TRANSPORT OF DANGEROUS GOODS
TECHNICAL COMMITTEE
14th session
20 June, Podgorica Montenegro

DETERMINATION OF POLLUTANTS AND PHYSICAL-CHEMICAL PARAMETERS IN DURRES PORT'S

Spiro Drushku, Aurel Nuro, Alma Shehu, Julian Shehu
Tirana University, Faculty of Natural Sciences, Department of Chemistry
E-Mail: spiro.drushku@fshn.edu.al

SCOPE OF OUR STUDY

ASSESSMENT OF STATE OF POLLUTION IN WATERS AND SEDIMENTS OF THE AREA OF DURRESI HARBOR.

- **Persistent organic pollutants**
- **Organochlorine pesticides (OCP)**
- **Polychlorinated biphenyls (PCB)**
- **Polycyclic aromatic Hydrocarbons (PAH)**
- **BTEX**
- **Nutrients and Physical-chemical parameters**

It is the largest seaport of Albania, situated in the city of Durres.

The port ranks as the largest passenger port in Albania and in the Adriatic Sea, with an annual passenger volume of approximately 1.5 million.

There is an intensive commercial and passenger activity.

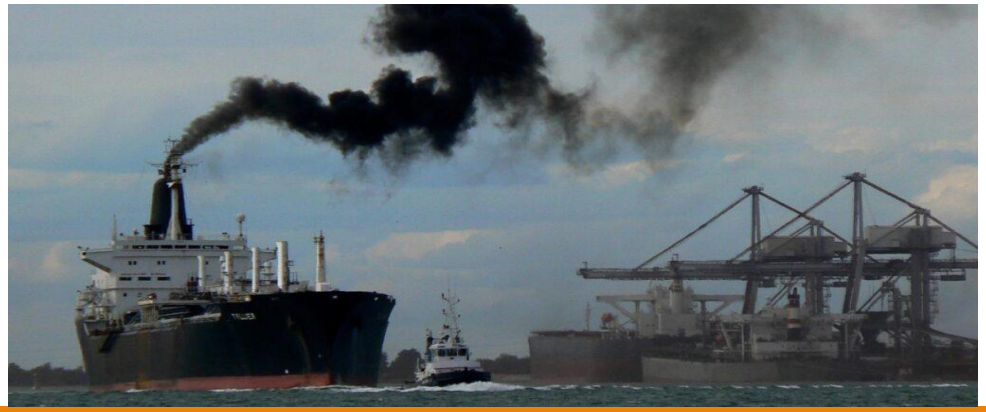
Pollution of ports

Ports are a significant source of global air, water and land pollution exposing people to serious health and environmental impacts.

Port emissions in air include greenhouse gases, notably carbon dioxide (CO_2), oxides of nitrogen (NO_x), oxides of sulfur (SO_x), methane (CH_4) and particulate matter (PM).

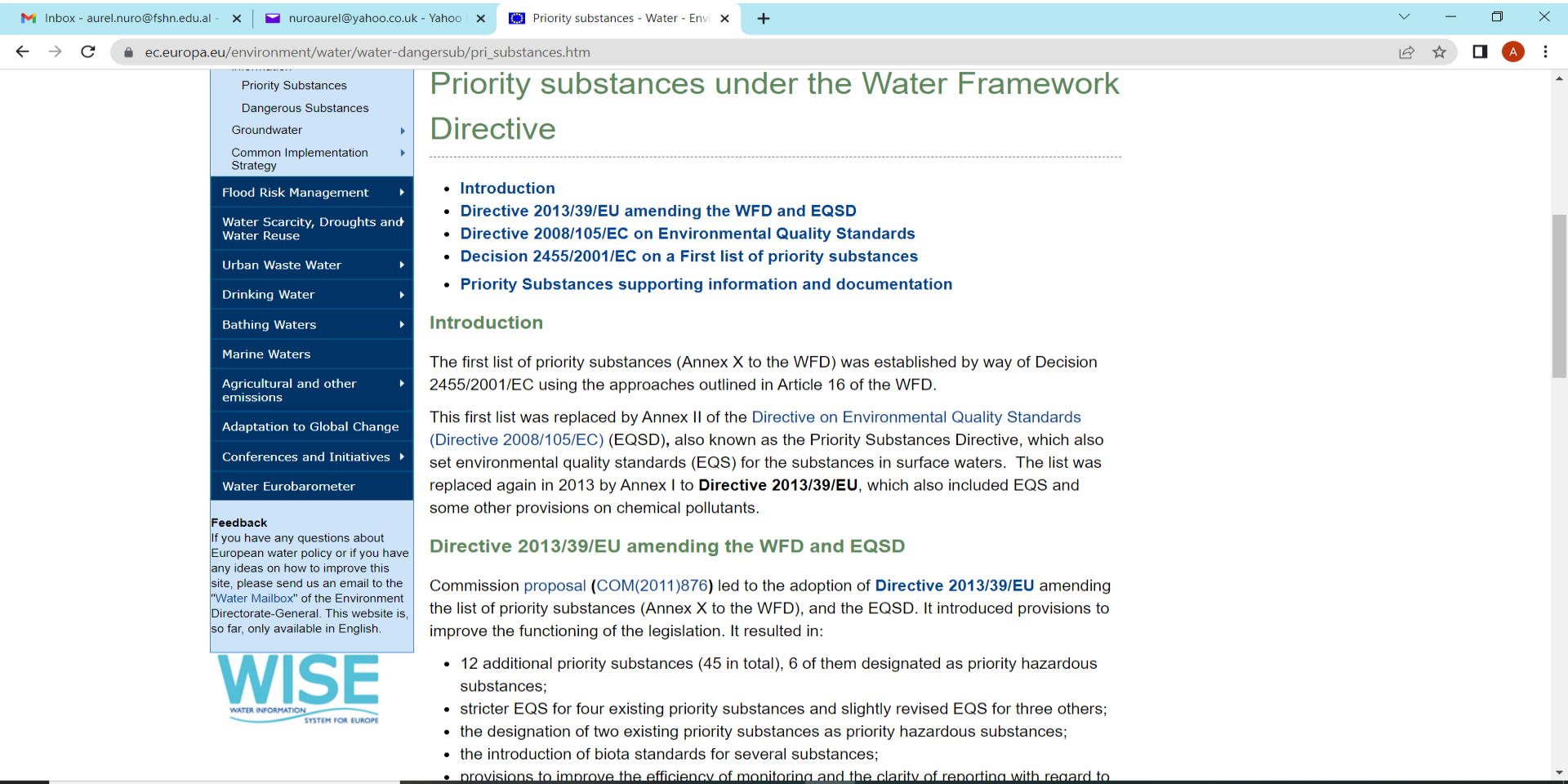
Port operations can cause significant damage to water quality—and subsequently to marine life and ecosystems, as well as human health. These effects may include bacterial and viral contamination of commercial fish and shellfish, depletion of oxygen in water, and bioaccumulation of certain toxins in fish.

Major water quality concerns at ports include wastewater and leaking of toxic substances from ships, stormwater runoff, and dredging.

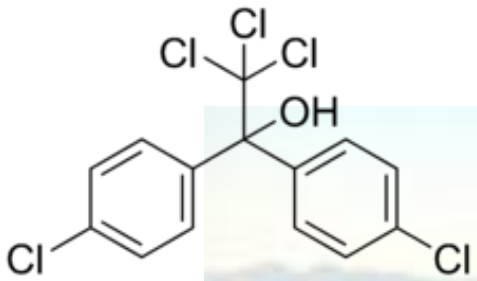


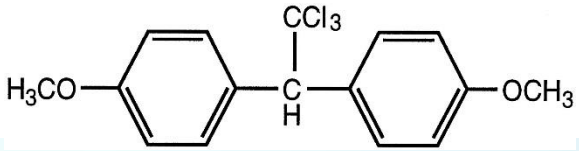
Persistent Organic Pollutants

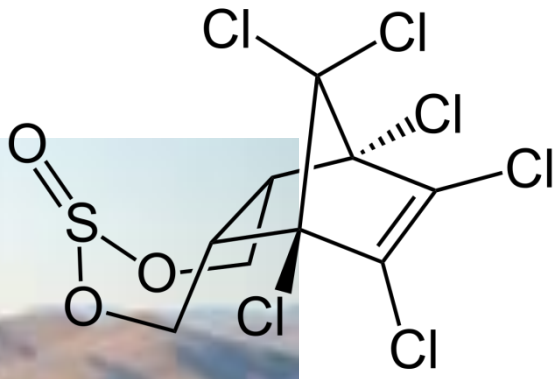
Organochlorine pesticides, polychlorinated biphenyls, some PAHs and benzene are classified as Persistent Organic Pollutants (POP) as well as priority substances because they are persistent for many years after their application and pose high toxicity.

