Marine Chemical Pollution

Institute of Oceanology PAN, Sopot
Marine Pollution Laboratory
http://www.iopan.gda.pl/MarPoLab/index-en.html

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Definition

'Pollution' – means introduction by man, directly or indirectly, of substances or energy into the sea, including estuaries, which are liable to create hazards to human health, to harm living resources and marine ecosystems, to cause hindrance to legitimate uses of the sea including fishing, to impair the quality for use of sea water, and to lead to a reduction of amenities (HELCOM http://www.helcom.fi).

According to this definition the pine pollen in the Gulf of Gdańsk waters (see front page) is not a pollution.

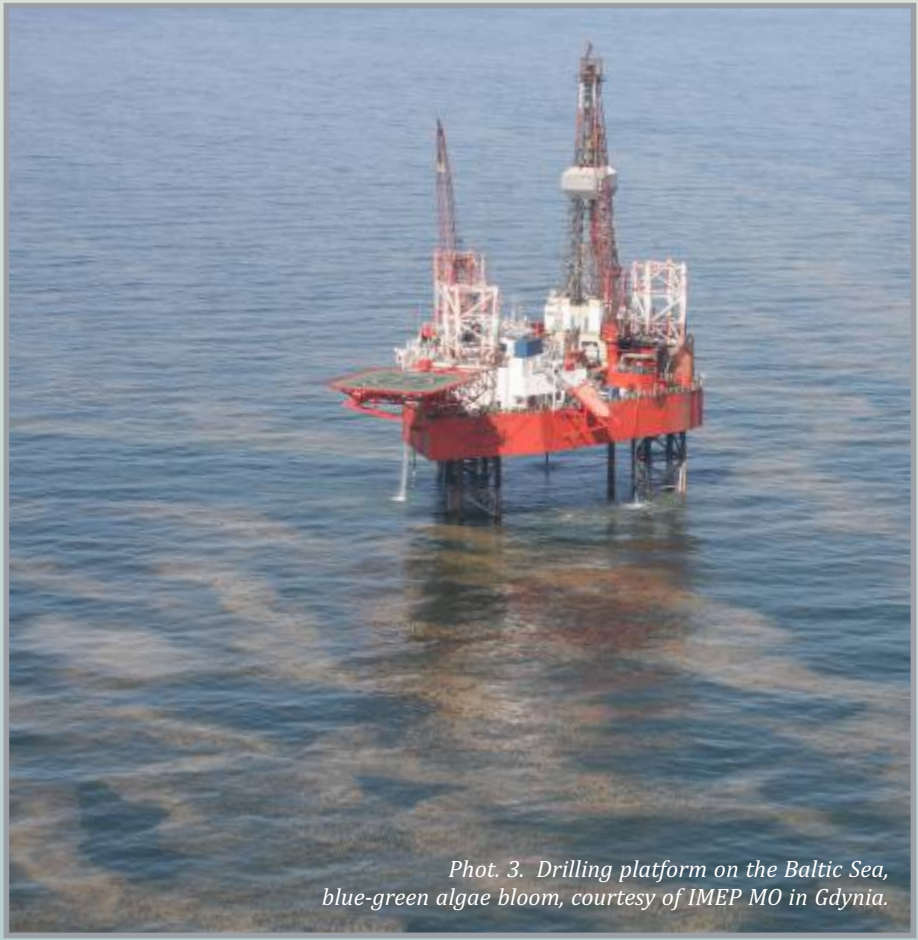
Phot. 1. Petroleum slick – a view from Maritime Office in Gdynia plane, courtesy of Inspectorate of Marine Environment Protection of Maritime Office (IMEP MO) in Gdynia.

Phot. 2. Petroleum slick in port, courtesy of IMEP MO in Gdynia.

This is a definition similar to that one accepted by GESAMP – Joint Group of Experts on the Scientific Aspects of Marine Environmental Protection, http://www.gesamp.org. It is an advisory body, established in 1969, that advises the United Nations (UN) system on the scientific aspects of marine environmental protection and also by other international legislation concerning protection of seas and oceans, e.g. OSPAR Convention (1974, 1992), regulating international cooperation on environmental protection in the North-East Atlantic, including the North Sea (http://www.ospar.org), European Union directives concerning the sea, like Marine Strategy Framework Directive – MSFD, 2008 (http://eur-lex.europa.eu). Poland as a member state of United Nations and European Union is also obliged to implement regulations arising from acceptance of these legislative instruments.

In Polish the same word 'zanieczyszczenie' means a substance which causes the mentioned at the beginning environmental effects (according to GIOS – Chief Inspectorate of Environmental Protection – 'substancja niebezpieczna = 'pollutant') and substance, which is in the environment but not necessary in concentrations causing the harmful effects (according to GIOS – 'substancja zanieczyszczająca' = 'contaminant').

There are known numerous substances/compounds, which theoretically could be the marine pollutants but to prove that



Phot. 3. Drilling platform on the Baltic Sea, blue-green algae bloom, courtesy of IMEP MO in Gdynia.

a compound is dangerous and put it on a list of harmful compounds needs many tests, environmental analyses and legislative efforts. Often the restrictions were circumvented by a slight change in chemical structure and the whole legislative procedure had to be started from the beginning, because the ban on usage did not concern this new compound. That is why the definition is so broad to include all the possible threats, to prevent pollution of seas and oceans and to punish those who pollute the marine environment.

At selection of the most harmful compounds for the marine environment the following criteria were considered: amounts in which they are transported and introduced to the sea, properties such as stability, volatility and ability to transfer to long distances, toxicity, tendency for bioaccumulation.

The compounds fulfilling the best all these criteria were put on the list of harmful substances of Stockholm Convention on persistent organic compounds (2001) signed by 180 states and organizations. The Convention is aimed to protect human health and the environment, not only the marine environment, from persistent organic pollutants (POPs) by restriction put on their production and applying. At present these are 23 compounds or groups of compounds, mostly chlorinated compounds and in majority pesticides, e.g. DDT – p,p-dichlorodiphenyltrichloroethane, and also chemicals for other usage and compounds produced as by-products in different processes, like combustion of organic materials, e.g. PCDD - dioxins, PCBs - polychlorinated biphenyls, PCDF – polychlorinated dibenzofurans.

