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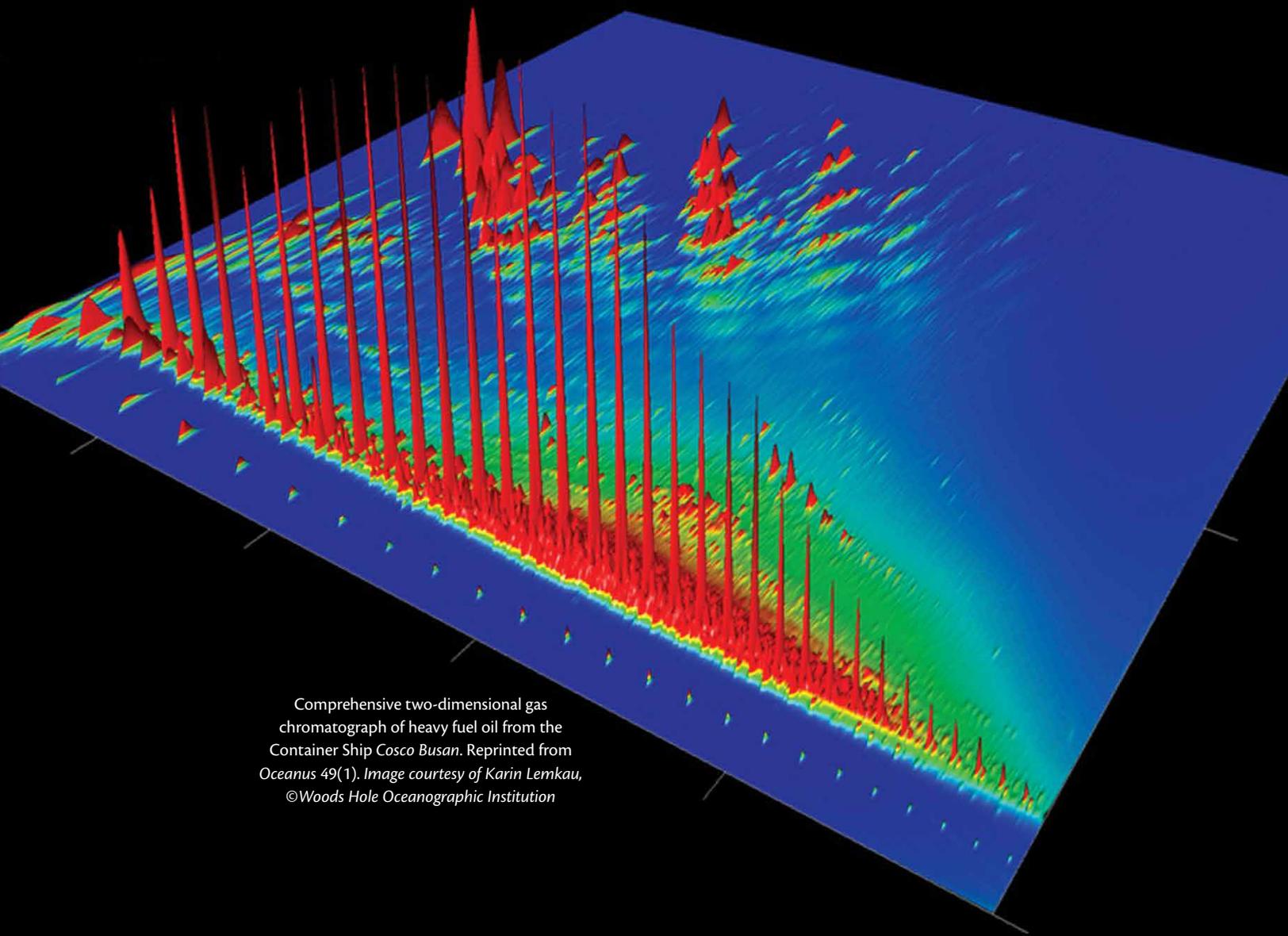
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Organic Chemicals of Environmental Concern

Water Sampling and Analytical Challenges

BY JOHN W. FARRINGTON



Comprehensive two-dimensional gas chromatograph of heavy fuel oil from the Container Ship *Cosco Busan*. Reprinted from *Oceanus* 49(1). Image courtesy of Karin Lemkau, ©Woods Hole Oceanographic Institution

A detailed understanding of the biogeochemical cycles of organic chemicals of environmental concern (OCEC) in the ocean requires measurement of their concentrations in the water column (Farrington and Takada, 2014, in this issue, and references therein). Obtaining these measurements remains a major challenge. Those of us who have attempted low concentration OCEC measurements in open ocean seawater know that research vessels can be considered a floating cloud of contaminants of the same or interfering compounds, as is true for trace metals (Froelich, 2014, this issue).