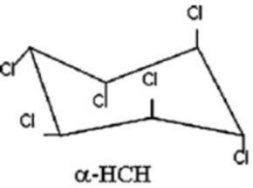


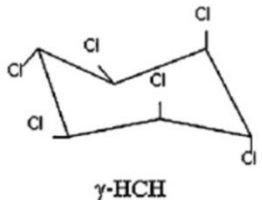
Organochlorinated pesticides (OCPs) are a group of compounds of great chemical stability and persistence whose presence in the environment is a clear indication of anthropogenic pollution. The massive use of pesticides for agricultural purposes caused their widespread diffusion to all environmental compartments including a wide range of organisms up to the humans. Before 90' organochlorine pesticides were used widely in Albania for agricultural purposes.

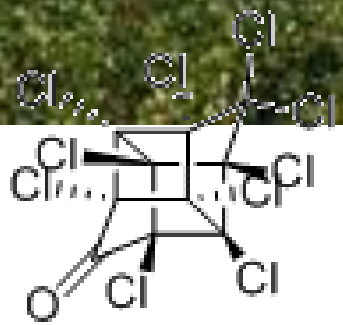


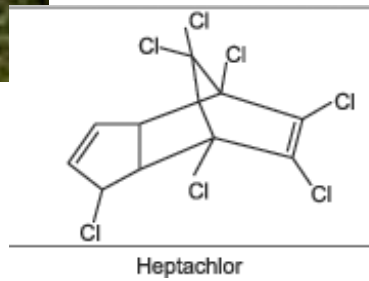




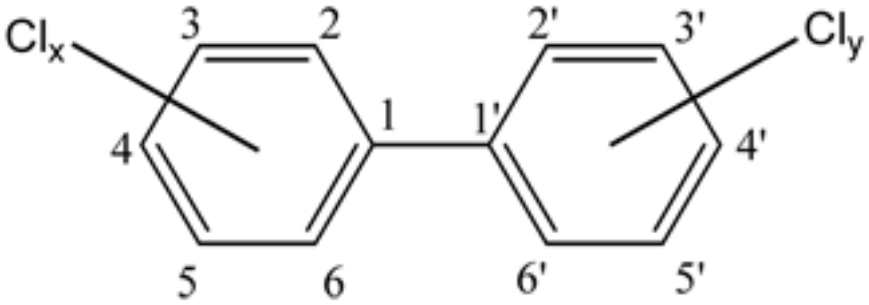






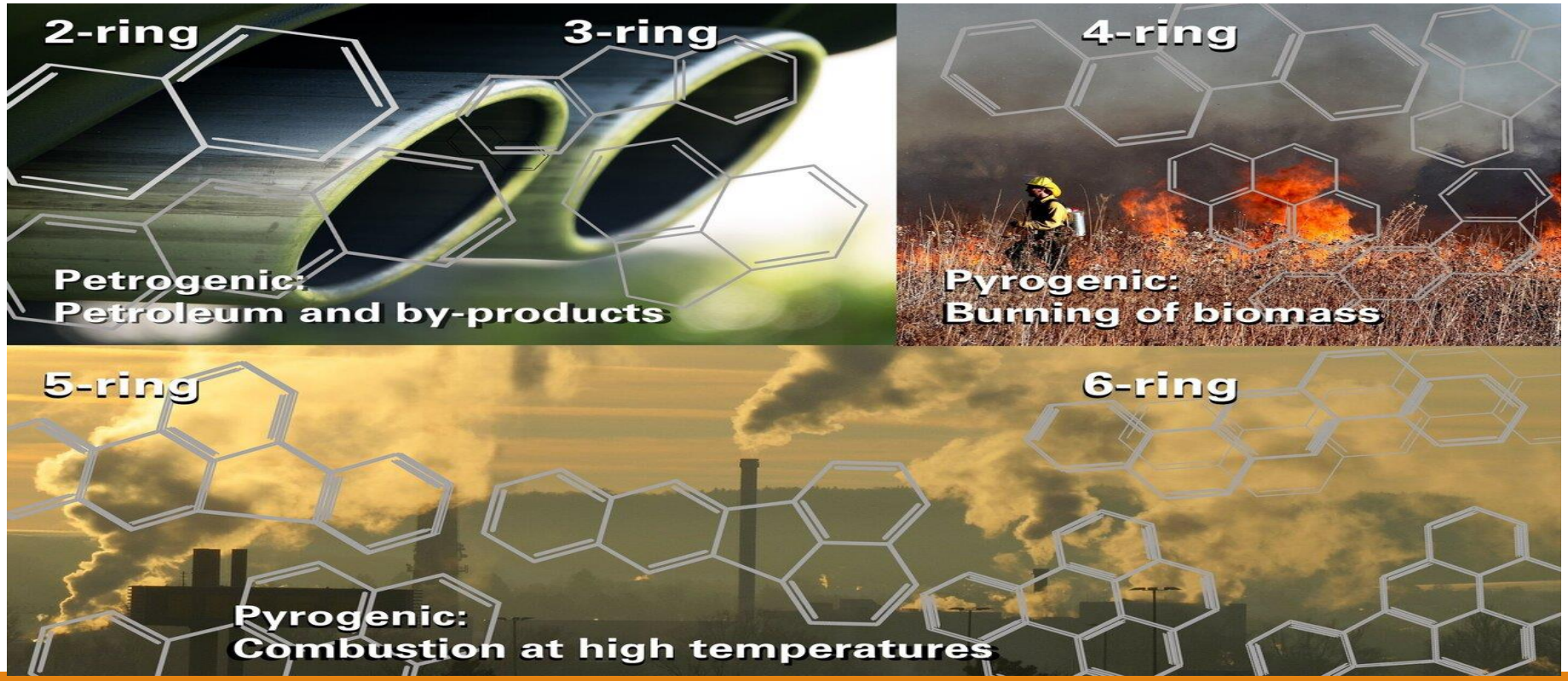


Commercial **PCB mixtures** were used in a wide variety of applications. They are chemically highly stable, lipophilic compounds and resist microbial, photochemical, chemical and thermal degradation (Lang, 1992). In Albania PCBs are used mainly in transformer oils after 90', but the source of pollution is mostly airborne origin with predominance of most volatile PCB congeners



Polycyclic aromatic hydrocarbons (PAHs)

PAH are priority organic pollutants, which are ubiquitously found in the atmospheric, aquatic, and terrestrial systems and therefore are closely monitored in the environment. Some of them such as Benzo[a]anthracene are genotoxic, mutagenic, carcinogenic, and/or teratogenic. Low molecular weight PAHs and BTEX move easily in nature with long range distances because of their volatility. Higher molecular members of this class of pollutants are relatively immobile due to their large molecular volumes and are less volatile, relatively insoluble in water, and more lipophilic than the lower molecular members. They also are known to stay longer in the environment.



Water sampling

Water samples from the port of Durres were taken in 12 different stations of the port of Durres (10 inside and 2 outside its area). Water samples were taken in July 2023. The sampling stations are presented in Figure 1. Volume of 2.5 l of seawater were taken from each station in Teflon bottles. The sampling method was based on ISO 5667-14:2016. Water samples were tranported and conserved at +4^{o}C before being analyzed.