Classification of contaminants

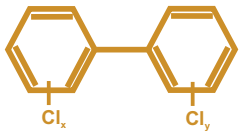
There are used different classifications depending on, e.g.:

1. Chemical composition
   - inorganic compounds (e.g. metal ions);
   - organic compounds (e.g. PCB – polychlorinated biphenyls, PAHs – polynuclear aromatic compounds).
2. Origin
   - natural substances, e.g. petroleum and its products;
   - anthropogenic compounds, i.e. synthetized, produced by man, e.g. NPs- nonylphenols, OTs – tin organics.
3. Toxicity or other toxic properties.
4. Usage – e.g. pesticides: fungicides, herbicides, insecticides.

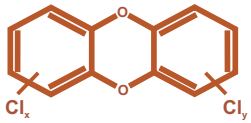
EXAMPLES OF ORGANIC POLLUTANTS

➢ **Chlorinated compounds**

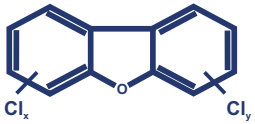
Polychlorinated biphenyls (PCBs)
x,y = 1÷5
x+y ≥ 1
(209 congeners)



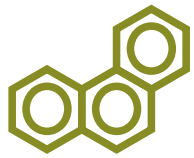
Dioxins (PCDDs)
x,y = 1÷4
x+y ≥ 1
(75 isomers)



Furans (PCDFs)
x,y = 1÷4
x+y ≥ 1
(135 isomers)



➢ **Polycyclic aromatic hydrocarbons (PAHs), e.g. –**



Phenanthrene

Fluoranthene

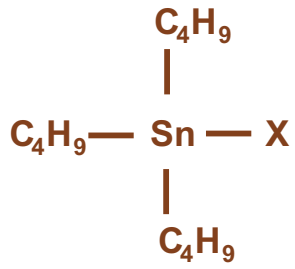
Benzo(a)pyrene

Indeno(1,2,3-cd)pyrene

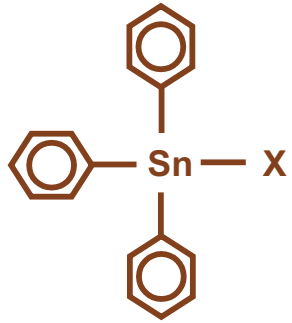
➢ **Nonylphenols (Nps), e.g. –**

4-nonylphenol (4-NP)

➢ **Organotin compounds (OTs)**



tributyltin (TBT)
X = e.g. Cl, OH



triphenyltin (TPhT)
X = e.g. Cl, OH

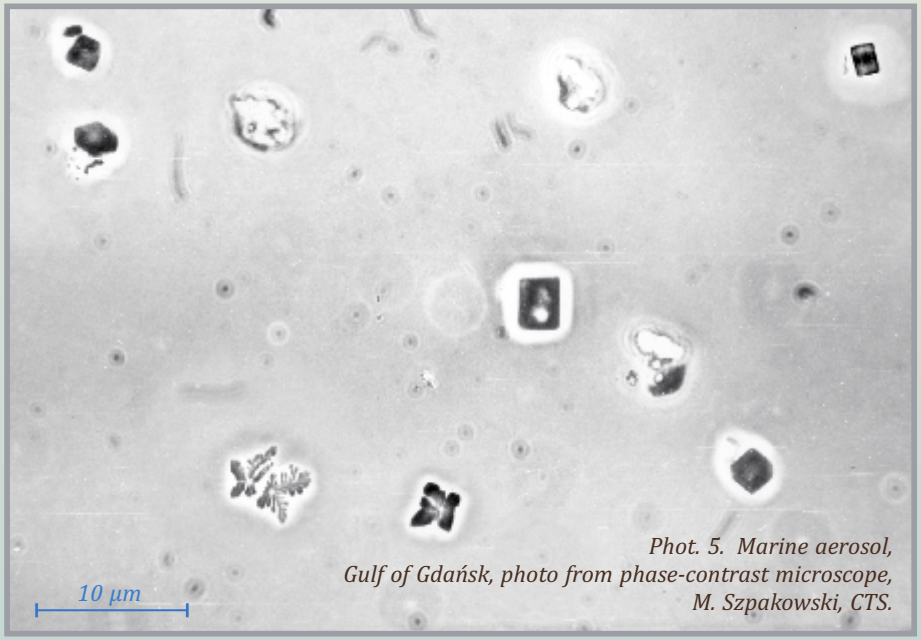
Sources of pollutants

There may be marine, land, riverine and atmospheric pollution sources. Pollutants may be introduced to the sea from ships (Phot. 1,2) and drilling platforms (Phot. 3), ports (Phot. 4), industry, different sorts of sewage but also sewage treatment plants, and others.

Phot. 4. Petroleum slicks in port, courtesy of IMEP MO in Gdynia.

Marine contaminant cycle

Some of contaminants, e.g. metals, while get to the marine environment stay there forever. The other ones may undergo degradation and decomposition. Contaminants may also get out from the sea to atmosphere with aerosol. In the sea contaminants



Phot. 5. Marine aerosol, Gulf of Gdańsk, photo from phase-contrast microscope, M. Szpakowski, CTS.

may undergo numerous reactions and processes, often various for different groups and even particular compounds from a group. Metal compounds and ions and majority of organic pollutants are taken and accumulated by organisms or adsorb on particulate matter (mineral particles, organic particles, phytoplankton), and next such associates settle on the bottom.

There, they may by absorbed and transformed by bacteria, phyto- and zoobenthos, and at hypoxia/anoxia may stay undecomposed for many years. Animals, moving in sediments and waves, cause resuspension of fine sediment fraction, next transported by

marine currents sometimes to long distances. Some pollutants can accumulate in organisms (bioaccumulation) or in the food chain (biomagnification).

