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NOVEL TANDEM MASS SPECTROMETRIC MEASUREMENTS OF ORGANOTIN COMPOUNDS AND IRGAROL 1051 ANTIFOULING AGENTS IN SELECTED WATER AND SEDIMENT SAMPLES IN THE NORTHWEST ATLANTIC ENVIRONMENT

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Fouling causes significant losses to the shipping industry. Numerous approaches to fouling control have been considered but the application of biocide(s)-laden antifouling paint remains the most important cost effective measure. Organotin biocides (*e.g.* tributyltin and triphenyltin) have been widely used in the formulations of antifouling agents in some paints for boats, ships and docks and have been found in areas of heavy boating and shipping traffic. These compounds are toxic to non-target aquatic biota and are responsible for the decreasing population of Pacific oysters and for causing the imposex defect observed in the neogastropod dog whelk. The wide environmental distribution of organotin compounds, in addition to their non-selective biotoxicity, led to the OECD countries in 1988 to prohibit their use in antifouling paints. Since then, copper based biocides, fortified with the herbicide IRGAROL 1051 (2-methylthio-tert-butylamino-6-cyclopropylamino-*s*-triazine) developed by Ciba-Geigy, have largely replaced organotins in antifouling paints worldwide. The use of IRGAROL 1051 in the copper based antifouling paints is essential because the copper salts themselves are not particularly effective in inhibiting the primary colonization of the hull surface by micro-algae and the subsequent growth of seaweeds. There is, however, no information in the open literature on the persistence, measurement and degradation of IRGAROL. This lack of information hinders the assessment of the impact of IRGAROL on the aquatic environment of the Northwest Atlantic

The high toxicity of organotin compounds to non-target organisms necessitates highly sensitive analytical protocols to quantify potentially toxic concentrations (<2 ng l^{-1}). The analytical protocols currently available for the determination of TBT and derived compounds are numerous and have been well documented. Despite the increased popularity of HPLC-ICP-MS, the coupling of GC with AAS, flame photometry (PFD) and MS remain the most preferred choices. The main hindrance of these gas chromatographic methods is the omnipresent need for separation of the analyte species from the analyzed matrix and their conversion to a form that is acceptable for presentation to a chromatographic column (*i.e.* derivatization is required prior to gas chromatographic separation). Although the previous methods once had merit, they are laborious and time consuming requiring extensive work-up including extraction, clean-up, and derivatization. Our preliminary investigations seem to indicate that the majority of the analytical methods used to determine TBT involving acid extraction contribute to its decomposition into dibutyl- and monobutyltin.

Analytical methods used to quantify IRGAROL 1051 are based on conventional methods developed for agricultural triazine herbicides and involve liquid-liquid or solid phase extraction. We have developed, in our laboratories, a state-of-the-art method for the detection of Irgarol 1051 and for organotin compounds that was refined and transformed into an MRM MS/MS method which has increased its detection ability to picomole/attomole levels in order to monitor these compounds in the environment. Ultimately, unique analytical methods for the quantitative determination of organotin and triazine antifouling agents in water and sediment was developed and optimized. The MS/MS results for quantification of organotin compounds and Irgarol1051 will be presented using different ionization sources such as electrospray (ES), atmospheric pressure chemical ionization (APcl) and metastable atom bombardment (MAB).

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