Fig. 1 Sampling site in the port of Durres, July 2022

Treatment of water samples for pesticide and PCB analyzes

Liquid-liquid extraction was used for extraction of organochlorine pesticide and polychlorinated biphenyls from water samples. One liter of water and 50 ml n-hexane as extracting solvent were added in a separatory funnel. After extraction, the organic phase was dried with 5 g of anhydrous Na_2SO_4 for water removal. A florisil column was used for the sample clean-up. 20 ml n-hexane/dichloromethane (4/1) was used for elution. After concentration to 1 ml, the samples were injected in GC/ECD.

Treatment of sediment samples for analyzes of chlorinated pollutants

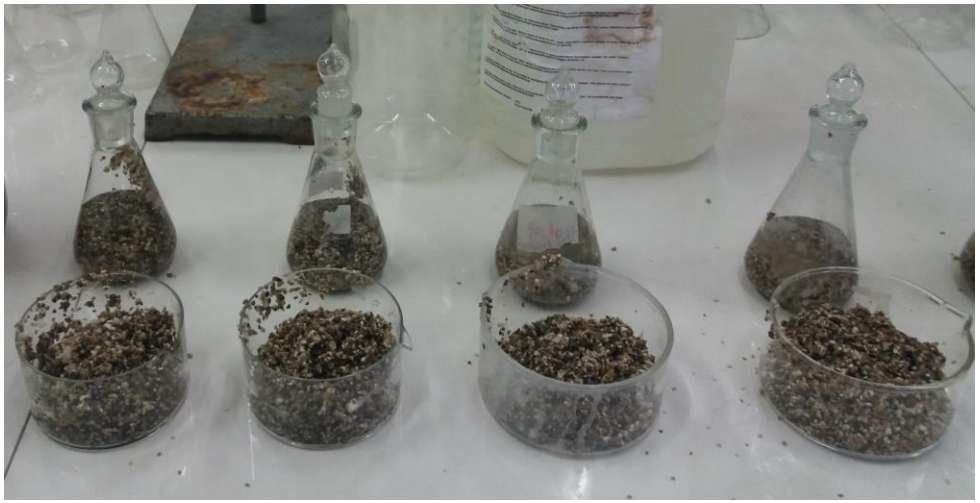
For the determination of chlorine-organic pollutants, 5 g of sediment sample was extracted with 40 ml of n-Hexane/Dichloromethane (3:1) in an ultrasonic bath for 60 minutes at 30oC. The solvent was evaporated using Kuderna-Danish to 10 ml. Metallic mercury was added to the test tube until the complete removal of sulfur compounds which are usually found in sediment samples and which hinder the gas chromatographic analysis. The extract is carefully transferred to an open glass column (10 cm x 0.8 cm) packed with florisil. The elution was carried out with 20 ml of n-Hexane/Dichloromethane (4:1) and collected in Kuderna-Danish where it was evaporated to block term to 2 ml. The extract was injected into the gas chromatograph equipped with an ECD detector.

Treatment of water samples for PAH analyzes

Two steps liquid-liquid extraction (LLE) was used for extracting PAHs from marine water samples. One liter of water with firstly 30 ml dichloromethane (first step LLE) and after that 30 ml hexane (second step LLE) as extracting solvent were added in a separator funnel. After extraction, the organic phase was dried with 5 g of anhydrous Na_2SO_4 for water removing. Extracts were concentrated to 1 ml hexane using Kuderna-Danish and then were injected in GC/FID for qualification/quantification of PAHs.

Treatment of sediment samples for PAH analyzes

Only the 63 micron fractions were taken into analysis. For the determination of chlorine-organic pollutants, 5 g of sediment sample was taken and thrown into a 100 ml beaker where 40 ml of n-Hexane was added as extraction solvent. Their extraction was carried out in an ultrasonic bath for 30 minutes at 30oC. After separation of the organic phase, 2 g of anhydrous sodium sulfate was added to remove traces of water. The solvent was evaporated using Kuderna-Danish to 2 ml. The extract was injected into the gas chromatograph equipped with FID detector.

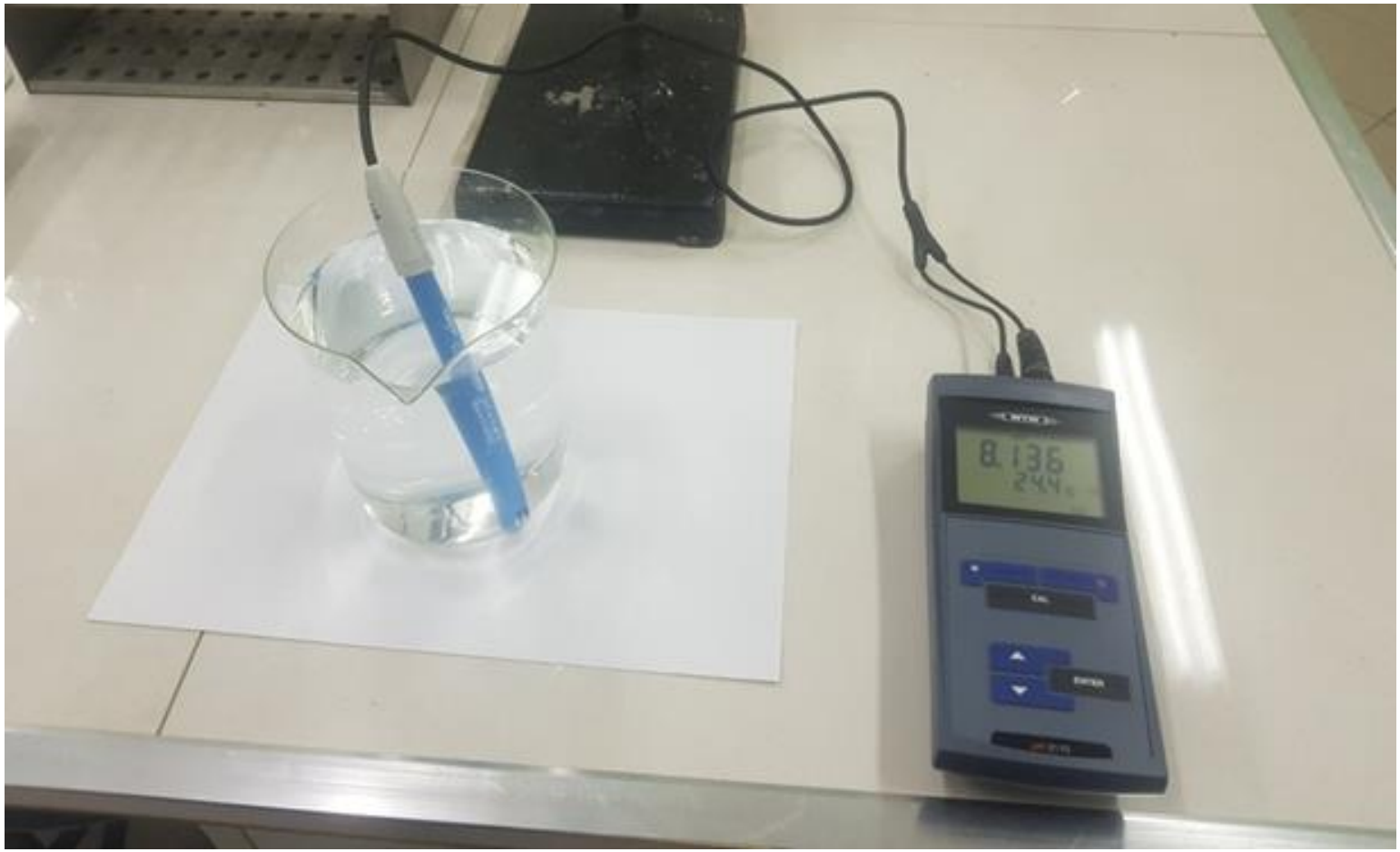


Gas chromatography analysis of pesticides and PCBs

Organochlorine pesticides and PCBs were analyzed simultaneously using capillary column model Rtx-5 (30 m long x 0.25 mm i.d. x 0.25 µm film thicknesses) on a gas chromatograph Varian 450 GC with ECD detector. Helium was used as carrier gas (1 ml/min) while nitrogen as make-up gas (24 ml/min). The manual injection was done in splitlesss mode at 280°C. The organochlorine pesticides detected were DDT-related chemicals (o,p-DDE, p,p-DDE, p,p-DDD, p,p-DDT), HCHs (a-, b-, γ- and d-isomers), Heptachlor's (Heptachlor and Heptachlorepoxide); Aldrin's (Aldrine, Dieldrine and Endrin) and Endosulfanes (Endosulfan alpha, Endosulfan beta and Endosulfan sulfat). Analysis of PCBs was based on the determination of the seven PCB markers (IUPAC Nr. 28, 52, 101, 118, 138, 153 and 180).