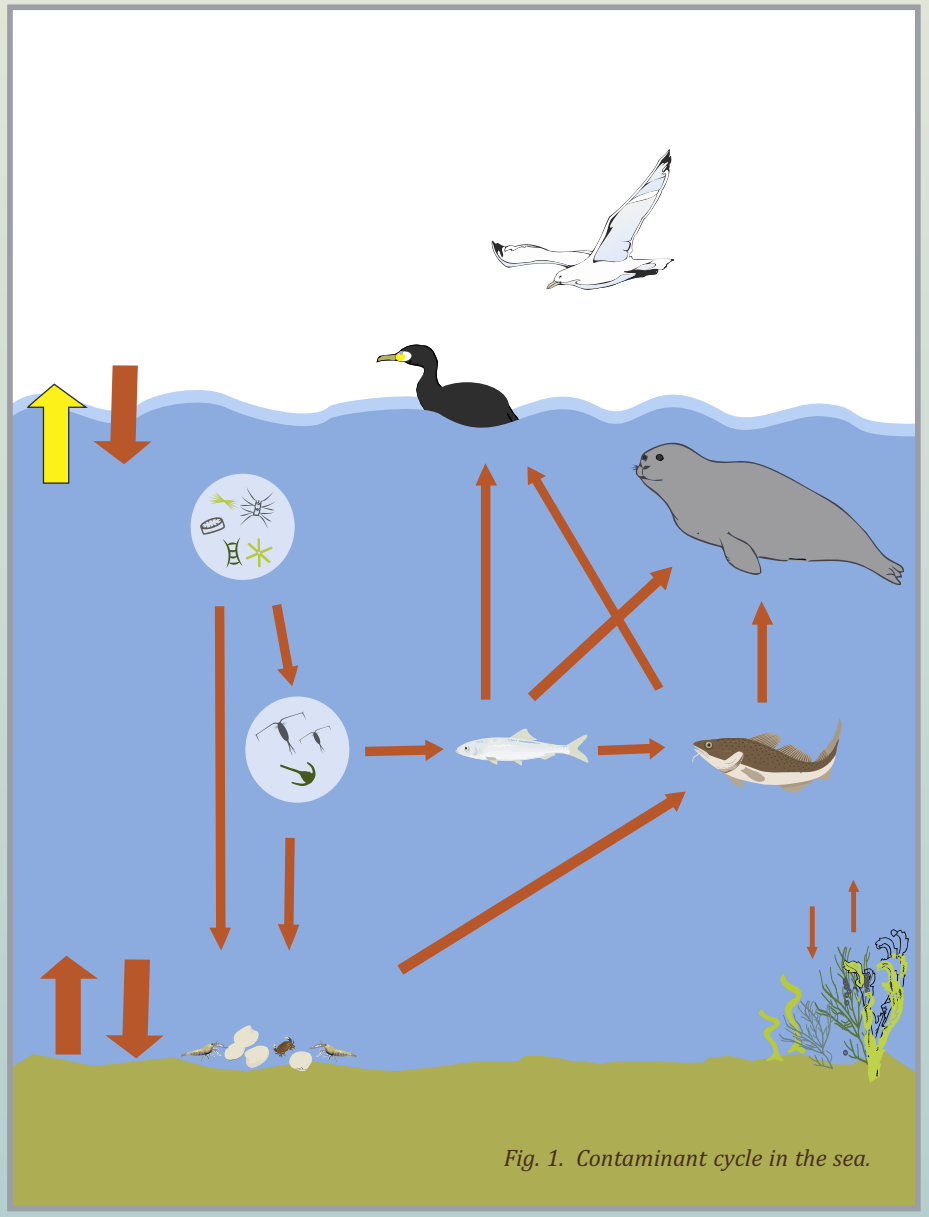


Fig. 1. Contaminant cycle in the sea.

Monitoring

» National Monitoring

Chief Inspectorate for Environmental Protection is responsible for coordination of environmental monitoring in Poland (http://www.gios.gov.pl, basing on legislative act Dz. U. Nr 0, 2013, p. 165), which is organizing also the marine environment monitoring, co-working with different institutions like Institute of Meteorology and Water Management, Maritime Branch in Gdynia (IMGW-PIB), Marine Fishery Institute in Gdynia (MIR-PIB), Maritime Institute in Gdańsk (IM). Monitoring is adjusted to the Baltic monitoring programme COMBINE, adopted by HELCOM, and that one is, in turn, agreed with EU in framework of MSFD implementation in European countries.

Selected contaminants are being analysed in seawater, sediments and organisms, according to accepted procedures, in samples collected at set sites and at set time periods. All the time, different international working groups carry on periodic assessments of the Baltic environmental state and analyse the accepted procedures.

This is impossible to monitor all contaminants occurring in the environment due to the fact that they are numerous and also to costly and time consuming analyses. That is why some groups of dangerous and harmful compounds have been indicated, and next the marker compounds of these groups have been selected. Procedures and frequency of monitoring have also been agreed.

According to MSFD eleven so called descriptors determine state of environment – good (GES – Good Environmental Status) or not good (sub-GES – sub Good Environmental Status). Four of them are connected with the marine chemical pollution. These are as follows:

