Estimation of Quality of the Black Sea Basin

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Black Sea – (Russian and Bulgarian *Chernoye More*, Ukrainian *Chorne More*, Turkish *Karadeniz* and Romanian *Marea Neagra*) is large roughly oval-shaped inland sea situated at the South-Eastern Europe and Asia. It is bordered by Ukraine to the north, Russia to the northeast, Georgia to the east, Turkey to the south and Bulgaria and Romania to the west.

The Black Sea occupies a large basin strategically situated at the southeastern extremity of Europe, but connected to the distant waters of the Atlantic Ocean by the Bosporus (which emerges sea's southwestern corner), the Sea of Marmara, the Dardanelles, the Aegean Sea, and the Mediterranean Sea. The renowned Crimean Peninsula thrusts into the Black Sea from north, and just to its east the narrow Kerch Strait links the sea to the smaller Sea of Azov. The Black Sea coastline is otherwise fairly regular. The maximum east-west extent of the sea is about 730 miles (1175 kilometers), while the shortest distance between the tip of the Crimea and the Kerempe Burmi Cape to the south is about 160 miles. The Black Sea greatest width is 350 miles (560 kilometers). The surface area excluding the Sea of Azov, is about 178 000 square miles (461 000 square kilometers). The Black Sea proper occupies about 162 280 square miles (420 300 square kilometers) – about one sixth the size of the Mediterranean. A maximum depth of 7 257 feet (2 212 meters) is reached in the south-central sector of the sea. The volume of the sea is about 548 055 cubic kilometers.

The temperature of the Black Sea's upper layer has a marked yearly periodicity. In winter, water temperature ranges from 31° F (-0.5° C) in the northwest to about 48° to 50° F (9° to 10° C) in the southeast. The winter cooling forms an upper mixed layer extending to depths of about 160 to 330 feet, with temperatures at the lower boundary of about 44° to 46° F (6.5° to 8° C). In summer the surface layer is warmed to between 73° and 79° F (23° and 26° C). At depths of about 160 to 240 feet, a cold layer remains at 45° F (7° C), and lower depths do not change from their winter levels.

The salinity of the surface waters in open sea averages between 17 and 18 parts per thousand, which is approximately half that of the oceans. A marked increase in salinity, up to 21 parts per thousand, occurs at depth of 160 to 500 feet, below which the salinity increase is much more gradual. The sea's deepest parts (below 1 300 feet) are distinguished by highly stable temperatures between 47° and 48° F (8.5° and 9° C) and salinities of 28 to 30 parts per thousand. Salinity increases to 38 parts per thousand at the Bosporus, where waters from the Sea of Marmara intrude. The chemical composition of Black Sea water is almost the same as that of the oceans.

The most important feature of the Black Sea is that oxygen is dissolved (and a rich sea life is made possible) only in the upper water levels. Nearly 87% of the entire Black Sea water volume is anoxic. Below a depth of about 230 to 330 feet at the centre and 330 to 500 feet, near the edge, there is no oxygen; below about 600 feet (180 meters) the sea's waters are stagnant and the sea is contaminated by hydrogen sulfide, which results in a saturated, gloomy "dead" zone frequented only by adapted bacteria.

Some of the main rivers which flow in to the Black Sea basin are the Danube, Dnieper, Dniester, Don, Kuban, Bug, Riomi, Kizil-Irmak, and Kamchiya. This large inflow of fresh water makes the upper levels of the sea less salty. But except all that, these huge fresh water sources are and the most Black Sea polluting factor too.

As a whole all rivers which empty into the Black Sea and their tributaries drain an area of about 2 500 000 square kilometers.