Determination of temperature and PH in the field

At each of the stations where the water samples were taken, field measurements were made with the PLOT 2 portable device for determining temperature and PH. Before field measurements, the device was calibrated with buffer solutions with pH = 4, 7 and 10. The measurements were made until the value of the device stabilized.



Determination of Dissolved Oxygen (DO)

The determination of dissolved oxygen in seawater is carried out by titration method. About 300 mL of seawater, magnesium sulfate solution, alkaline/iodine/azide solution, and H_2SO_4cc are added to a Winkler container. The solution is titrated with a sodium thiosulfate solution in the presence of starch until a stable blue color is formed.

Determination of BOD_5

VELP brand automatic sensors (respirometers) were used to estimate the 5-day biological oxygen demand (BOD_5) in seawater. The measurement was carried out at a level of 250 ppm. The samples were placed at 20°C for 5 days, and a direct reading of the BOD value was made for each sample.

Determination of COD

For the determination of chemical oxygen demand (COD), SPEC COD digestion tubes were used, which use standard 16-mm tubes pre-prepared with mercury sulfate ($HgSO_4$). 2 ml of seawater was taken in the pre-filled COD digestion tube, close the cap and mix vigorously for 1 minute. The tube is placed in the thermoreactor ECO 16, set at 150^oC. After being heated for 2 hours, the samples were allowed to cool, then measured in a PF-3 spectrophotometer at wavelengths suitable for COD analysis.

UV-VIS analysis of nutrients and sulfates

The analysis of $N\text{-}NO_3$ in water is based on the ISO 7890-3: 1988 method for their determination with the spectrophotometry technique at a wavelength of 420 nm.

The analysis of $N\text{-}NO_2$ in water is based on the ISO 6777: 1984 method for their determination by the colorimetric method at 543 nm.

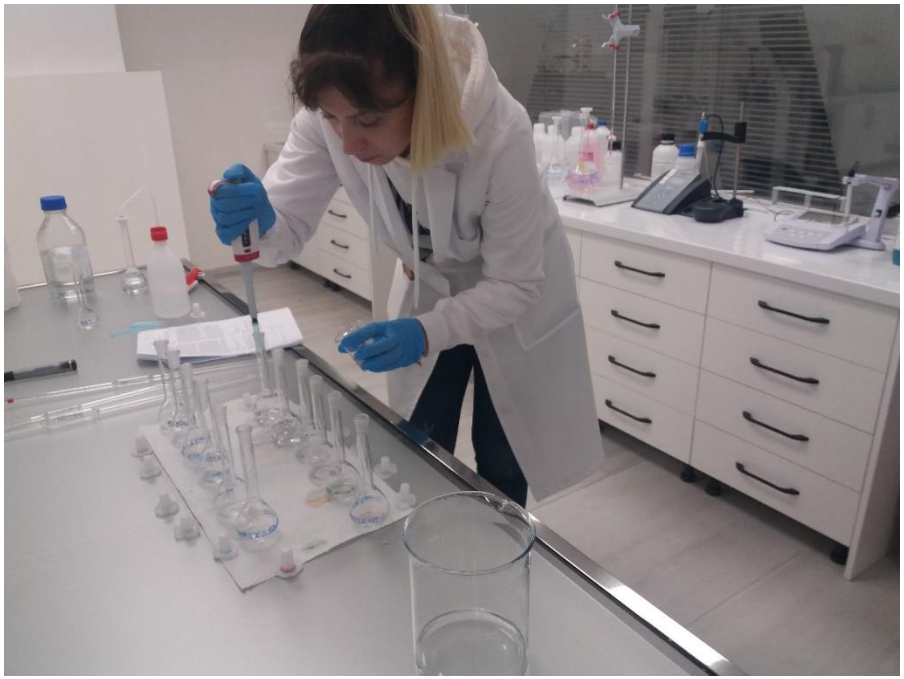
The analysis of $N\text{-}NH_4$ in water is based on the ISO 7150/1:1984 method for their determination with the spectrophotometry technique at 655 nm.

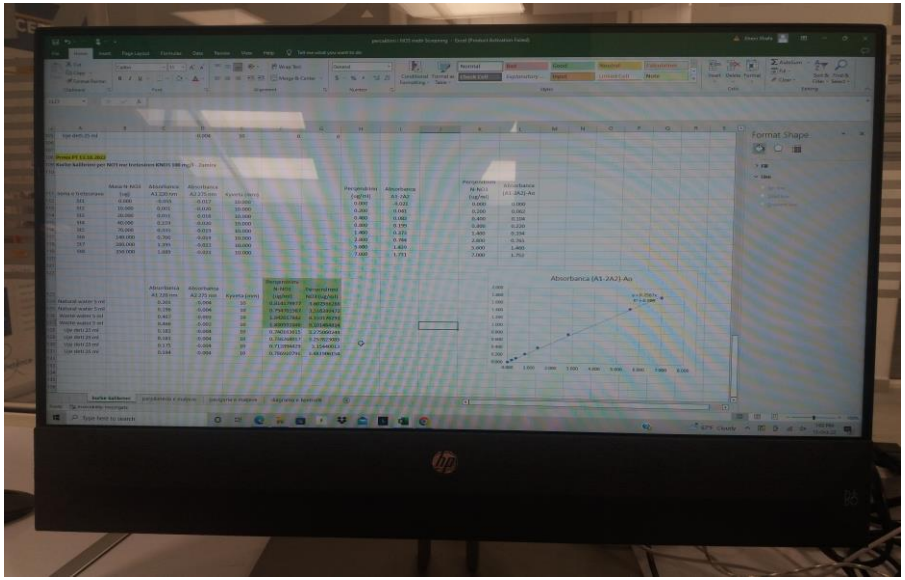
N-total was determined using complete disaggregation of the sample with $K_2S_2O_8$ and determination of nitrogen at two wavelengths: 220 nm and 275 nm. All forms of nitrogen are oxidized and measured as $N\text{-}NO_3$.

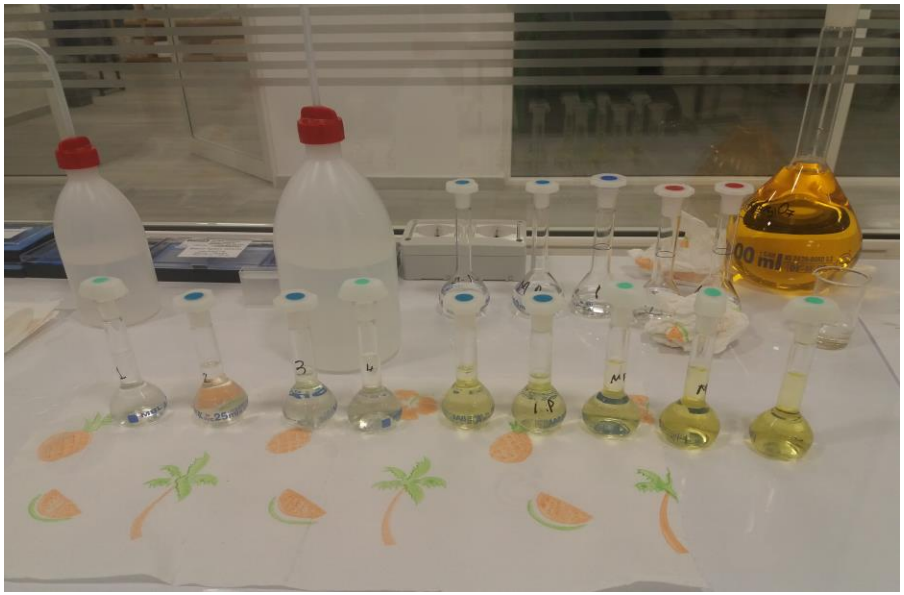
P-total was determined using the disaggregation method, which aims to oxidize all forms of phosphorus into PO_4 ions and further make their determination using the spectrophotometer method at 880 nm.