Descriptor 5 – Eutrophication,

Descriptor 8 – Contaminants level in marine environment,

Descriptor 9 – Pollutants in fish and other seafood,

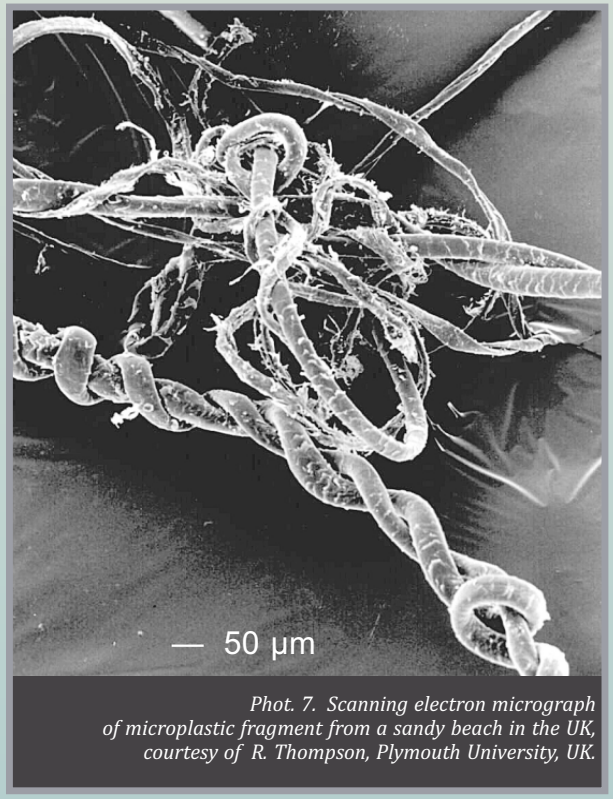
Descriptor 10 – Marine litter.

Phot. 6. Plastic litter thrown on the coast by waves and tides, Norwegian Sea, Norway, courtesy of MPL IOPAN.

● Marine litter

Problem of litter in the marine environment was noticed not so long ago. It concerns mainly plastics. This problem indicates distinctly that capacity of seas and even of oceans is not unlimited like people had thought before. While chemical compounds, even the most toxic ones or radionuclides, may be detected only after applying analytical methods, so everybody can see with bare eye eg. plastic packagings on the shore. Especially visible they are on these coasts where are tides. There, plastics consist 50–80% of litter thrown around (Phot. 6).

Some of plastic litter is floating on seawater surface but after a time the weight of fouling organisms and water filling up make them sunk and settled on the seabed. Their amounts in different parts of World Ocean are estimated to be equal to hundred thousand tons, and stability of plastic objects – to thousands years, and even more, in deep areas. Different plastic objects and plastic packagings, damaged fishing nets cut loose by fishermen, can be a death trap

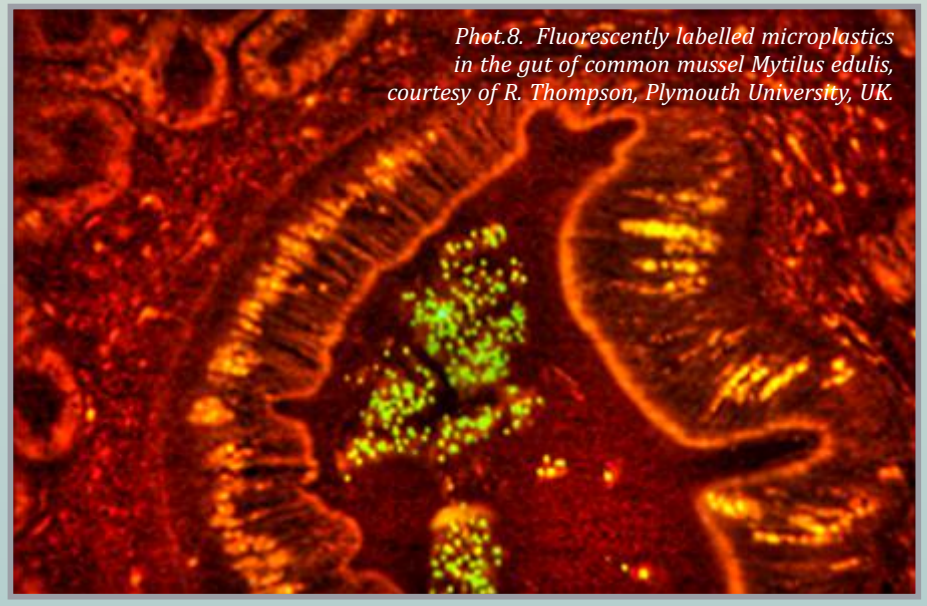


Phot. 7. Scanning electron micrograph of microplastic fragment from a sandy beach in the UK, courtesy of R. Thompson, Plymouth University, UK.

for marine animals like fish, mammals or turtles which may swallow them or become entangled and/or drown.

Besides, the plastics in the sea may break down to smaller pieces; those which are smaller than 5 mm, are called 'microplastics'. Such small fragments mayn also get to the sea from land, e.g. fine plastic fibers (Phot. 7), parts of packagings and construction materials, etc. The microplastics may be swallowed by small marine organisms like mussels (Phot. 8), zooplankton. Moreover, plastics may introduce to the marine environment different harmful compounds, which are added in production process, e.g. PAHs, PCBs or NPs, also adsorb contaminants from seawater and transfer them to other parts of the World Ocean or inside of organisms after their consumption.

The recent evaluation of state of the marine environment of the Polish Baltic zone for harmful substances (Descriptors 8 & 9) was good (GES) and for eutrophication and marine litter (Descriptors 5 & 10) was not satisfactory (sub-GES), http://www.gios.gov.pl.



Phot.8. Fluorescently labelled microplastics in the gut of common mussel Mytilus edulis, courtesy of R. Thompson, Plymouth University, UK.