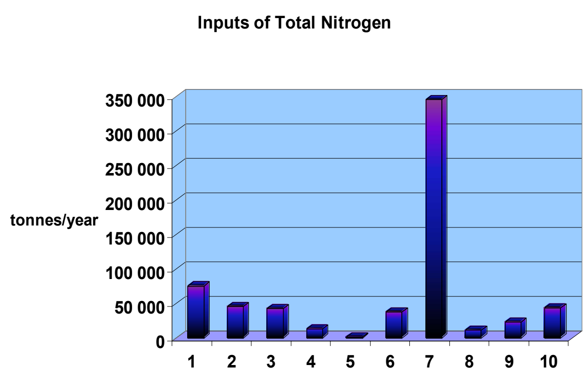
Except that for some climate peculiarities, water exchange between Sea of Marmara and the Black Sea through the Bosporus is relatively slow, and a complete recycling of Black Sea waters takes about 2 500 years.

For these reasons the Black Sea is Europe's most polluted sea and it takes polluting sources by 17 countries or by the live activity of 165 millions of people. As a result of that about 90% of the water is polluted, mainly by agricultural fertilizers.

Chart's legend: 1 – Bulgaria; 2 – Romania; 3 – Ukraine; 4 – Russian Federation; 5 – Georgia; 6 – Turkey; 7 – Danube; 8 – Dnieper; 9 – Dniester; 10 – Sea of Azov;

Some of the main polluting sources are:

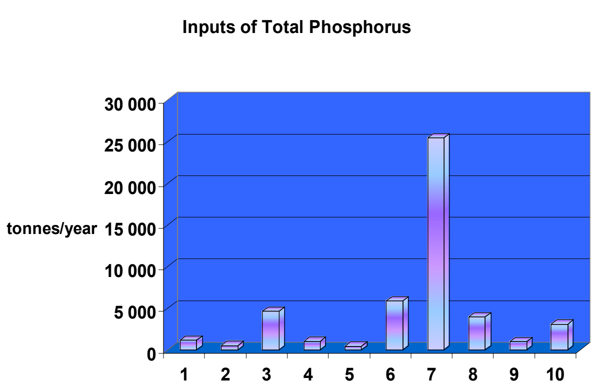
The inputs of Total Nitrogen (TN) to the Black Sea:



stations

The international rivers provide the majority (ca 60%) of the total TN input to the Black Sea, and of the three major rivers it is the Danube which dominates (with ca 53% of the total input). One country (Bulgaria) provides a significant contribution (10%) to the total input of TN to the Black Sea.

Overall the biggest contribution to the total national input of TN to the Black Sea arises from the industrial discharge (68%) followed by river discharges (23%) and the domestic discharges (9%). Four countries (Bulgaria, Romania, the Ukraine and Turkey) provide nearly all of the total national input of TN to the Black Sea. However, it should be stressed that most of the Bulgarian and Romanian TN inputs comes from one single industrial source (oil refineries at Bourgas and Petromidia). In view of this these inputs need to be verified by actual measurement of TN in the oil refinery effluent. Georgia contributes less than 1% to the total input.



The inputs of Total Phosphorus (TP) to the Black Sea:

The international rivers account for over 70% of the TP input into the Black Sea, and of the three major rivers it is Danube which dominates with 54% of the total. National inputs from Ukraine and Turkey account for 12% and 10% respectively of the total load, while Bulgaria, the Russian Federation, Romania and Georgia together account for the remaining 7%. Domestic sources account for half of the total TP input, followed by riverine sources (36%) and industrial sources (15%). Ukraine and Turkey together account for over three quarters of the total national input of TP, with the remainder coming from Bulgaria (8%), the Russian Federation (8%), Romania (4%) and Georgia (3%).

Radionuclides in the Black Sea:

The convention on the protection of the Black Sea Pollution (Bucharest 1992) classified radionuclides as "Hazardous Substances and Matter" due to their toxicity, persistence in the environmental and bioaccumulation characteristics.

Among the anthropogenic radionuclides which have been introduced to the Black Sea environment, from the point of view of radiological significance, the following need to be considered when evaluating its state of pollution: ^{137}Cs, ^{90}Sr and $^{239-240}Pu$. These radionuclides have long physical and environmental half-lives and their biogeochemical behavior makes them available for delivering radiological doses to human through various specific exposure pathways (e.g. seafood consumption, external exposure through leisure or professional activities, inhalation of resuspended sediment and sea spray). Among the above-mentioned radionuclides ^{137}Cs can be expected to be the most significant. Plutonium however is the most radiotoxic.

