

Nontargeted comprehensive two-dimensional gas chromatography/time-of-flight mass spectrometry method and software for inventorying persistent and bioaccumulative contaminants in marine environments

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ABSTRACT

Analytical methods for contaminant monitoring are generally targeted; i.e., they measure defined lists of compounds. Routine monitoring projects using targeted methods are not usually designed to screen for unrecognized or novel contaminants and therefore miss compounds within the region or population of study that cause, or have the potential to cause, adverse biological impacts. We describe a nontargeted analytical method utilizing direct sample introduction coupled to comprehensive two-dimensional gas chromatography with time-of-flight mass spectrometry. To test the capabilities of this instrumental method within the context of marine contaminant surveys, we characterized a broad array of nonpolar, persistent, and bioaccumulative contaminants in Atlantic common dolphin (*Delphinus delphis*) blubber, including compounds that are not typically monitored. Compound identifications were made by searching a standard reference database, by contemporaneously analyzing mass spectra from reference standards, and by de novo interpretation. We identified a total of 271 compounds belonging to 24 classes; all compounds but 1 were halogenated. Anthropogenic contaminants and halogenated natural products were concurrently detected. A total of 86 compounds were anthropogenic contaminants that are not routinely targeted in environmental surveys, and 54 compounds were halogenated natural products. A total of 112 spectra were identified de novo, demonstrating that exclusive reliance on commercially available reference standards and mass spectral libraries may miss a significant fraction of identifiable compounds. We also cataloged 27 halogenated mass spectra that were not able to be identified. Due to the volume and complexity of the identification data, we developed custom software to organize and provide shared access to the identified mass spectra and related information. The nontargeted analytical method and data reporting system, in combination with the analysis of a high-trophic-level sentinel species, demonstrates a framework for creating an inventory of persistent and bioaccumulative contaminants in marine environments, with the future goal of suggesting new compounds for further investigation by targeted monitoring and risk assessment.

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