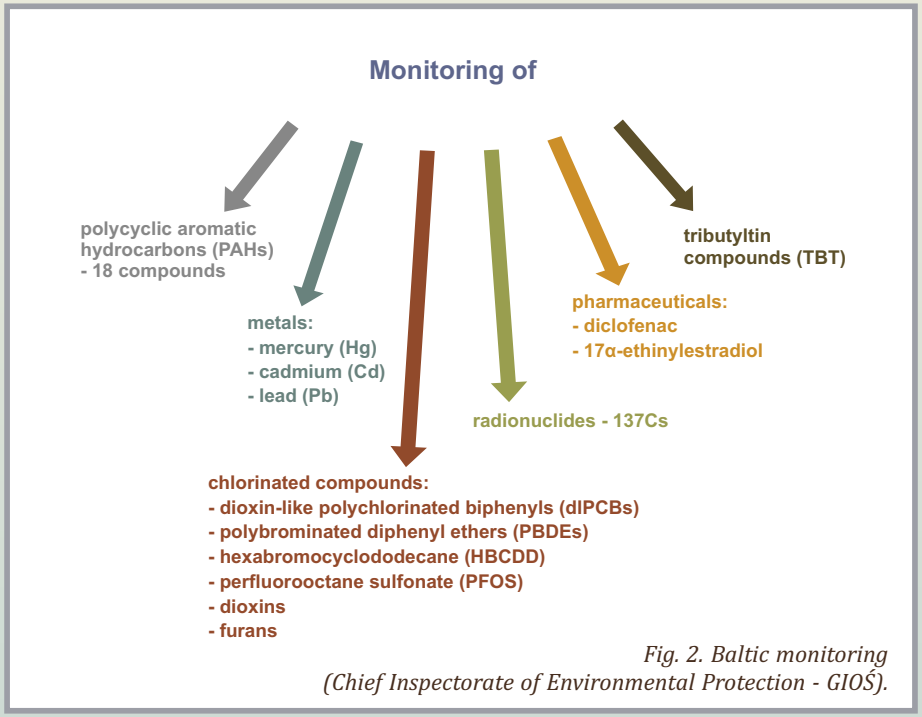


Fig. 2. Baltic monitoring (Chief Inspectorate of Environmental Protection - GIOŚ).

» Research driven monitoring - examples

Besides the official national monitoring the crucial role in recognition of marine pollution plays also the monitoring carried on in framework of research. Examples of compounds studied in MPL IOPAN are given below.

- **PAHs** – constitute large group of compounds included to the main pollutants of the environment. They may be the by-product of not full combustion of organic matter, occur also in petroleum and its products. They may be introduced to the sea in result of natural phenomena such as natural wood fires or leakage of petroleum from seabed. However, the main cause of their abundance in the environment is human activity. In MPL IOPAN are being analysed PAHs of marine origin. These were the first results for the Polish economic zone of the Baltic for the bottom

sediments which were included into HELCOM reports. Basing on marker PAH analysis we may determine with high probability if they origin from fuel combustion or from petroleum slicks. From correlations with other environmental parameters one can conclude on sources and cycle of PAHs in the sea.

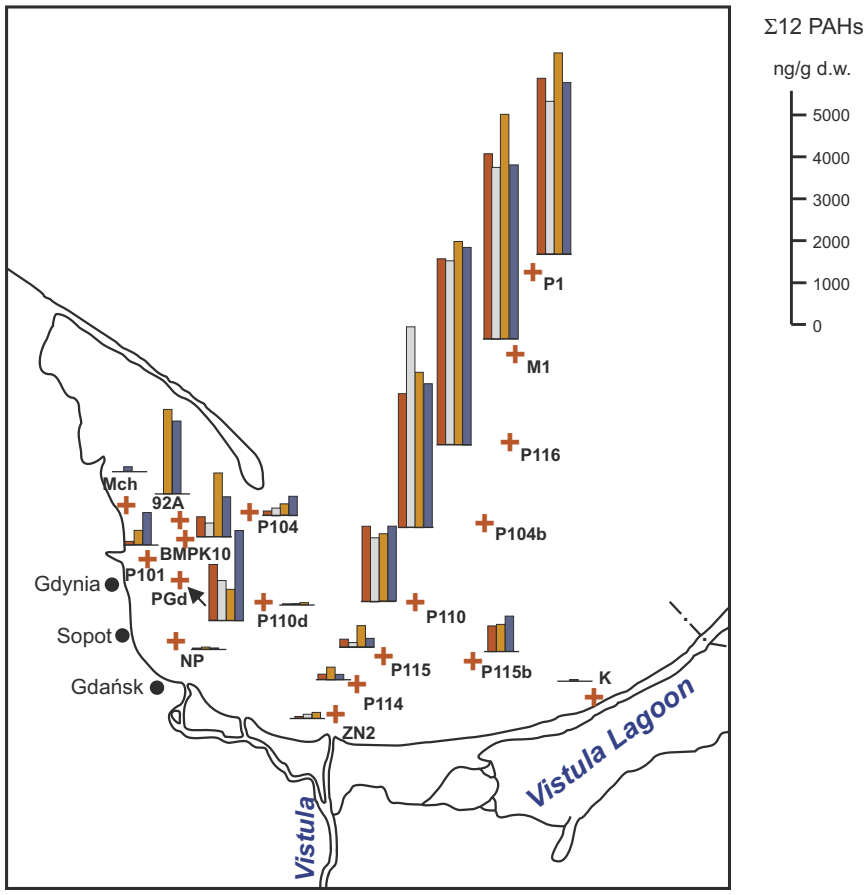


Fig. 3. PAHs in sediments (0-10 cm) of the Gulf of Gdańsk, L. Lubecki, MPL IOPAN.