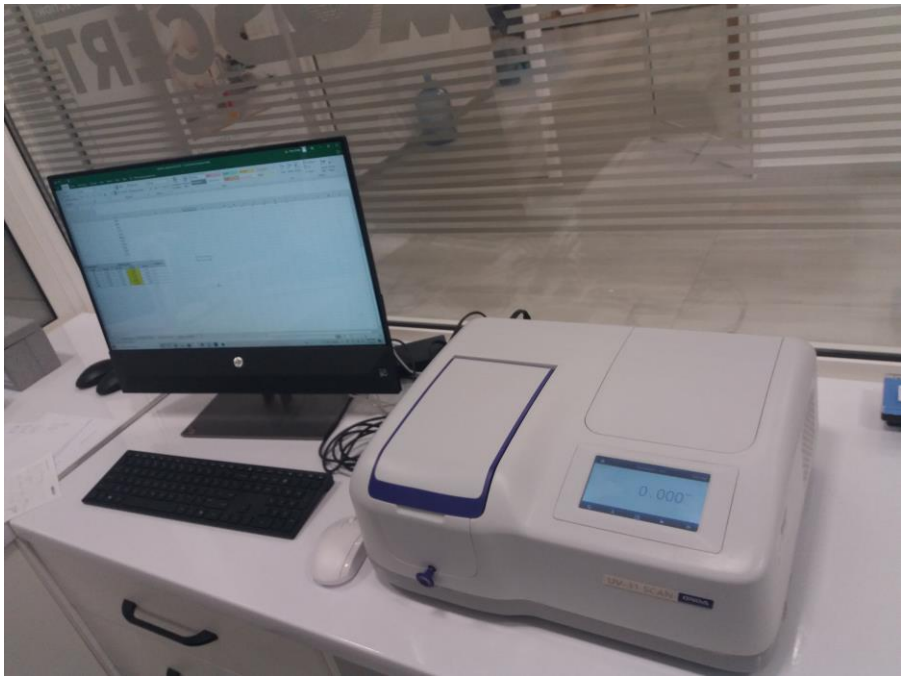
The analysis of sulfates in water is based on method 9038 for the determination of sulfates by the turbidimetric method at a wavelength of 420 nm.

The UV-VIS measurements were carried out in the UV 31 SCAN ONDA model spectrophotometer.







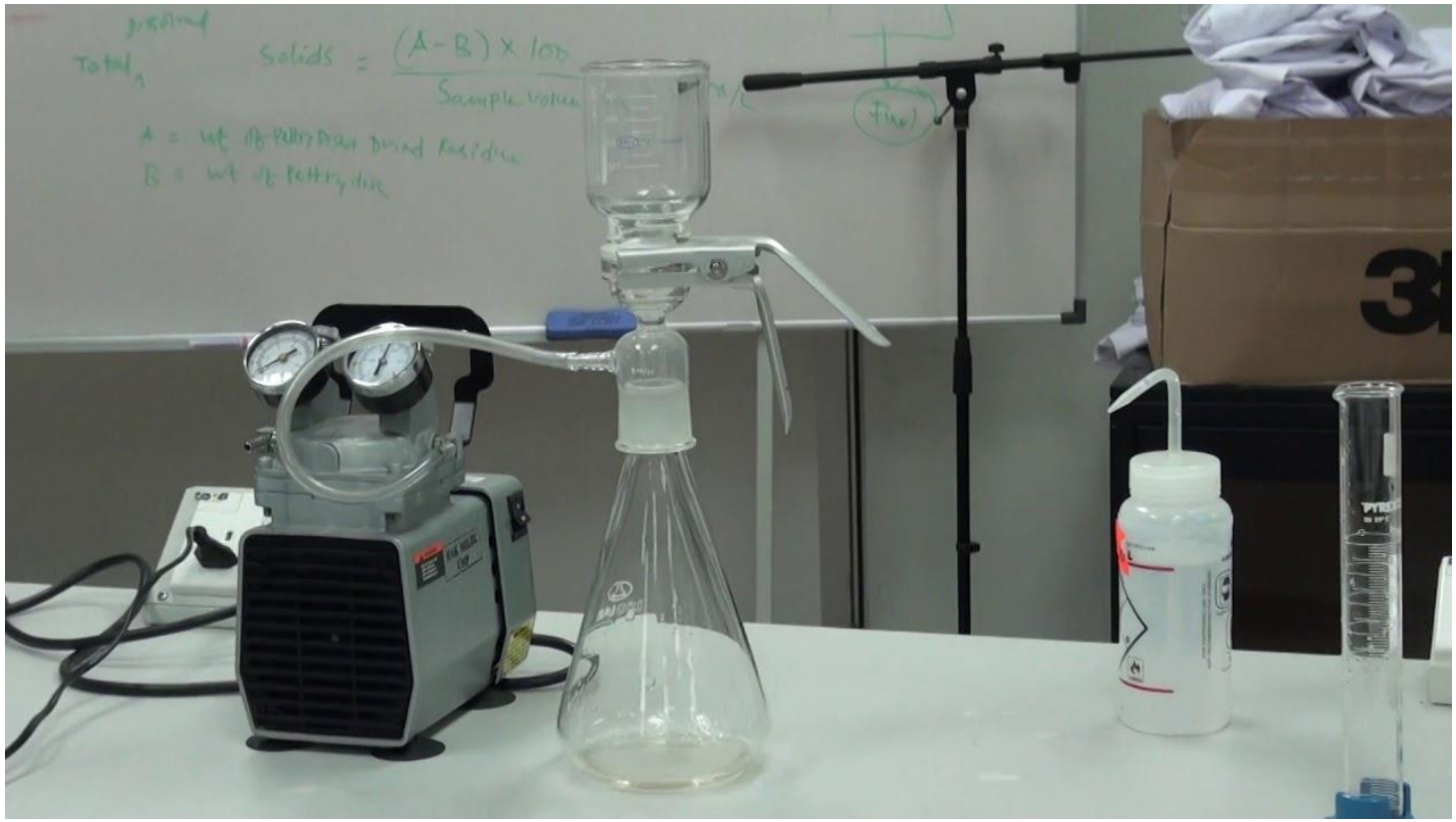


Determination of Cl^- (salinity), Ca^{2+} and Mg^{2+} by titration methods

Chloride ions were determined in seawater samples using the argentometric method (4500-Cl^- B, Argentometric Method, known as the Mohr method). The data obtained for chloride ions in seawater were used to calculate the salinity of the samples using the formula: S (ppt) = 1.805 [ppt Cl–] + 0.03. The concentration of calcium ions in seawater was carried out using the titration method with EDTA in the presence of the indicator Ericrom black T (3500-Ca B). Magnesium ions have been determined in seawater using the titration with $MgCl_2$ of the complex forming Mg^{2+} with EDTA (3500-Mg B, C).

