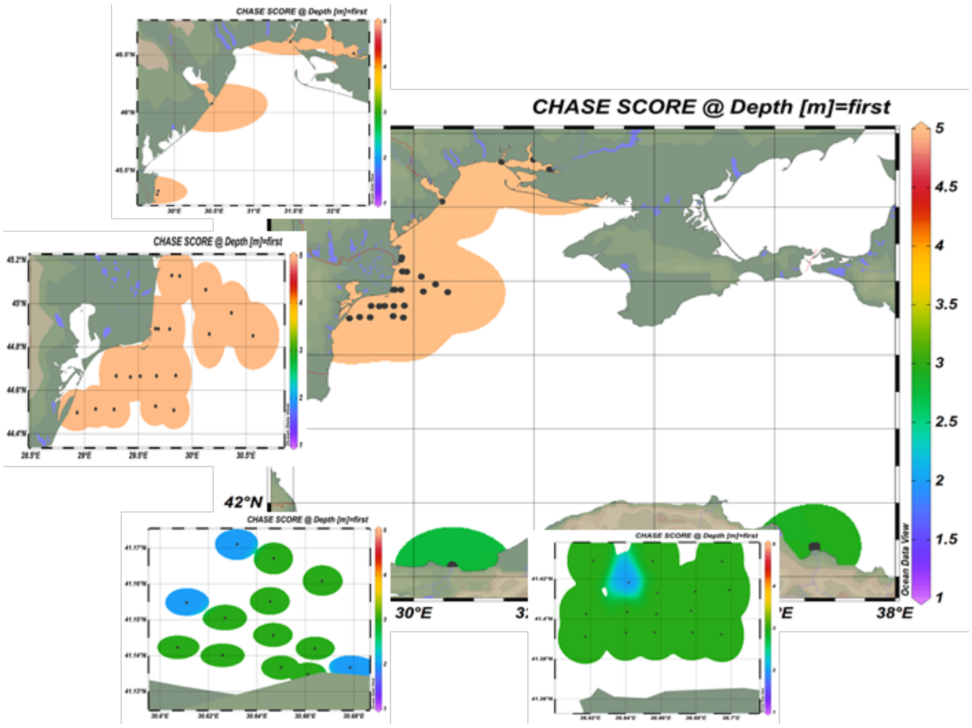

Fig. 14. Overall, CHASE results in the rivers influenced area of the north-western, western, and southern part of the Black Sea

There are many differences between the studied areas regarding indicator substances or threshold values used in the assessment, but even so, the Black Sea quality seems to be better in the southern part where the status was moderate comparative with the other areas, which were in bad status. Therefore, we identified the chemical pressure coming from organic pollutants input from north-western rivers. The results can contribute to evaluate the measures efficiency in the Black Sea region.

A common agreed set of indicators and threshold will give a better understanding of the pressures of the Black Sea.

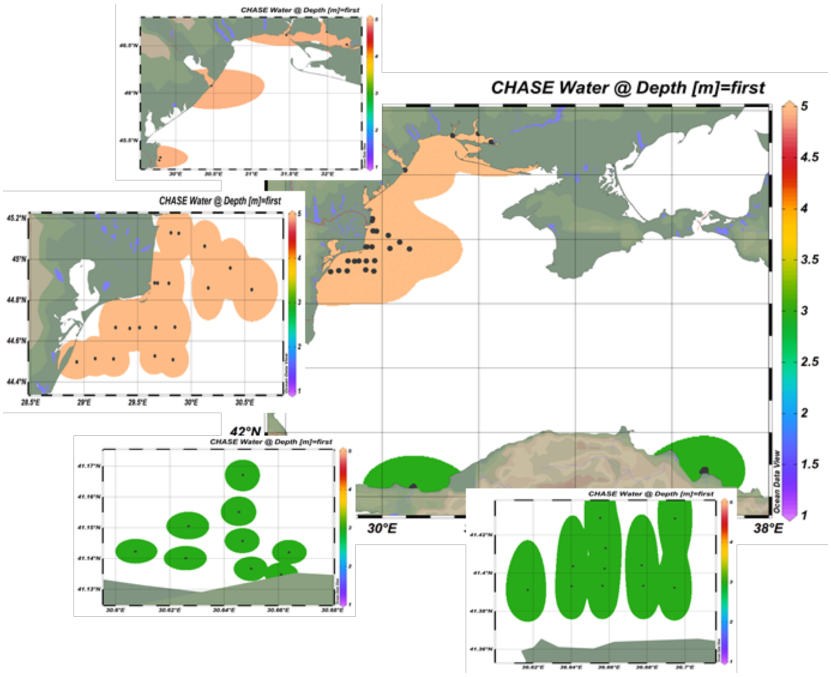

Fig. 15. Water CHASE results in the rivers influenced area of the north-western, western, and southern part of the Black Sea