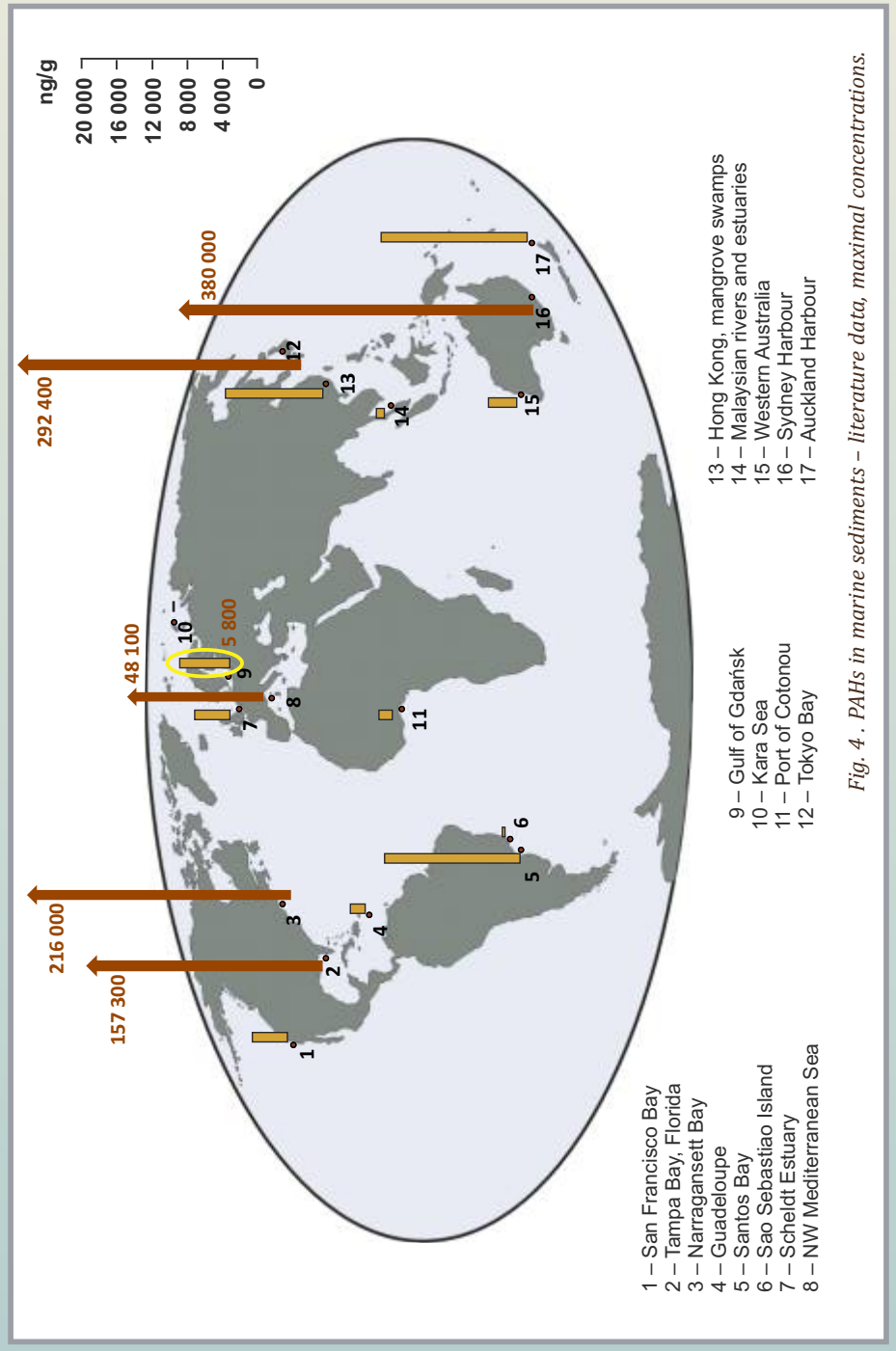


Fig. 4 . PAHs in marine sediments – literature data, maximal concentrations.

• Endocrine disruptors – OTs and NPs

Organotins (OTs) and nonylphenols (NPs) are the compounds highly toxic towards aquatic organisms, characterized also by high stability in the marine environment. These compounds are changing functioning of endocrine system: OTs cause their masculinization and NPs – feminization.

The most dangerous for the marine environment OTs are tributyl- (TBT) and triphenyltins (TPhT), which are used for composites of antifouling paints to protect hulls of vessels and underwater

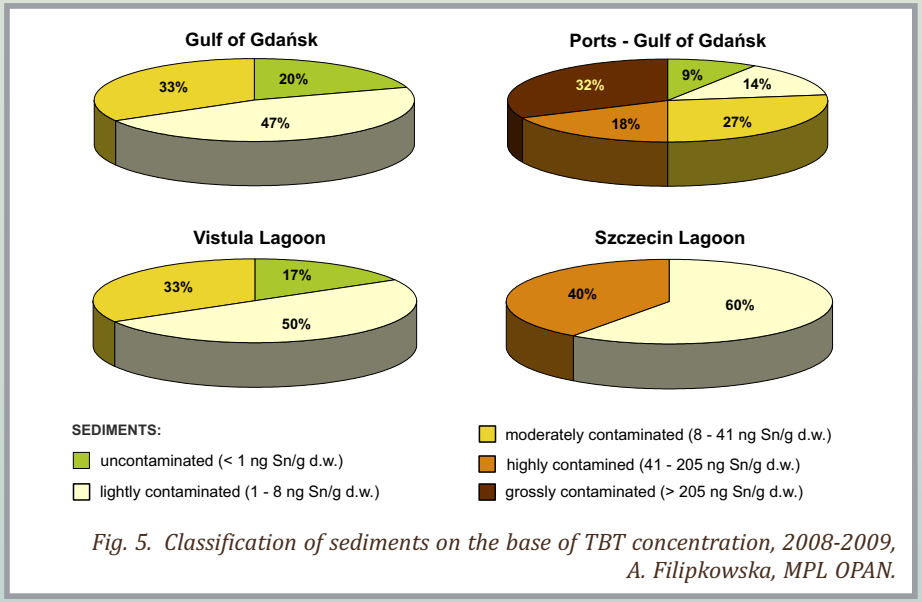


Fig. 5. Classification of sediments on the base of TBT concentration, 2008-2009, A. Filipkowska, MPL OPAN.

constructions. In many countries, in that the Baltic ones, their usage has been banned but still these compounds stay in the sea. NPs, in turn, occurring in the marine environment origin from decomposition of nonylphenol etoxylates (NPE), the compounds widely used in different branches of industry in production of e.g. detergents, fabrics, paints, varnishes, paper, and others. The sewage treatment plants do not remove these pollutants.

These are hydrophobic pollutants, which adsorb on particulate matter and accumulate in sediments in marine environment. OTs and NPs deposited in sediments, may be released to water in result of diffusion, resuspension of sediments and chemical reactions caused by hydrological and biological factors or human activity. Due to that they still pose a serious threat to marine organisms (especially benthos and bottom dwelling fish); may cause disorder in reproduction; endocrine disruptors interfere with hormone (endocrine) system of organisms, what may result in sterility and species extinction due to reproduction and developmental disorders. That is why there is a necessity of monitoring of these compounds. The HELCOM data indicate however, that monitoring of TBT, TPhT and NPs in the Baltic is realized in non-satisfactory range, though these are ones of the most harmful pollutants.