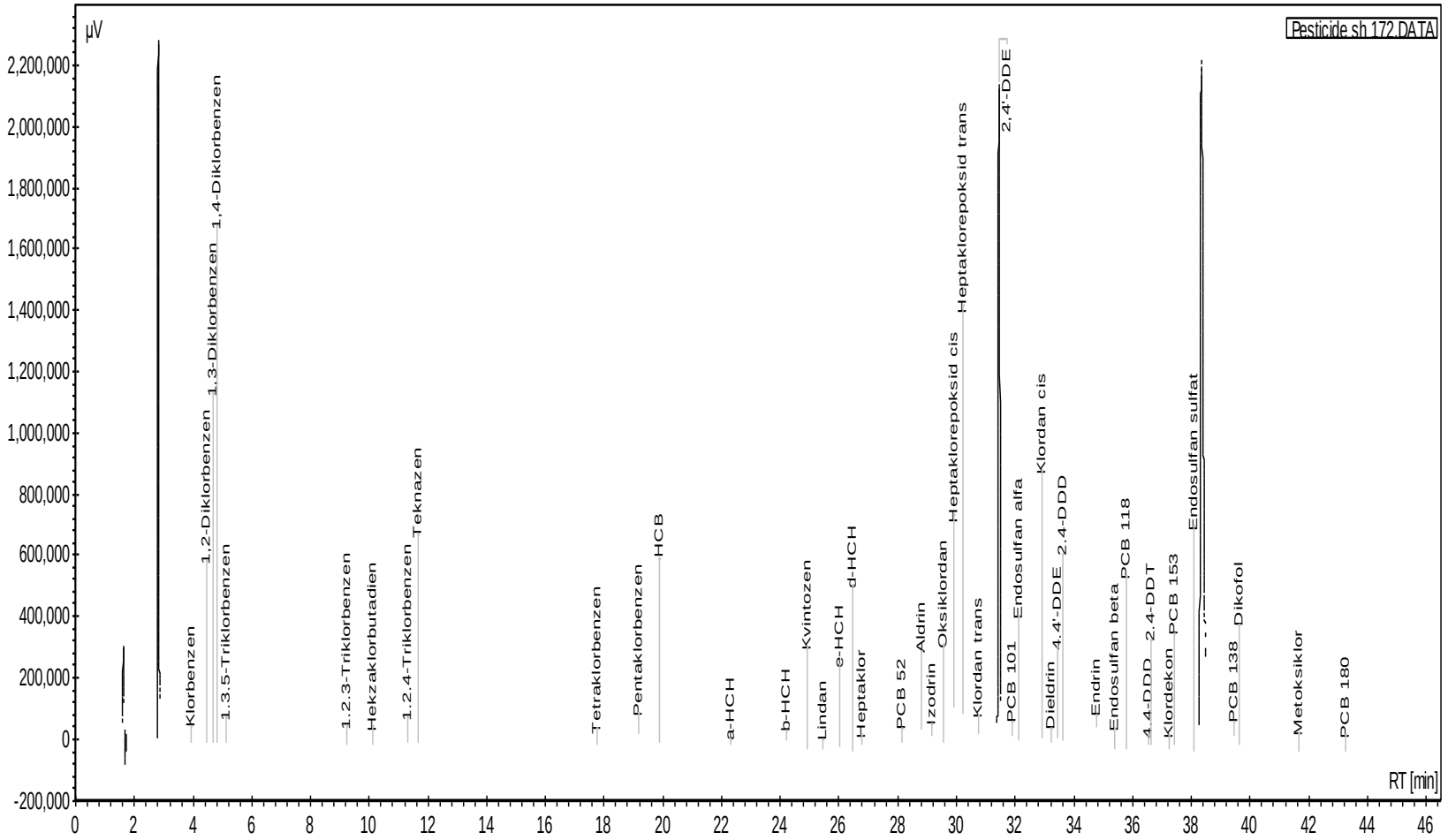
DETERMINATION OF TSS (TOTAL SUSPENDED SOLIDS) IN WATER SAMPLES

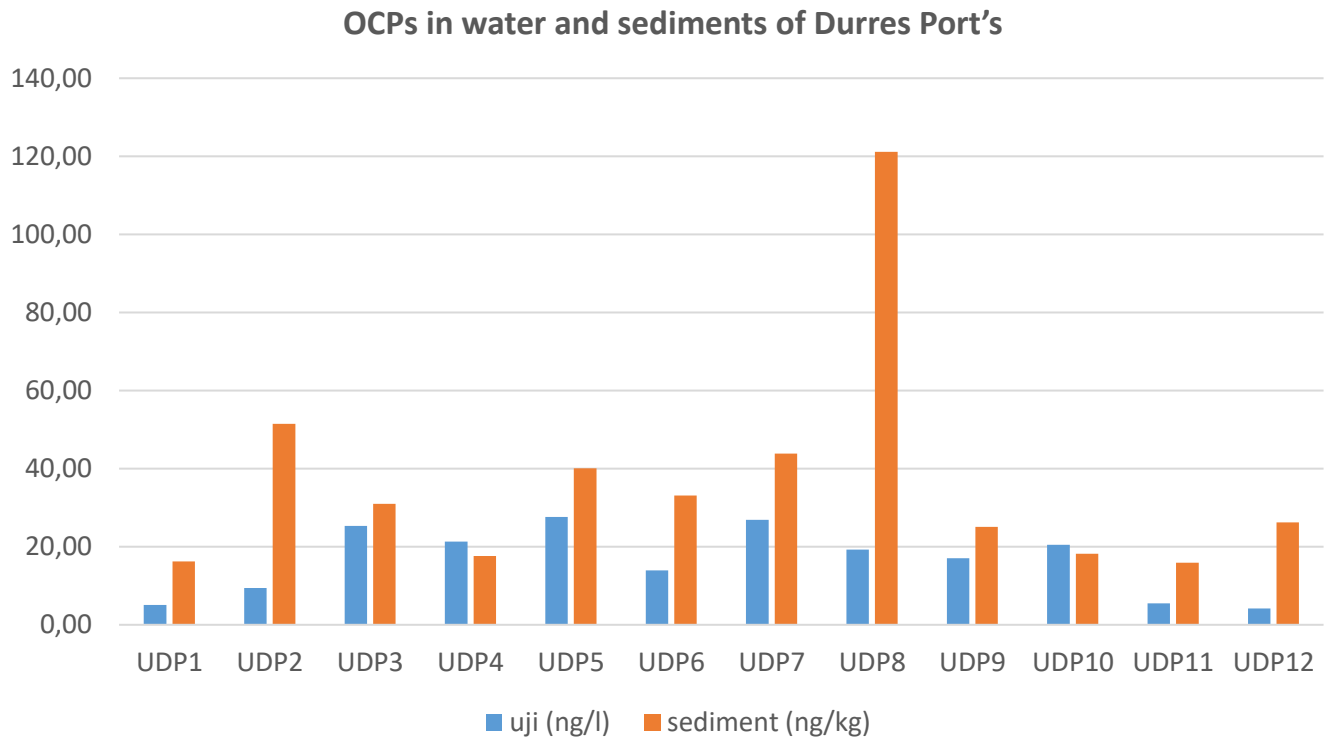
The analysis of solid particles in suspension (TSS) in water is based on their determination by the gravimetric method. 200 ml of seawater sample is taken for analysis. The water is filtered using 32 mm diameter glass filters with 0.45 um pores in a vacuum filtration system. TSS is calculated from the difference of the weights before and after filtration. The conditioning and drying of the filters was done in the thermostat for 8 hours at 105^{o}C