In addition to the man-made radionucliedes, some of the natural ones are equally interesting, either from a radiological point of view (e.g.^{210}Po in seafood) or as ratio tracers (^{210}Pb, ^{234}Th). Reports and publications issued from scientific groups in practically all Black Sea countries extensively document ^{137}Cs concentrations in seawater, sediments and biota. The data on ^{90}Sr are less comprehensive, with most of them coming from Russia and Ukraine. Very few data have been reported for $^{239-240}Pu$.

When compared with levels elsewhere in the world's oceans the Black Sea shows relatively high concentrations of anthropogenic radionuclides. Average ^{137}Cs concentrations in seawater (about 30 Bq/m^3) and fish (about 3 Bq/kg fresh weight). On average ^{137}Cs concentrations in surface sediments of the Black Sea are 30-50 times higher than those in the Mediterranean. In Black Sea surface sediments the ^{137}Cs concentrations ranges from a few to a few hundred Bq/kg dry weight given in a report by the European Commission as the average value for surface sediments in the Black Sea is based on data reported for the shelf areas offshore the Danube and Dnieper river mouths.

The Danube, besides being a major source of non-nuclear contaminants, also represents an important source of radionuclides, with ^{137}Cs, dominating the man-made ones.

Pollution with Hydrocarbons:

The distribution of hydrocarbons in the environment can vary greatly from one area to another.

Biological sources include land plants, animals, bacteria, macroalgae and microalgae. Certain hydrocarbons such as phytenes, hopenes and sterens are produced from bacterial and chemical degradation of naturally degradation of naturally accruing lipids. Bush fires, agricultural burn-off, vehicle exhausts and combustion products in factory emissions are also significant sources of hydrocarbons in some areas. Considerable amounts of petroleum products are discharged into the marine environment through runoff, industrial and sewage effluents, storm water drains, shipping activities, spillage, etc. Some of the hydrocarbons are taken up by the biota; others are lost by evaporation, dissolution and photo-chemical degradation, but many because incorporated into the sediment, where they remain for years.

Isoprenoid hydrocarbons:

Pristane (C_{19}) and phytane (C_{20}) are common isoprenoids detected in coastal marine sediments. Thus, they are often considered as good indicators of petroleum contamination.

In relatively unpolluted sections of the Black Sea (e.g. the Ukrainian coastline) the concentrations of pristine ranged from 0.4 to 5.5 ng/g. Phytane concentrations ranged from undetectable to 2.5 ng/g. However in the Danube coastline and around Sochi, higher concentrations were detected. In these latter areas, concentrations of pristine ranged from 23 to 170 ng/g and phytane from 16 to 170 ng/g.

Polycyclic aromatic hydrocarbons (PAHs):

PAHs are a group of chemical compounds which have a huge polluting meaning. It has been estimated that on a global scale each approximately a quarter of million tones of PAHs reach the marine environment.

PAHs are primary products of incomplete combustion processes. They are composed of two or more fused aromatic rings. The low molecular weight, two and three ring, PAHs have a significant acute toxicity, whereas some of higher molecular weight PAHs show a high carcinogenic potential.
The primary source of anthropogenic PAHs to the environment is pyrolysis of fossil fuels. Combustion-derived PAHs are mainly transported to the sea by two routes, via the atmosphere and rivers. Other sources include domestic and industrial wastewater run-off from land and the spillage of petroleum products by ships. The solubility of PAHs in water is low and decreases with increasing molecular weight. Thus due to their hydrophobic nature, the concentrations of dissolved PAHs in seawater are very low.

Concentrations of total PAHs in sediments from the Black Sea are generally quite low (from 7 ng/g to more than 630 ng/g dry weight). The greatest concentrations of total PAHs in sediments were observed at sites along the Danube coastline (638 ng/g), Odessa (635 ng/g), Port of Sochi (368 ng/g) and station 10 (Bosporus) (531 ng/g).