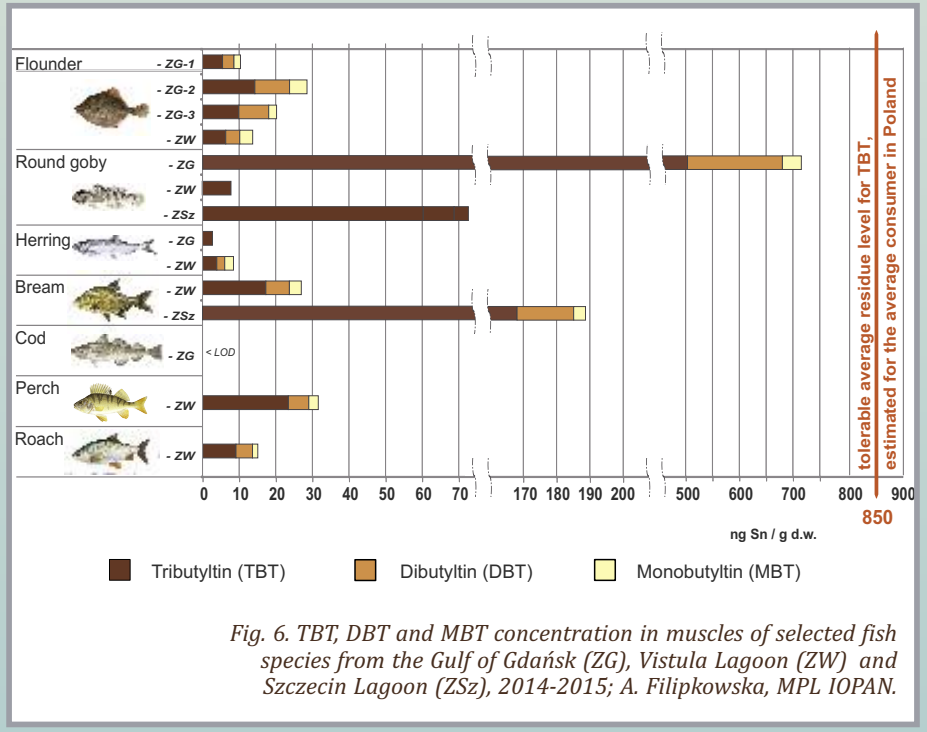
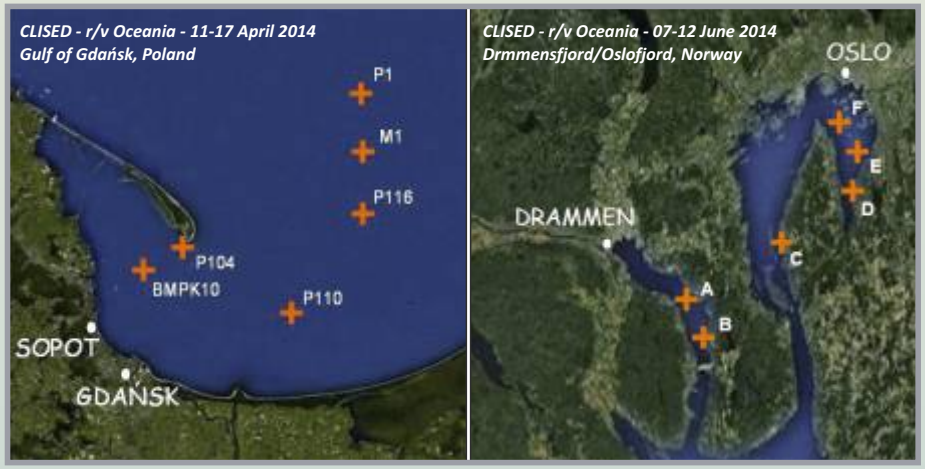


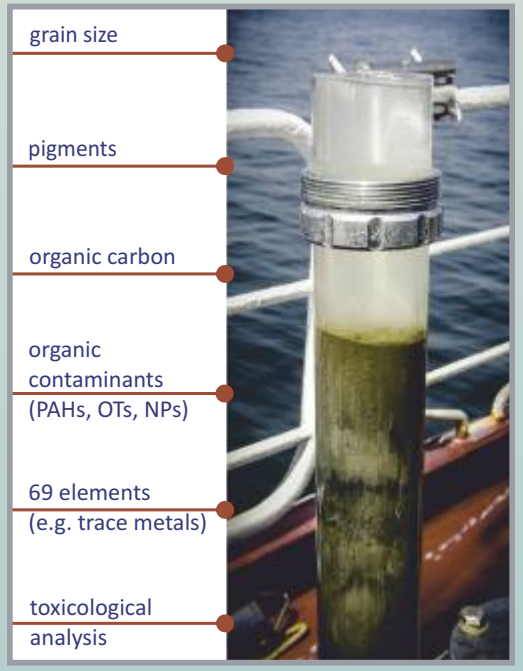
Fig. 6. TBT, DBT and MBT concentration in muscles of selected fish species from the Gulf of Gdańsk (ZG), Vistula Lagoon (ZW) and Szczecin Lagoon (ZSz), 2014-2015; A. Filipkowska, MPL IOPAN.

Project CLISED

Climate Change Impact on Ecosystem Health – Marine Sediment Indicators (02/2014–01/2017), www.iopan.gda.pl/clised; sampling sites are indicated in the maps below.



The aim of the project is among others, the comparison of trends and cycles of contaminants in the Gulf of Gdańsk and Norwegian fjords. The studied contaminants are heavy metals, PAHs, endocrine disruptors OTs and NPs, in sediments. Their toxicity depends on the form and environmental conditions; in sediments they may stay undecomposed, undergo degradation or may be released to water column.