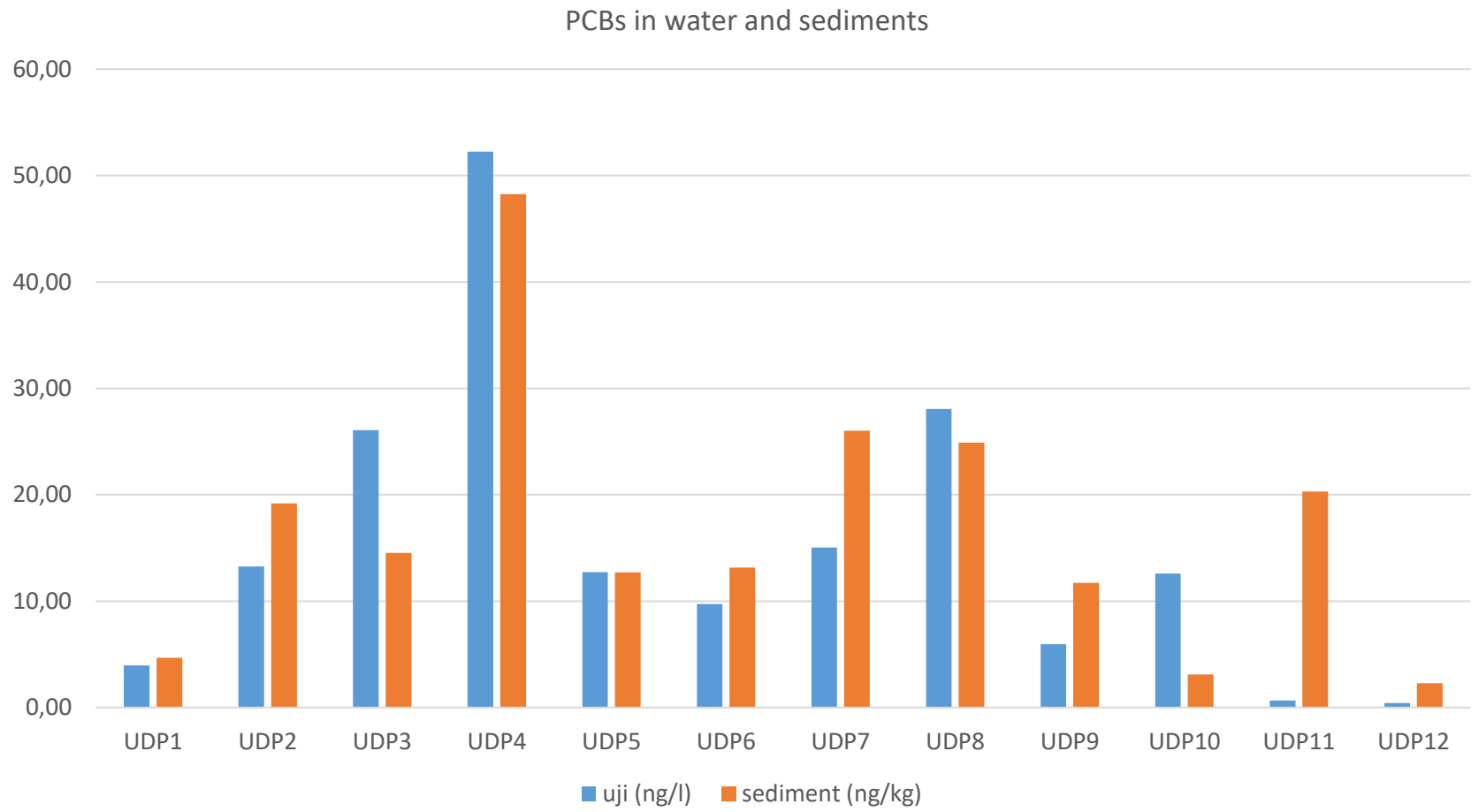


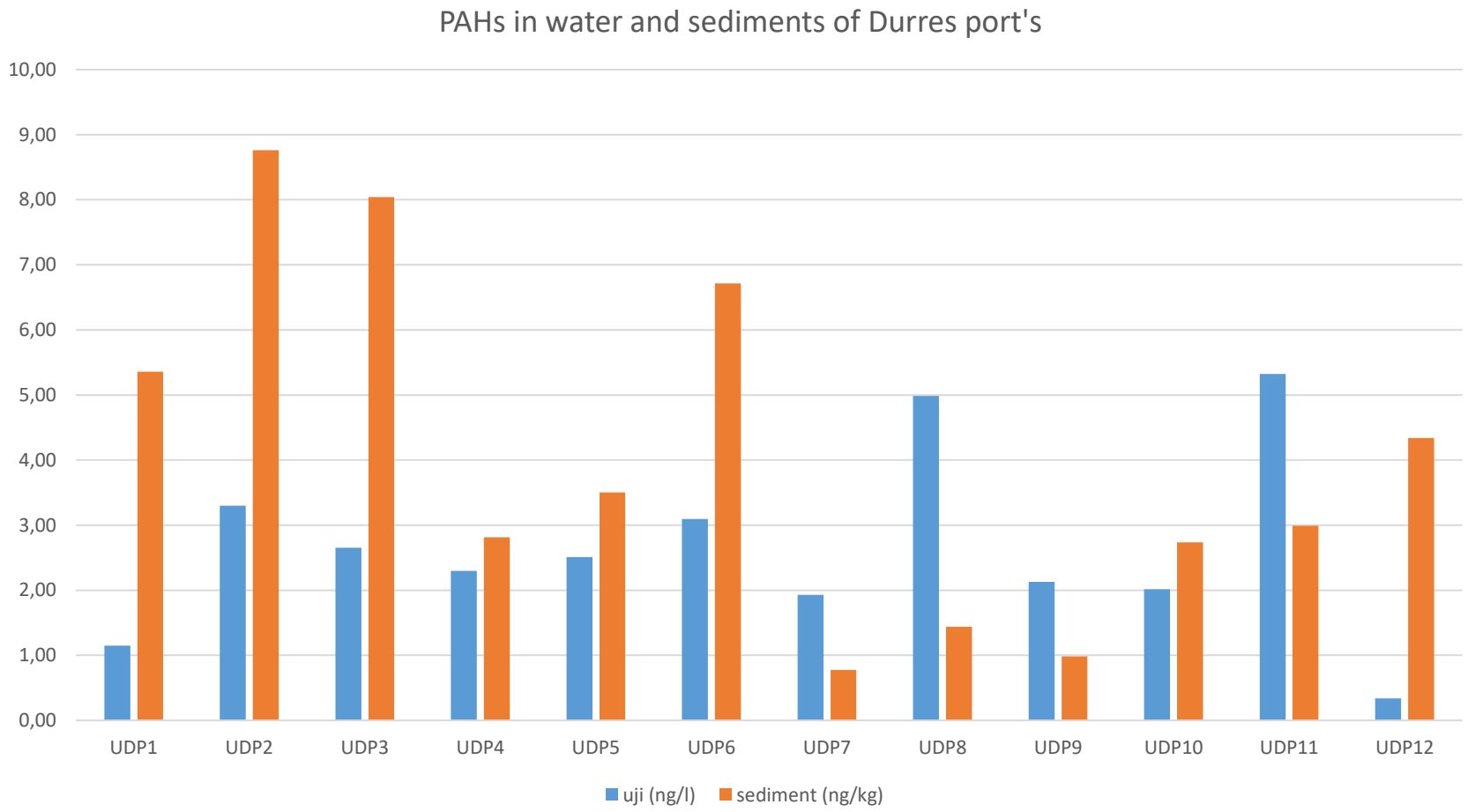
RESULTS AND DISCUSSIONS

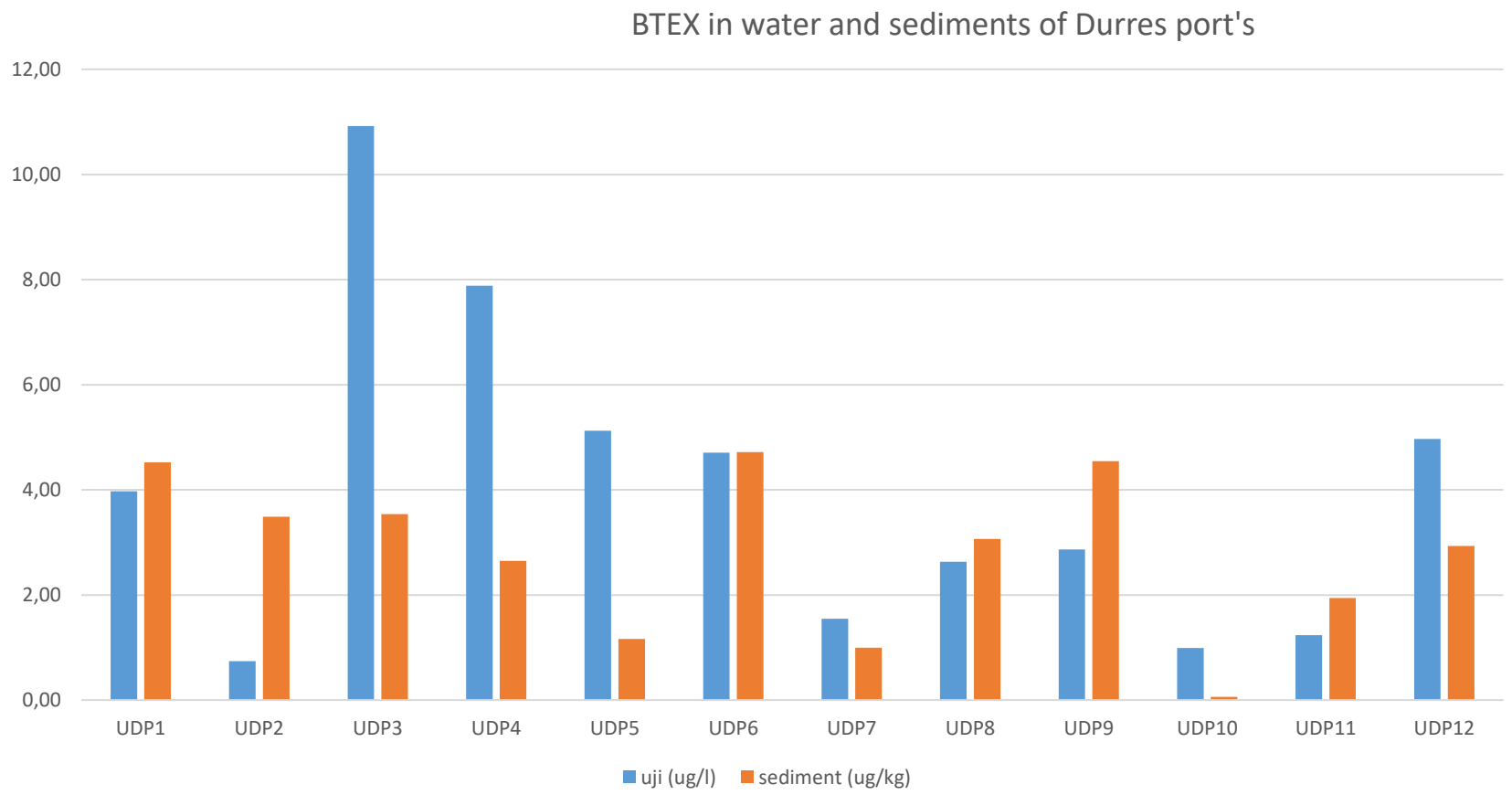
CHROMATOGRAM OF PESTICIDES. SAMPLE 6




OCPs in water and sediments of Durres Port's
140,00
120,00
100,00
80,00
60,00
40,00
20,00
0,00
UDP1
UDP2
UDP3
UDP4
UDP5
UDP6
UDP7
UDP8
UDP9
UDP10
UDP11
UDP12
uji (ng/l)
sediment (ng/kg)


PCBs in water and sediments
60,00
50,00
40,00
30,00
20,00
10,00
0,00
UDP1
UDP2
UDP3
UDP4
UDP5
UDP6
UDP7
UDP8
UDP9
UDP10
UDP11
UDP12
uji (ng/l)
sediment (ng/kg)


PAHs in water and sediments of Durres port's
10,00
9,00
8,00
7,00
6,00
5,00
4,00
3,00
2,00
1,00
0,00
UDP1
UDP2
UDP3
UDP4
UDP5
UDP6
UDP7
UDP8
UDP9
UDP10
UDP11
UDP12
uji (ng/l)
sediment (ng/kg)


BTEX in water and sediments of Durres port's
12,00
10,00
8,00
6,00
4,00
2,00
0,00
UDP1
UDP2
UDP3
UDP4
UDP5
UDP6
UDP7
UDP8
UDP9
UDP10
UDP11
UDP12
uji (ug/l)
sediment (ug/kg)

Physical-Chemical parameters	Durres port, 2023				
	Mean	Min	Max	Median	STDEV
PH	7.833	7.450	8.620	7.665	0.419
Temperatura (oC)	22.236	21.840	22.570	22.350	0.267
Konduktiviteti (ms/cm)	42.299	25.360	68.320	41.610	12.138
DO (mg/l)	4.887	4.120	5.720	4.820	0.423
BOD 5 (mg/l)	88.950	75.200	105.200	87.200	9.864
COD (mg/l)	112.497	75.260	169.060	101.795	32.093
TSS (mg/l)	118.443	76.320	151.320	120.020	20.010
NO3 (mg/l)	1.278	0.484	2.289	1.209	0.645
NO2 (mg/l)	0.477	0.035	1.255	0.367	0.382
NH4 (mg/l)	0.660	0.025	2.014	0.499	0.610
N-total (mg/l)	2.603	0.952	6.262	1.897	1.508
PO4 (mg/l)	13.773	8.247	21.547	13.250	4.067
P-total (mg/l)	7.490	4.485	11.719	7.206	2.212
SO4 (mg/l)	94.626	22.494	224.394	85.784	65.919
Cl- (g/l)	21.353	21.199	21.554	21.404	0.123
Salinity (g/l)	38.478	38.200	38.840	38.570	0.222
Ca+2 (mg/l)	1.133	0.848	1.498	1.136	0.171
Mg+2 (mg/l)	0.592	0.446	0.767	0.576	0.097

CONCLUSIONS (ORGANIC POLLUTANTS)

- The highest level of pesticides was found in sediment samples 2-5 times higher than for water samples. The most polluted stations are inside the port area due to sea currents and its depth. Their individual levels in water samples generally do not exceed the standards set by Directive 2008/105/EC. The exception is the levels of Endosulfan sulfate for 2 sediment samples.
- Concentration of 7 polychlorinated biphenyls (PCB) markers in water and sediment samples were almost the same. Again, the most polluted areas are inside the port. Concentration of PCB exceeded the recommended value, according to Directive 2008/105/EC in water of station 4.
