



An overview of organic pollutants concentrations in the port of Durres, Adriatic Sea

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Cite this study:

Halo E., Nuro A., Myrtaj B., Tahiraj J., & Kane S. (2023). An overview of organic pollutants concentrations in the port of Durres, Adriatic Sea. *Advanced Engineering Days*, 6, 100-103

Keywords

Port of Durres
OCPs
PCBs
PAHs
Water analyze
GC/ECD/FID

Abstract

The findings reported here belong to a study on determination of organochlorine pesticides (OCPs), polychlorinated biphenyls (PCBs) and polycyclic aromatic hydrocarbons (PAH) concentrations in water samples of the port of Durres which is the largest port of Albania. In it are processed the main part of commercial and passengers shipping in Albania. These substances that present high risks are classified as priority substances. Although the production and use of these substances has been banned for decades, their presence continues to be reported due to their high persistence in the environment. Water samples were taken in 12 different stations of the port of Durres in two periods (May and July 2022). Organochlorine compounds were extracted simultaneously using liquid-liquid technique using hexane as extracting solvent. Also, PAHs were extracted also using liquid-liquid technique using dichloromethane and hexane (two steps) as extracting solvent. Chlorinated pollutants were determined by gas chromatography electron capture detection (GC/ECD) while PAH by gas chromatography flame ionization detector (GC/FID). Organochlorine pesticides (mostly their metabolites) were detected almost in all water samples because of their previous use. Also, PCBs and PAHs were found almost for all analyzed samples. Their presence could be because of elevated activity and ship transport in port area. The found levels for these priority substances in waters of Port of Durres was higher / comparable with reported levels of them from others stations of Adriatic Sea, Albania part.

Introduction

In this study was determined some priority substances concentrations in water samples of the port of Durres. The Port of Durres is the largest seaport of Albania, located in Adriatic Sea. It is an artificial basin that is formed between two moles. The Port is located at the north end of the Bay of Durres, an extensive body of water between Castel of Turra and Cape Durres. As of 2014, the port ranks as the largest passenger port in Albania and one of the largest passenger port in the Adriatic Sea, with annual passenger volume of more than 1.5 million.

Organochlorine pesticides (OCPs), polychlorinated biphenyls (PCBs), polycyclic aromatic hydrocarbons (PAH) and some other pollutants are classified as Persistent Organic Pollutants (POP), because they are persistent for many years after their application [1, 2]. Great concern was caused by chlorinated compounds, which proved to be extremely persistent in the environment and after that in the food chain [2, 3, 5]. For more than 50 years (after the Second World War to 90') organochlorine pesticides were used widely in Albania against malaria vector and for agricultural purposes. PCBs have not been used in Albania since 90s. They can only be found in some electrical transformers that were used in the early 1990s, but they were reported in many water ecosystems of our country because of atmospheric depositions. PAHs are pollutants generated by automobiles transport, extracting/processing of oil industry, coal mine and other industries. PAH could be found in marine water because of ship transport or some accident spills of hydrocarbons. Forest burning and their natural background make them very often in environment. Organochlorine pollutants (OCP and PCB) and PAHs have high stability, high bioaccumulation capacity and the ability to spread out far away from the application site. Generally, these compounds are difficult to degrade and can persist for many years in particular in water ecosystems [3, 6, 7, 8].

Material and Method

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 two sampling periods (May and July 2022). A volume of 2.5l of water were taken from each station in Teflon bottles. The sampling method was based on UNEP/MED Wg. 128/2, 1997. Water samples were transported and conserved at +4°C before being analyzed.