» CLISED - examples of results

• Metals

Trace elements are inherent components of marine ecosystems. They have an essential influence on functioning of organisms as the nutrition components but in higher concentrations may be toxic. In result of human activity considerable amounts of trace elements got to waters and sediments and their natural equilibrium in the sea has been disrupted. Besides, the progressing climate changes may also influence their bioavailability in the sea. Trace elements may be bounded with different sediment fractions, and the total content of an element does not define its mobility nor bioavailability; a lot depends on species, in which it occurs. From trace metals in the sediments studied in

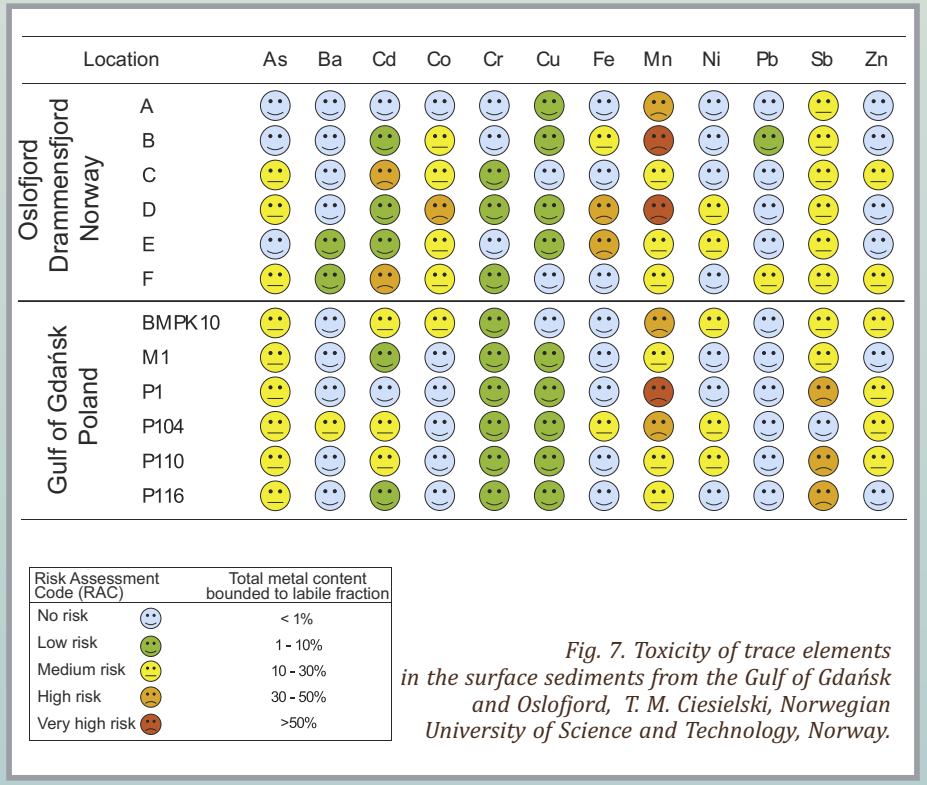


Fig. 7. Toxicity of trace elements in the surface sediments from the Gulf of Gdańsk and Oslofjord, T. M. Ciesielski, Norwegian University of Science and Technology, Norway.

framework of CLISED project, the highest mobility (fraction soluble in acids – a possibility to get into food chain) had manganese (Mn), while the lowest – chromium (Cr) and copper (Cu). High and moderate risk was estimated for metaloids – antimony (Sb) and arsenic (As) (Fig. 7).

• Endocrine disruptors

In the basins studied the highest NP concentrations in the recent sediments (0-10 cm) were found at stations D and E, localized in Oslofjord. At the other Norwegian sites and in the Gulf of Gdańsk the NP concentrations were considerably lower than the limit of no effect concentration, according to tentative guideline proposed in the framework of Common Implementation Strategy for the EU WFD to protect benthic communities (Fig. 8).

Scientists are the first who draw attention to a threat from uncontrolled compounds, new contaminants and their sources. They are studying the contaminant stability in the sea and ways

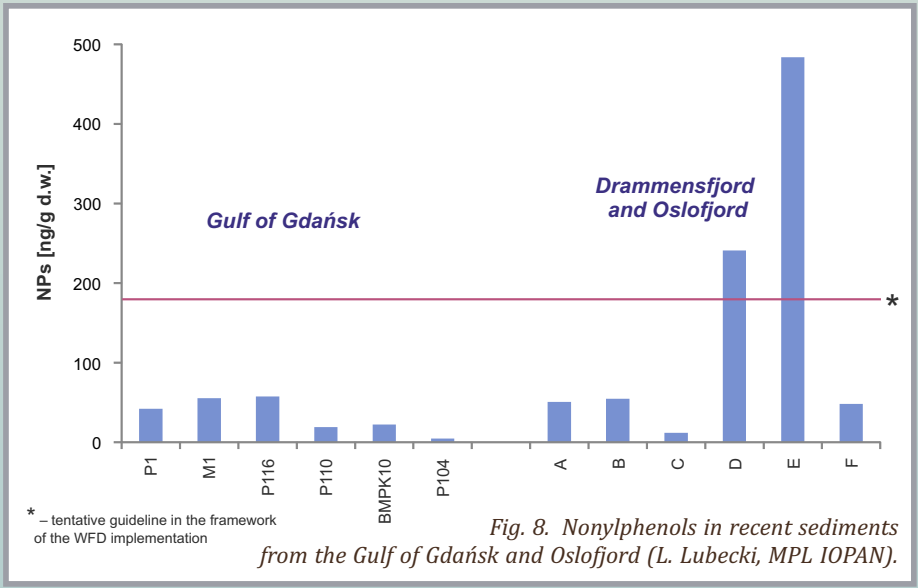


Fig. 8. Nonylphenols in recent sediments from the Gulf of Gdańsk and Oslofjord (L. Lubecki, MPL IOPAN).

of transfer, and develop new monitoring methods. So, the research driven monitoring supports and supplements the official national monitoring, and helps in protection of this common human heritage which are seas and oceans.