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METAL POLLUTION IN THE BALTIC



Metals are useful raw materials used in various industries. But one of the side-effects of their production is pollution of the marine environment.

The "Oceania"
research vessel of the PAS
Institute of Oceanography

MARTA KASPRZAK, TAKEN FOR PAS IO AS PART OF THE MODUM PROJECT

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Hheavy metals are elements that naturally occur in the environment, but they are now found in the seas and oceans in concentrations so high that they can be dangerous to the health of many organisms. Metals, including heavy metals, can exist in various forms in the environment. Minerals containing them form in various ways, including by diagenesis (slow processes that have been ongoing since the Earth's formation, gradually turning sediment into rock). Metals can also be found as impurities in various rocks and minerals, usually in small concentrations. For millions of years, metals on Earth were kept "trapped" in their most stable forms and had relatively little impact on the environment. Only in a few geothermal areas or during volcanic eruptions could they change into forms more accessible to living organisms.

Since ancient times, however, humans have been working to reverse this state of affairs. Initially, metals were harnessed in limited ways, as dyes, components of "magical" tinctures, or medicines. A good example is the use of mercury compounds for mummifying corpses. The rise of mining technology and metallurgy led to the extraction of metals from minerals and rocks on a broader scale – a trend that gained further momentum with the industrial revolution. However, metal production has the side-effect of releasing other, often toxic elements. In the latter half of the twentieth century, it was discovered that such commonly used chemical elements as mercury, cadmium, and arsenic are actually highly toxic. When they are present in living organisms, they cause various disruptions, including brain damage. Something similar can be said for coal-fired electric power generation: burning coal releases all the metals contained in it straight into the air we breathe.

The price of progress

The technological progress of the twentieth century ushered in a whole new era in terms of such environmental pollution. Humanity found numerous applications for many metals – iron, copper, nickel, zinc, chromium, noble metals, and more. Aluminum proved to be an excellent construction material, lead

was used as an additive to boost the performance of gasoline. The potential of mercury was discovered by the rapidly developing electrochemical and cellulose industry. Metals like cadmium, arsenic, molybdenum, and vanadium came to be widely used in almost all branches of the economy. After World War II, industry developed at a rapid pace, and untreated wastewater, both municipal and industrial, was discharged into rivers or directly into the sea. This occurred globally, including the countries around the Baltic Sea. In those days, it was assumed that heavy metals would simply sink to the bottom of the sea or ocean and thus be excluded from the cycle. But this theory was wrong. Even before heavy metals reached the sea, they caused damage in the environment, and after settling on the seabed, they did not simply stay there forever but found their way back into the water and the organisms living in it.

As a result of subsequent reports raising the alarm about the effects of polluting the environment with metals, research began to be done on metal concentrations in fish. Norms were also established for permissible concentrations in fish caught for the food industry. To identify sources of pollution, the contamination levels of particular areas of water were studied, but the metal concentrations found in water, even highly polluted, are still much lower than in the bodies of fish, sometimes by several orders of magnitude. Early research methods used in the 1960s and



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is an Associate Professor at the University of Gdańsk. Her research concentrates on the circulation of toxic metals (especially mercury) in the marine environment – especially the exchanging of metals between air and water, as well as water and sediment. She also studies the bioaccumulation and biomagnification of elements in the marine food chain, from planktonic organisms to up seabirds and marine mammals. She is a member of the PAS Committee on Marine Research and chairwoman of the Committee's Marine Chemistry Section.

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Jacek Bełdowski out on
the Baltic Sea, with
a sediment core sampler

1970s were unable to detect such quantities in water in a replicable and accurate manner.

Initially, it was decided to analyze sea-floor sediments, and this approach is still in use today. It forms the basis of existing global programs monitoring quantitative changes in harmful substances. However, this method is not without its flaws: it does not take into account metals present directly in water or in suspension, and these are precisely the ones that can enter the pelagic food chain, directly accumulating in fish.

New research methods

In 1975, the American marine chemist Edward D. Goldberg proposed a simple solution – studying water-filtering organisms that inhabit the sea floor. The International Mussel Watch program was born, in which mussels are caught annually worldwide in order to analyze the concentrations of various pollutants they contain: not only metals but also organic pollutants such as pesticides, polychlorinated biphenyls, and polycyclic aromatic hydrocarbons.