Analyzes of pesticides and PCBs by GC/ECD: Liquid-liquid extraction was used for extraction of OCPs and PCBs from water samples. One liter of water and 40 ml n-hexane as extracting solvent were added in a separator funnel. After extraction, the organic phase was dried with anhydrous Na₂SO₄ for water removing. A florisil column was used for the sample clean-up. 20 ml n-hexane/dichloromethane (4/1) was used for their elution. After concentration up to 1 ml, the samples were injected in GC/ECD. OCPs 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 model Varian 450 GC equipped with µECD detector. The organochlorine pesticides detected were DDT-related chemicals (o,p-DDE, p,p-DDE, p,p-DDD, p,p-DDT), HCHs (α-, β-, γ- and δ-isomers), Heptachlor's (Heptachlor and Heptachlorepoxyde); Aldrin's (Aldrine, Dieldrine and Endrin) and Endosulfanes (Endosulfan alfa, 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). Their quantification was based on external standard method [4-9].

Analyzes of PAHs by GC/FID: Liquid-liquid extraction was used for extracting PAHs from marine water samples. In a volume of 1 liter of water that was put in a separation funnel was added 30 ml dichloromethane first and after that 30 ml hexane as extracting solvent were added in it. After extraction, the organic phase was dried and concentrated to 1 ml using Kuderna-Danish and then were injected in GC/FID for their quantification. Gas chromatographic analyses of PAH in water samples were realized with a Varian 450 GC instrument equipped with a flame ionization detector and PTV detector. VF-1 ms capillary column (30 m x 0.33 mm x 0.25 µm) was used to isolate and determine 13 PAHs according to EPA 525 Method. Acenaphthylene, Fluorene, Phenanthrene, Anthracene, Pyrene, Benzo [a] anthracene, Chrysene, Perilene, Benzo [b] fluoranthene, Benzo [k] fluoranthene, Indeo [1,2,3-cd] pyrene, Dibenzo [a, b] anthracene and Benzo [g, h, i] perylene were determined in seawater samples. Quantification of PAH was based on external standard method [7, 9].

Results

In this study were analyzed marine water samples from port of Durres, which is located in Adriatic Sea. Samples were taken in May and July 2022. This is the main port of Albania for passengers and commercial shipping. Organochlorine pesticides and PCB markers were analyzed using GC/ECD while PAH by using GC/FID techniques. These substances were classified as priority substances because of their stability and toxicity. The processed data on OCP classes, total of pesticides, PCBs and PAHs were shown in Table 1.

Table 1. Statistical data on OCPs, PCBs and PAHs for water samples of the port of Durres in May and July 2022

	May 2022					July 2022				
	Mean	Median	STDEV	Min	Max	Mean	Median	STDEV	Min	Max
HCHs	0.19	0.09	0.25	N.D.	0.66	1.37	0.54	1.67	0.09	5.65
DDTs	0.08	0.06	0.08	N.D.	0.25	0.47	0.23	0.58	N.D	2.15
Aldrin's	0.49	0.28	0.52	0.05	1.46	0.61	0.43	0.56	0.05	2.10
Heptachlor's	0.06	0.02	0.08	N.D.	0.26	0.49	0.28	0.56	N.D.	1.72
Endosulfane's	0.11	0.08	0.10	N.D.	0.34	0.27	0.12	0.35	N.D.	1.25
Pesticides	1.17	1.05	0.79	0.29	2.22	3.61	3.56	1.51	1.63	6.59
PCBs	2.14	1.48	2.08	0.27	7.63	1.73	0.66	3.82	0.15	13.79
PAHs	1.03	0.83	0.91	0.29	3.35	4.57	4.86	2.22	1.97	8.61