Surface water and surface films or slicks can be sampled from inflatable rafts deployed from research vessels to travel upwind well away from the ship, or surface waters can be sampled with great care from the deck of the ship by pumping through specially cleaned tubing or through intake systems mounted in the bow of the ship (e.g., De Lappe et al., 1983). In the 1970s, most subsurface, deeper (below 10 m) water samples for OCEC analyses were obtained from lowering standard Niskin bottles, large 90 L or 160 L stainless steel or anodized aluminum Bodman bottles (Bodman et al., 1961), or similar large samplers, all cleaned with care and lowered, open, through the surface slick, with the attendant risk of the slick and its components contaminating the interior of the bottle and eventually the deepwater samples. Boehm (1980) was among the first to report on the use of large Bodman bottles modified to enter the surface ocean closed and then opened under

the surface to avoid surface slick contaminations. Eventually, in situ pumping systems employing glass fiber filters for particulate matter sampling and sorbent materials to sample the dissolved phase were developed for sampling both surface and deep waters (e.g., Petrick et al., 1996). Deployment time to pump a thousand or more liters of deepwater samples can be 10 hours or longer. This may be the reason that very few high-quality deepwater samples for OCEC measurements have been obtained. Another reason may be the focus on the continental shelf and coastal ecosystems where OCEC concentrations are the highest and pollution has been severe in some locations.

Clean samples were and are just the beginning of the challenge. Obtaining OCEC quantitative data for all samples—from deep, surface, continental shelf, and coastal waters—involves extraction of samples with various organic solvents followed by column chromatography, thin layer chromatography, and high performance liquid chromatography (HPLC) to separate classes of OCECs from the myriad other compounds (e.g., lipids) in the extract. However, some of the OCEC classes enter the environment as complex mixtures of individual chemicals. For example, PCB commercial mixtures contain of up to 50 individual chlorobiphenyls, and the mixture of medium and higher molecular weight hydrocarbons in petroleum, including polycyclic aromatic hydrocarbons (PAHs), contains hundreds of individual compounds (Erickson, 1997; see Example Chemical Structures box in Farrington and

Takada, 2014, in this issue).

In the early days, the gas chromatography columns in routine use could not resolve these mixtures of PCBs and PAHs into individual compounds to allow quantitative measurements of each of the components. Beginning in the mid-1970s, gas chromatography–mass spectrometry–computer systems (GC-MS) or mass spectrometry–computer systems did allow quantitative measurements of several of the PAHs and entered into frequent use in the 1980s (Giger and Blumer, 1974; Hites and Biemann, 1975).

Progress in the development and use of high-resolution capillary gas chromatography columns then improved the separation of individual compounds and, when coupled with mass spectrometry–computer systems or selective detectors such as electron-capture detectors for halogenated compounds, provided a powerful means to quantify many, but not all, components of OCEC complex mixtures such as PCBs. The application of multidimensional gas chromatography using two GCs and high-resolution capillary columns with different internal liquid phase coatings provided the means for separation and quantitative measurements of individual components in PCB mixtures (e.g., Duinker et al., 1988).

Comprehensive two-dimensional gas chromatography is now available (Frysiner et al., 2003) and is being applied to several environmental samples

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to provide quantitative measurements of individual components of complex mixtures of organic chemicals in the environment, including OCEC in samples from marine ecosystems. Techniques are now available for isolating sufficient quantities of individual OCEC, for example, an individual PAH, to measure an individual compound's C-14 activity. The data enable discernment of organic chemicals with a fossil carbon source, such as PAH from fossil fuel combustion versus PAH from recent forest fires (Reddy et al., 2002). Ultrahigh-resolution mass spectrometry and liquid chromatography with tandem mass spectrometry has been applied recently to quantify a key ingredient in a dispersant used at the Deepwater Horizon oil spill (Kujawinski et al., 2011). Added to this is the report of recent coupling of two-dimensional gas chromatography to time-of-flight mass spectrometry and new software to inventory OCEC in environmental samples (Hoh et al., 2012).

Thus, clean sampling capabilities exist. High-resolution analytical chemical methods are available. Yet, very few studies have combined these new methods to obtain open ocean deepwater data for OCEC. Significantly more field sampling campaigns and accompanying high-quality analyses are needed if we are to have a much needed understanding of the biogeochemical cycles of OCEC in the ocean and the global environment as a whole—both for legacy contaminants (e.g., persistent organic pollutants, or POPs) and emerging contaminants. Assessment of the intercomparability (in a quality assurances/quality control mode) of results from different laboratories will need to be a first step in such an effort. The sparse number of such assessments to date constrain any attempt, such as that of Farrington and Takada

(2014, in this issue), to synthesize data and conclusions from different studies into a more comprehensive view of the biogeochemical cycles of OCEC in the marine environment. 

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