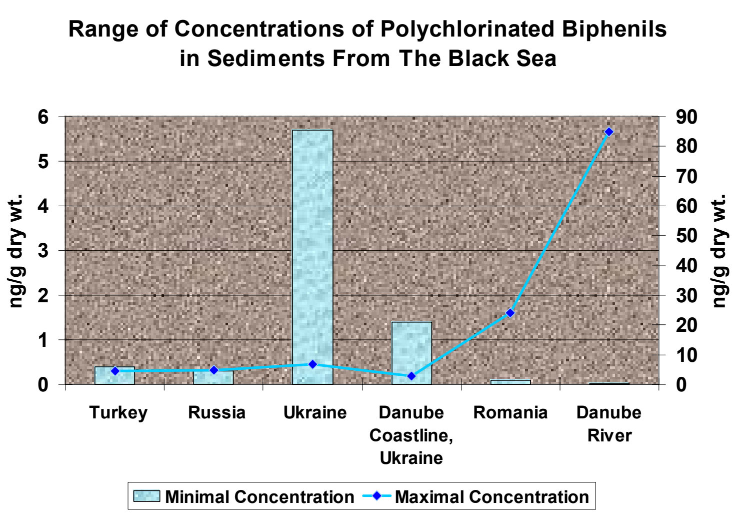
Organoclorines:

The organochlorines selected for study belong to a group of compounds often referred to as "Persistent Organic Pollutions" (POPs). There are, by definition, organic compounds that are:

- Highly resistant to degradation by biological, photolytical or chemical means;
- Liable to bioaccumulate;
- Toxic and probably hazardous to human health or the environment;
- Prone to long-range transport;

These compounds are also typically characterized as having low water solubility and high-fat solubility. The UNEP Governing Council at its meeting in May 1995 identified 12 specific POPs that require urgent attention. They are **PCBs**, dioxins and furans, aldrin, dieldrin, **DDT**, endrin, chlordane, hexachlorobenzene, mirex, toxaphene and heptachlor. All of these POPs are synthetic organochlorines.

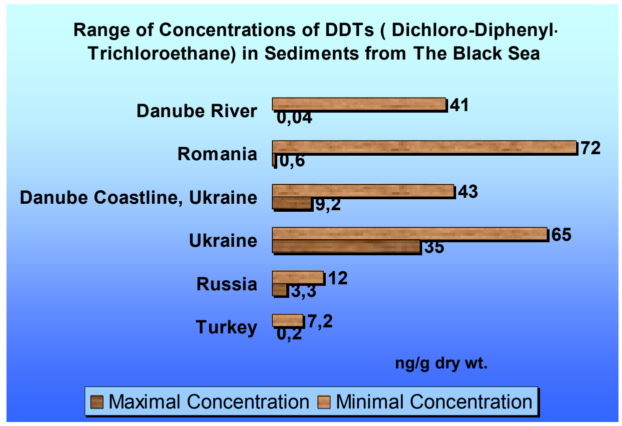
Over 80% of the total input into the sea is via the atmosphere, the remainder is via rivers. Nevertheless, those (the majority) used in agriculture are also washed off the land into rivers, thence to the sea, or directly into the sea via outfalls on run-off. Many organohalogens follow quite complex biogeochemical pathways.



Polychlorinated biphenyls (PCBs) are mixtures of chlorinated hydrocarbons which are or have been produced for industrial use (especially as dielectrics in transformers and large capacitors, as coolants in refrigerators, and as plasticizers in some paints). They are globally ubiquitous in all environmental compartments. In aquatic systems, these compounds partition onto particulates and bioconcentrate in the lipids of organisms.