Discussion

Pesticides were present in all water samples of Durresi's port. Their maximum was in water samples of July around 3 times higher than in May 2022. Their presence could be because more intense agricultural activity in this period. New arrival from the rivers (rivers of Ishmi, Erzeni, Shkumbini, Semiani, etc.) could be another factor in found concentrations. Their total for all analyzed samples was lower than 50 ng/l, a limit values for the total of pesticides in surface waters based on 2013/39 EU Directive. Lindane and its isomers (α-, β-, and δ-hexachlorocyclohexanes-HCHs) were found in higher concentrations (around 8 times higher) in July seawater samples. Notes that Lindane was found only in 25% of all analyzed samples. Delta-, α- and β-HCH isomers were found to be in majority for all seawater samples. Their origin could be because of their presence as an impurity in other pesticide formulations or because it's physical – chemistry properties. Also, HCH isomers could

be found because of degradation of other pesticides, new arrivals by rivers and urban wastes. For all stations, total of HCHs was lower than permitted level (0.04 ug/l) conforming to EU Directive 2013/39. DDTs (4,4'-DDT, 4,4'-DDD and 4,4'-DDE) were found in 67% water samples for the port of Durres for both periods. The higher DDT levels were found in July (around 3 times higher than in May). Note that DDT degradation products (DDD and DDE) were found in higher concentration in all stations, Average of DDTs in port area was lower compare with other stations on Adriatic Sea [5, 6, 8]. DDT was lower than permitted level (0.01 ug/L) in marine water based on Albanian and EU norms. Aldrine's were found almost in all water samples for the port of Durres. A slight higher levels of Aldrines were found in May 2022. This fact is connected with the use of Aldrins in this period, any punctual source or because on new arrival by rivers or effluents near the port area. Sweater currents inside/outside the port and momentum values are not excluded. Aldrins were found in lower levels than EU directive 2013/39 and Albanian norms. Heptachlors were found in higher concentrations in July. The higher levels in all analyzed samples were found Heptachlor epoxide, its degradation products. This fact is connected with the previous use of Heptachlor. Heptachlors in all samples were lower than EU Directive 2013/39. Total of Endosulfanes were 2 times higher in July samples. Their total was higher at stations inside the port area. These data could be the result of their previous use or and Endosulfan's punctual source near port of Durres. Endosulfan concentrations for water samples of Durresi port were lower than permitted level based on EU Directive 2013/39.

PCBs were found in all analyzed water samples. Their total was higher in May 2022. Presence of PCB markers in seawater samples can be related to the elevated mechanical and industrial activity in port area. For all water samples, volatile congeners (PCB 28 and PCB 52) were found at higher level. PCB concentrations for water samples of Durresi's port were comparable levels than the reported data on previous studies on the same stations [6, 7, 8].

PAHs were detected for all analyzed water samples. PAH were found 3 times higher in July 2022. Their presence could be because of elevated ship transport in this area. Automobilist transport and any possible accident could be another source of PAH pollution in marine water samples of Durres port. The presence of some individual PAHs in higher level was noted. Also, this could be a momentum value of PAHs. PAH levels in seawater samples were in the same range/higher than the reported levels for other stations of Adriatic Sea, Albania [8, 9]. The presence of some individual PAHs was higher than permitted level according to Albanian and EU norms.

Conclusion

Organochlorine pesticides, their residues, PCBs and PAHs were found in all water samples of Durresi port, for both periods. The higher levels of these pollutants were found mostly in July 2022. It was noted presence of degradation products of pesticides in higher levels compare to their active products. This fact is related with the previous use of pesticides in Albania and their degradation process. Aldrine's (in May) and HCHs (in July) were shown to be in high level in all samples. This pesticide could be in use in near port area or because of new arrivals by terrestrial or water currents inside-outside port of Durres. PCBs volatile were found at high levels for all seawater samples. Their presence could be because of their atmospheric deposition. Some water samples were detected heavy PCB. This could be connected with punctual sources of PCBs in these stations. PAHs were found in all water samples because of ship transport, automobilist transport and any possible accident of hydrocarbons near the area of Durres port. Momentum values of them are not excluded. Generally, concentrations of organochlorine pesticides, PCBs and PAHs were lower than permitted levels for surface waters according to EU Directive 2013/39 and Albanian norms. Monitoring of organic pollutants in water of Durres port should be continuous because of its importance in Albanian economy overall.

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