- Concentration of total polycyclic aromatic hydrocarbons (13, PAH) in water and sediment samples showed that the highest level was found in the sediment samples for some stations and in some others there is a high level of them in the water compared to the sediments. This is related to instant pollution that occurred during the sampling period for these stations. Maritime and automobile transport, hydrocarbon spills (intentional or not) and mechanical activity are their main sources. Some of the individual PAHs (Anthracene, Benzo[a]anthracene and Benzo[k]fluorenthrene) exceeded their limit according to Directive 2008/105/EC.
- The total concentration of Benzene, Toluene, Xylenes (ort, meta and para) and Ethylbenzene known together as BTEX for water and sediment samples were higher in water samples. This is related to instant pollution that can occurred during sampling, just like for PAH. Maritime and automobile transport, hydrocarbon spills (intentional or not) and mechanical activity are also their main sources. These are volatile hydrocarbons common to fossil fuels and released from the emissions of their combustion in car and ship engines. Benzene levels were exceeded at stations 2 and 3 (in water samples) based on Directive 2008/105/EC.

CONCLUSIONS (PHYSICAL-CHEMICAL PARAMETERS)

- The water in port area has a slightly basic PH as a result of urban water discharge in port of Durresi area.
- The average values for DO, BOD_5 and COD indicate that the harbor water is suitable for the growth of organisms in this area. The high value for COD should be mainly related to the presence of chemicals in the seawater which come mainly from the intensive activity in this area.
- The levels found for nutrients ($N\text{-}NO_3$, $N\text{-}NO_2$, $N\text{-}NH_4$, N-total and P-total) were higher than previous reports for this area. Population growth, urban spillovers and intensive transport (ships and cars) are the main factors behind the levels found. The impact of agriculture may also be a significant factor in found levels.
- The presence of sulfates must be mainly related to urban pollution, hydrocarbon spillages and/or impact of ship and automobilistic transport.
- Concentrations of analyzed ions (Cl^-, Ca^{2+} and Mg^{2+}) could be related to the natural beckground of the Adriatic Sea or influenced by external factors such as seawater currents inside/aoutside the port and the impact of flow for some important rivers of Albania.
- The levels found for the water of the port of Durres classify these waters as moderately good.
- Analyzes of the physico-chemical parameters in the water of the port of Durres should be realized periodically by the laboratories of the respective agencies because their monitoring keeps the pollution of these areas under control.

Thank You!

Acknowledgments

The Authors want to thanks **University of Tirana** for the financial support in the framework of the program “UT-Research, Excellence and Innovation”.