Due to the toxic effects of organochlorines in humans and aquatic organisms, the use and/or sale of most organochlorine pesticides has been banned or restricted in many European countries since the mid-1970's. DDT (dichlorodiphenyltrichloroethane) is still used to control mosquito vectors of malaria in numerous countries of the world. In most countries of the Black Sea, however, the use of these pesticides has also been banned or restricted. Despite this restriction, recent studies have shown that DDT is present in Turkish rivers, streams and domestic and industrial discharges, which indicates their illegal use. Also lindane and DDT are usually found in the mouth of the Danube River in spring. Concentrations of DDTs , HCHs and PCBs in Black Sea fish and mammals are high by comparison with those reported for other regional seas.

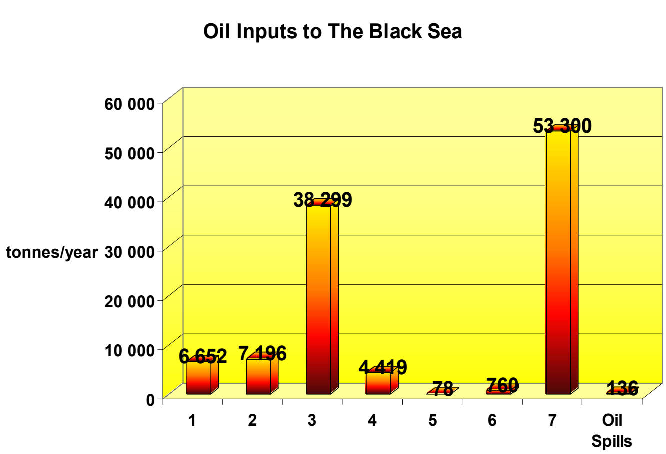
Relatively higher concentrations of 4.8 and 8.8 ng/g were, however recorded for the Romanian stations. These locations are influenced by discharges from the River Danube, whose sediments have been reported to contain relatively high levels of PCBs. The highest concentration of PCBs in sediments (24.3 ng/g) was found in a sample taken from the Port Constanta on the Romanian Coastline. The sediments of Odessa and Sochi were also found to contain relatively higher concentrations (6.8, 5.7 and 4.7 ng/g respectively).



Concentrations of DDT related compounds in sediments from Black Sea are shown to be generally lower than those reported for the Baltic Sea and most Asian sites. They are comparable, or slightly higher, than those reported for other regions of Russian Federation (e.g. Baikal Sea), The USA and Mexico. Highest concentrations of DDTs in the Black Sea are associated with lipid rich sediments in the Ukraine (43 ng/g dry weight basis of 476,500 ng/g fat weight basis) and Romania stations under the influence of River Danube discharges (34 and 72 ng/g dry weight basis or 137,080 and 146,184 ng/g fat weight basis). The Danube and adjacent coastal areas indicate that the river is a major source of contamination to the Black Sea.

According to Tuncer *et al.* (1998), approximately 100 tones of DDT are discharged annually via rivers into the Black Sea suggesting continued illegal usage of this insecticide.

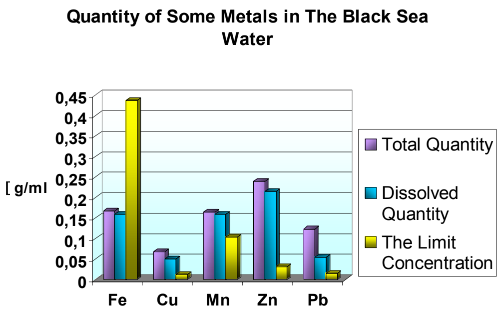
Oil inputs to the Black Sea:



Total oil pollution inputs to the Black Sea is estimated 110.840 t/y. Off the 111 thousand tons of oil entering the Black Sea each year. 48% is transported by the Danube River most of remainder is introduced from land-based sources through inadequate waste treatment and poor handling of oil products. Total oil discharges from the Black Sea Coastal Countries are 57 404 t/y and this value is about 52% of the total oil pollution. Accidental oil spills are 136 t/y and it is calculated as an average of the last years and is excluded illegal discharges from shipping. The amount reaching the Black Sea from ballast water discharges by ship is unknown (the practice is illegal) but though to be considerable.