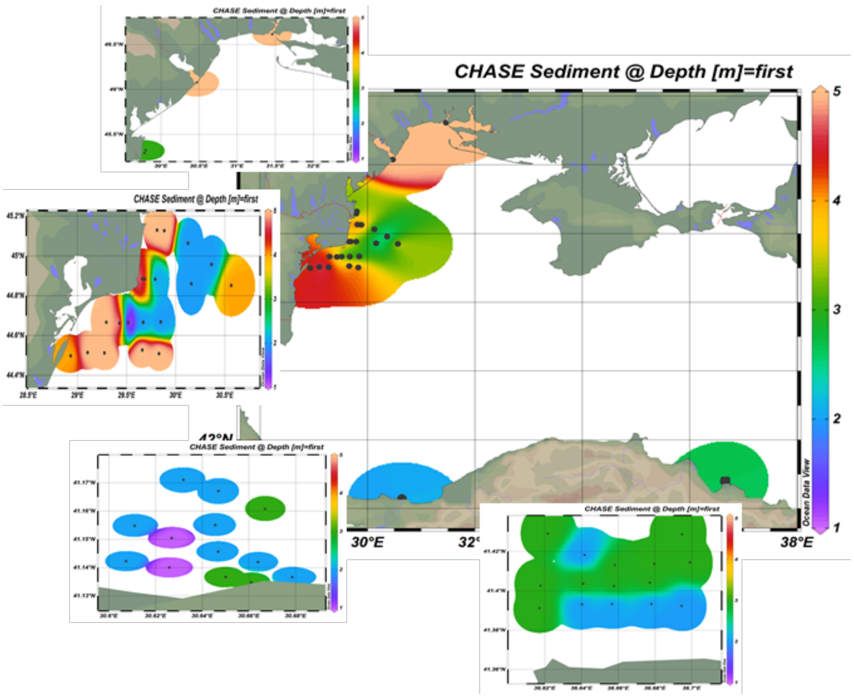

Fig. 16. Sediment CHASE results in the rivers influenced area of the north-western, western, and southern part of the Black Sea

CONCLUSIONS

The integrated assessment tools CHASE makes a clearer image of the pollution level, being more useful for the coastal managers.

Even though there are many differences between areas regarding indicator substances or threshold values used in assessment, the Black Sea quality is better in the southern part where the status was moderate comparative with the other areas which were in bad status.

A common agreed set of indicators and threshold will give a better understanding of the pressures of the Black Sea.

Acknowledgment. This study has been supported by the ANEMONE project (funded by the EU under ENI CBC Black Sea basin Programme 2014-2020, grant contract 83530).

We would like to express our very great appreciation to Dr. Ciaran Joseph Murray, NIVA Denmark, for his valuable guidance and constructive suggestions for testing the Contaminants Status Assessment Tool (CHASE) in the Black Sea region. His willingness to give his time so generously has been very much appreciated.

REFERENCES

Andersen J. H., Murray C., Larsen M. M., Green N., Høgåsen T., Dahlgren E., & Garnaga-Budrė G., & Gustavson K., Haarich M., Kallenbach E.M.F., Mannio J., Strand J. and Korpinen S. (2016), Development and testing of a prototype tool for integrated assessment of chemical status in marine environments. *Environ Monit Assess*, 188:115.

Boicenco L., Abaza V., Anton E., Bișinicu E., Buga L., Coatu V., Damir N., Diaconeasa D., Dumitrache C., Filimon A., Galațchi M., Golumbeanu M., Harcotă G., Lazăr L., Marin O., Mateescu R., Maximov V., Mihailov E., Nenciu M., Nicolaev S., Niță V., Oros A., Pantea E., Radu G., Spinu A., Stoica E., Tabarcea C., Timofte F, Țiganov G., Țoțoiu A, Vlas O., Vlăsceanu E., Zaharia T. (2018), Study on the elaboration of the report regarding the ecological status of the Black Sea marine ecosystem according to the requirements of Art. 17 - Strategy Framework Directive for the Marine Environment (2008/56/EC), 331 pp (*in Romanian*).

CHASE (2019), https://niva.shinyapps.io/ANEMONE_CHASE

Da, C., Liu G., Tang Q., and Liu J. (2013), Distribution, sources and ecological risks of organochlorine pesticides in surface sediments from the Yellow River Estuary, China. *Environmental Science Processes & Impacts*, 2013, 15, 2288.

DIRECTIVE 2000/60/EC of the European Parliament and of the Council, establishing a framework for Community action in the field of water policy, *Official Journal of the European Communities*, L 327, 22 December 2000, 1-71.

DIRECTIVE 2013/39/EU of the European Parliament and of the Council, amending Directives 2000/60/EC and 2008/105/EC as regards priority substances in the field of water policy, *Official Journal of the European Communities*, L 226, 24 August 2013, 1-17.

Laane R.W.P.M., Slijkerman D., Vethaak A.D., Schobben, J.H.M. (2012), Assessment of the environmental status of the coastal and marine aquatic environment in Europe: A plea for adaptive management, *Estuarine, Coastal and Shelf Science* 96, 31-38.

Long E.R, Field L.J., MacDonald D.D. (1998), Predicting toxicity in marine sediments with numerical sediment guidelines. *Environmental Toxicology and Chemistry* 17 (4), 714–727.

Miladinova S., Stips A., Macias Moy D., Garcia-Gorriz E. (2020), Pathways and mixing of the north western river waters in the Black Sea, *Estuarine, Coastal and Shelf Science* 236, 106630.

Ministry of Environment and Urbanization (MoEU), TUBITAK- National Monitoring Report (MRC), (2020), "Integrated Marine Pollution Monitoring 2017-2019 Programme: 2019 The Black Sea Report, TUBITAK-MRC Press, Kocaeli.

Ojaveer H., Eero M. (2011), Methodological Challenges in Assessing the Environmental Status of a Marine Ecosystem: Case Study of the Baltic Sea. *PLoS ONE* 6(4): e19231. doi:10.1371/journal.pone.0019231

OSPAR (2008). Coordinated Environmental Monitoring Programme – Assessment manual for contaminants in sediment and biota.

UNEP MAP (2011). Development of Assessment Criteria for Hazardous substances in the Mediterranean. *UNEP(DEPI)/MED WG.* 365/Inf.8.

US Environmental Protection Agency (1998). EPA's contaminated sediment management strategy. *EPA-823-R-98-001*. Washington, DC.