LEIBNIZ-INSTITUT FÜR OSTSEEFORSCHUNG WARNEMÜNDE

IOW

IOW press release from December 14, 2020

First-time detection of glyphosate in the sea: IOW develops new method and successfully applies it to Baltic Sea samples

Glyphosate is one of the world's most widely used weed killers. The disputed herbicide, which is suspected to be carcinogenic among other things, gets transported from the on-land application areas into rivers, which wash it into the sea. So far it was unclear, however, how much can be found in marine environments, because glyphosate and its metabolite aminomethylphosphonic acid could not be measured in saltwater due to methodological reasons. Marisa Wirth from the Leibniz Institute for Baltic Sea Research Warnemünde has now developed a new method, with which both substances can reliably be measured in seawater and for the first time was able to detect glyphosate and AMPA in the Baltic Sea.

Glyphosate, which is used as a broad-spectrum herbicide primarily in agriculture, horticulture and industry, but is also frequently used in private households, is transported from the areas of application into streams, rivers and lakes by rain and wind erosion. Accordingly, it can be detected in freshwater ecosystems worldwide, together with its metabolite, aminomethylphosphonic acid (AMPA). Researchers from the Leibniz Institute for Baltic Sea Research Warnemünde (IOW) have been able to detect both substances in estuaries that discharge into the Baltic Sea, but never in the sea itself. How toxic the herbicide is to marine organisms has not been conclusively clarified.

"The basic prerequisite for assessing the hazard potential of a substance for an ecosystem is to find out whether it is present at all and in what concentrations it can be detected," emphasises Marisa Wirth, who has specialised in the detection of glyphosate in environmental samples as part of her PhD work at the IOW. "The starting point for our current study was, therefore, the question of whether glyphosate and AMPA in fact do not reach the sea – be it due to biodegradation or sedimentation along its paths towards the sea – or whether methodological difficulties have so far prevented their detection in marine ecosystems," the marine chemist explains.

One obstacle to reliably detect the two target substances in marine waters is known from the previous estuarine studies: Glyphosate and AMPA become increasingly diluted with increasing distance from river mouths towards the open sea. "Before you can measure glyphosate and AMPA with common instrumental methods – liquid chromatography and mass spectrometry – the samples have to be pre-concentrated to such an extent that the instrument can detect the analytes," Wirth describes an important step in glyphosate analytics. In the case of seawater samples, the presence of salt has so far proved to be a problem for this step: In solid-phase extraction, which is used to achieve the necessary pre-concentration and in which the target substances in the liquid water sample are first bound to a solid substrate and then transferred back into a much smaller volume of liquid, the salt ions prevent the glyphosate and AMPA molecules from binding to the solid phase. "Our target substances 'rush' through the solid phase virtually unhindered and are lost because the salt blocks all the binding sites," Wirth points out. Moreover, during the actual measurement, the salt can interfere by shifting or suppressing instrumental signals, preventing reliable analysis, the chemist elaborates.

To overcome the salt interference during sample pre-concentration, Wirth tested various substrates for solid phase extraction and was finally able to identify a polymer as a suitable material, which binds glyphosate and AMPA with high selectivity due to so-called molecular imprinting and is at the same time unaffected by sea salt. Furthermore, she successfully established an additional purification step prior to instrumental measurement, which allows interference-free analysis.

After thorough validation of the new method, for salinities between 5 and 20, as they typically occur in the Baltic Sea, as well as for a salinity of 35 typical for the world's open oceans, the method was tested on environmental samples from seven sampling sites in the Western Baltic Sea. Both substances, glyphosate and its metabolite AMPA, could be detected – for the first time in the sea. Glyphosate concentrations between 0.42 and 0.49 ng/l were quite constant, regardless of the distance from the coast, with the exception of one measurement of 1.22 ng/l in the inner Lübeck Bight. AMPA concentrations (maximum 1.47 ng/l) were significantly higher near river mouths compared to sampling sites further out to sea, where AMPA fell below the detection limit of the new method.

"With the glyphosate and AMPA analytics developed at the IOW, we can for the first time measure in concentration ranges below 1 ng/l, as they can be expected in marine ecosystems – and without interference from the salinities that can be found in the different marine areas of the world," says Marisa Wirth. The glyphosate concentrations now measured in the Baltic Sea are far below the concentrations that are discussed as being harmful to humans or marine organisms. But since only very few data are available so far, no assessment of the extent to which the Baltic Sea is endangered is possible as of yet, Wirth adds. "However, we now have a sufficiently sensitive and reliable method with which to conduct monitoring in marine environments. Furthermore, studies are now possible that address current research questions, regarding transport, persistence and degradation of glyphosate and AMPA in the sea," the IOW researcher concludes.

The results can be read in detail at: Marisa A. Wirth, Detlef E. Schulz-Bull, Marion Kanwischer: *The challenge of detecting the herbicide glyphosate and its metabolite AMPA in seawater – Method development and application in the Baltic Sea.* Chemosphere (2021); doi.org/10.1016/j.chemosphere.2020.128327

Scientific Contact:
Marisa Wirth | Tel.: +49 381 5197 - 237 | marisa.wirth@io-warnemuende.de
Dr. Marion Kanwischer | Tel.: +49 381 5197 - 382 | marion.kanwischer@io-warnemuende.de

Contact to the IOW press relation office:
Dr. Kristin Beck: +49 381 5197 135| kristin.beck@io-warnemuende.de
Dr. Barbara Hentzsch: +49 381 5197 102 | barbara.hentzsch@io-warnemuende.de

The IOW is a member of the Leibniz Association that connects 96 independent research institutions that range in focus from natural, engineering and environmental sciences to economics, spatial and social sciences and the humanities. The institutes are jointly financed at the state and national levels. The Leibniz Institutes employ a total of 20,000 people, of whom 10,000 are scientists. The total budget of the institutes is 1.9 billion Euros. *www.leibniz-association.eu*