Some metals in The Black Sea:

- Copper (Cu) and Zinc (Zn):



Whilst essential at low concentrations, both copper and zinc are toxic at elevated levels. The concentrations measured in the Black Sea are relatively low and comparable to other coastal areas of the world. They are between 2 and 49 µg/g for copper and between 5 and 186 µg/g for zinc. Anthropogenic inputs are the major source of copper and zinc contamination in the marine environment.

- Lead (Pb):

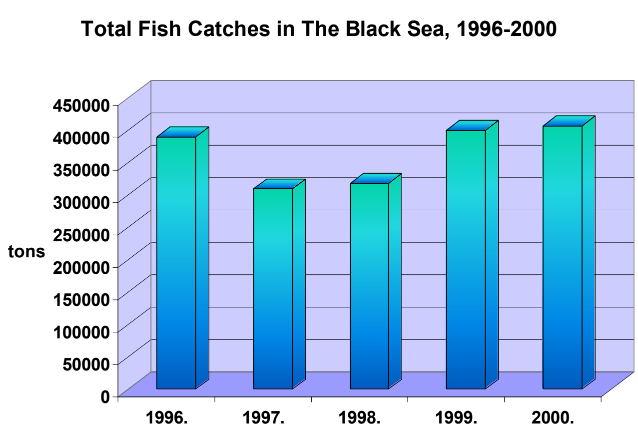
Lead is regarded as potentially of greatest concern among pollutant metals and is classified as an EC “Black List Substance”. For this metal, inputs through the atmosphere are an important pathway. The importance of this route mainly reflects the use of petrol containing tetraethyl lead. In absolute terms, the concentrations of lead obtained for the Black Sea are not exceptionally high. They vary between 2.3 and 60 µg/g and offshore concentration is around 12 µg/g. The concentrations obtained near the Danube outlet are between 11 and 30 µg/g and are comparable to the lower range of earlier results for the Danube, between 23-420 µg/g (IAEA, 1992). Concentrations measured in Turkey coastal sediments in the present study are comparatively higher (between 16 and 60 µg/g). In comparison concentrations in the open Mediterranean Sea are in the range 20-25 µg/g and contaminated sediments of the Venice Lagoon contain around 350 µg/g.

All these show a real picture of the Black Sea. Picture, which is full with “pain” and “sorrow”.

Optimistic Signals:

The environment of the Black Sea and its fragile and vulnerable ecosystem, with their recreational and aesthetic value that benefits the coastal population, are showing the first signs of recovery: fewer instances of less intense algal blooms have been reported by all Black Sea coastal states; total fish catches in the Black Sea are increasing mostly due to the stocks of small pelagic fish species, and the number of introduced species is continuously increasing.

Along with the first signs of recovery of the Black Sea ecosystem, the economies of the Black Sea coastal states in transition have begun to recover, according to the available macroeconomic indicators. The envisaged accession of Bulgaria, Romania and Turkey to the European Union and the related need for those countries to comply with strict European legislation is also contributing to the health of the Black Sea environment.



These optimistic signals should not hinder the pursuit of existing problems. The Black Sea is still a sea in trouble: algae blooms are still heavy and pollution – although localized – affects the biological communities. Fish stocks of commercially valuable species, such as sturgeons and turbots, suffer from illegal fishing and from pollution and destruction of their habitats. The process of recovery of the Black Sea will take a long time and will require the implementation of all measures envisaged by the Black Sea Strategic Action Plan as well as some future provisions.

In conclusion I can say that Black Sea suffered because of us and if we don't stop treat it like a litter-bin soon it will be too late to save it. Black Sea protection is in our hands. Let's use this chance.

Used materials: 1. Black Sea pollution; GEF Black Sea Environmental Program, Edited by Laurence D. Mee and Graham Topping, 1998
2. Environmental Protection Technologies For Coastal Areas – Second international Black Sea Conference – 21-23 October 1998, Varna, Bulgaria
3. Encyclopedia "Britannica" 2002
4. "Danube Watch", The Magazine of The Danube River, #1/2002

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