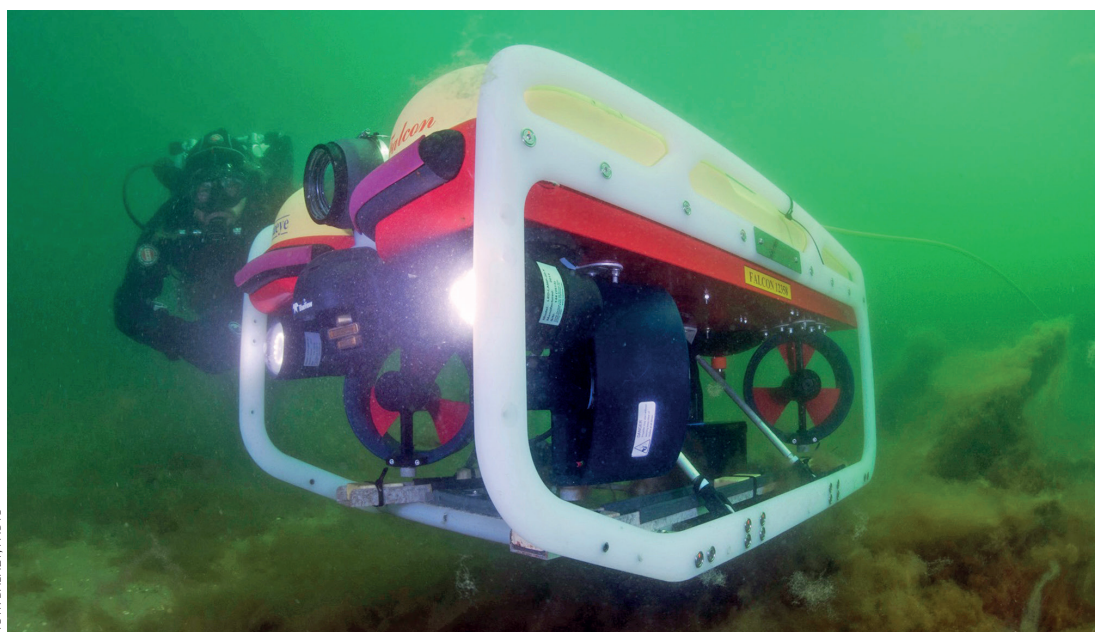
Atomic absorption and fluorescence spectrophotometry came to be used in environmental analyses in the 1980s, followed by mass spectrometry in the 1990s. However, both methods require many conditions to be met to obtain precise and repeatable results. The method of sample collection itself had to change. In the 1980s, scientists did not fully realize how micro-pollutants could affect the result. For instance, even a glove touching a part of the ship's equipment for just a moment could disturb the result: talc, used to powder latex gloves, could be a source of error in the analysis of trace elements. After many trials and errors, special analytical protocols were

developed, known as the “Clean hands / dirty hands” techniques, whereby any person having direct contact with a sample essentially does not touch anything else. It was realized that vessels used to store samples in the laboratory needed to be made of special materials. Ordinary laboratory glass can sometimes “remember” previously prepared samples or reagents, which may diffuse back out of the vessel walls into the tested sample. Depending on the element being analyzed, various materials are used instead of ordinary glass – some are only analyzed in vessels made of special plastics (e.g. Teflon), others only in borosilicate glass or quartz, and some only in metal vessels, e.g. made of pure platinum or tungsten carbides. There are now standardized methods for each metal being analyzed in water. The International Atomic Energy Agency (IAEA) and the US Environmental Protection Agency (EPA) have developed methods and procedures that are now widely used.

Heavy metals in the Baltic

In the 1980s, some areas of the Baltic Sea – such as the inner part of the Bay of Puck – were considered to be dead zones. Fortunately, in the early 21st century, restrictions mandating the purification of industrial wastewater came into force. Additionally, new state-of-the-art municipal sewage treatment plants were built in Baltic countries, and still continue to be. More sustainable use of fertilizers in agriculture is also an essential improvement. All these actions have significantly reduced the amounts of pollution reaching the Baltic Sea. The aforementioned inner zone of the Bay of Puck has revived, with species preferring a clean environment returning there.

A submarine instrument for bottom sediment sampling



PIOTR BALAZY, PAS 10

Despite all the efforts to clean up the Baltic Sea, however, the problem of heavy metal pollution still persists. Metals that were excessively present in marine sediments in the past are still there and are slowly diffusing back into the water and the organisms living there. Climate warming is unfortunately conducive to this process, specifically in the late autumn / winter / early spring season. As recently as the 1990s, parts of the Bay of Puck would freeze over during the Christmas season and the ice would remain until the first calendar days of spring – for almost three months. Currently, winters are warm enough that the coastal zone of the southern Baltic usually does not freeze at all, or if ice does appear, it lingers for a much shorter time. When the water surface is frozen, biological and chemical processes are inhibited and living organisms fall into a lethargic state. Back when the sea used to freeze over for about three months, pollutants were largely unable to move from sediments into seawater and organisms during that time. When winters are warm, on the other hand, organisms can continue to develop and absorb chemical substances from sediments. They do not do so selectively – together with useful nutrients, they also absorb toxic substances. Therefore, due to climate warming, plants and animals living on the sea floor accumulate chemical substances for a much longer time compared to the years when the bay froze over for months.

In recent years, if the weather is warm enough, phytoplankton blooms have been observed even in January. In winter months, this has particularly harmful consequences because phytoplankton accumulates toxic elements being released into the atmosphere from coal combustion (which many people use to heat their homes in this part of the world). Climate warming at our geographical latitude is therefore doubly dangerous, because chemical elements that we ourselves once extracted from minerals and introduced into Baltic sediments are gradually re-entering circulation.

Research contribution

The Institute of Oceanology of the Polish Academy of Sciences and the Faculty of Oceanography at the University of Gdańsk have been studying metals in the marine environment for over 40 years. Initially, measurements were taken of the concentration of metals in individual environmental components (sediments, organisms, water, suspension), then they were expanded to study speciation – the occurrence of metals in their various physicochemical forms, and processes leading to transformations of these forms. Currently, research topics also include the impact of climate change on the return of metals from contaminated bottom sediments and hazardous objects introduced by humans into the sea back into nature's



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Samples of bottom sediments retrieved from the sea floor, on board the research vessel

circulation. Research is done not only on the Baltic Sea but also on other marine areas, including the Arctic and Antarctica. The techniques used include many spectroscopic methods, and sample preparation takes into account the latest guidelines for trace analysis put forward by the EPA and IAEA. Sample collection is performed with great precision, using remotely operated submarine vehicles and systems for pure water sampling with a depth resolution in the single centimeters.

Despite significant progress in environmental protection, the problem of heavy metal pollution in the seas persists. Polish research is contributing to gaining a better understanding of the processes involved and making progress towards future solutions. ■

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Further reading:

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