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REGIONAL MONITORING PROGRAM FOR WATER QUALITY IN SAN FRANCISCO BAY

RMP

A BROAD SCAN OF BAY CONTAMINANTS: Cutting Edge Analysis Identifies Low Levels of Five Unmonitored Compounds in Wildlife of San Francisco Bay

SUMMARY

San Francisco Bay wildlife were tested for previously unmonitored contaminants using a non-targeted analysis that screens mainly for long-lived, fat-soluble, chlorine- and bromine-rich chemicals.

Bay mussel and harbor seal samples contained five contaminants not previously identified in wildlife, and for which toxicity is largely unknown.

Most of the Bay chemical contamination was from high priority contaminants that the RMP already monitors, or closely related compounds.

Future non-targeted analysis could include techniques that examine water-soluble compounds.

PROTECTING SAN FRANCISCO BAY FROM POLLUTION

The RMP tracks well-known toxic compounds like PCBs, as well as chemicals that have only recently been identified in the environment, and for which we often have little information regarding sources, occurrence, or toxicity. These contaminants of emerging concern (CECs) are broadly defined as man-made or naturally occurring chemicals that are not regulated or commonly monitored, but have the potential to enter the environment and harm ecological or human health. Over a decade of investigations on CECs in San Francisco Bay were summarized in the 2013 Pulse of the Bay report.

THE REGIONAL MONITORING PROGRAM FOR WATER QUALITY IN SAN FRANCISCO BAY (RMP) is an independent, long-term monitoring program providing policymakers with the information they need to protect this vital urban ecosystem. The RMP is an innovative collaboration between the San Francisco Estuary Institute, the San Francisco Bay Regional Water Quality Control Board, and regulated dischargers.

USING NON-TARGETED ANALYSIS TO SEARCH FOR UNEXPECTED CONTAMINANTS

Traditionally, scientists monitor water, sediment, or organisms for contamination using a specific list of chemicals already identified as potentially problematic. This means the measurement tools are tuned to only look for these specific "target" chemicals. Could toxic chemicals we haven't identified yet be lurking in the Bay and in wildlife?

To explore this question, the RMP collaborated with scientists at the National Institute of Standards and Technology (NIST) to conduct a "non-targeted" scan for many thousands of chemicals in a sample, not just those on a targeted list. This technique, called two dimensional gas chromatography time-of-flight mass spectrometry, was used by NIST scientists to conduct a broad scan of Bay samples, comparing signals found to those present in the NIST Mass Spectral Library, an indispensable resource containing information on over 200,000 compounds. This analysis focused on carbon-based chemicals with chlorine or bromine atoms, which are not very water-soluble and tend to build up in fatty tissues in wildlife and people. Members of this chemical family include well-known toxic contaminants such as PCBs, pesticides like DDT, and flame retardants like PBDEs.

We examined samples of Bay mussels and blubber from Bay harbor seals that had stranded and died, and compared them to samples from relatively unpolluted areas (mussels from Bodega Bay and seals from Alaska). These two animals occupy different places in the Bay food web, and can harbor different types or concentrations of contaminants.

Founded in 1901 and now part of the U.S. Department of Commerce, NIST is one of the nation's oldest physical science laboratories.

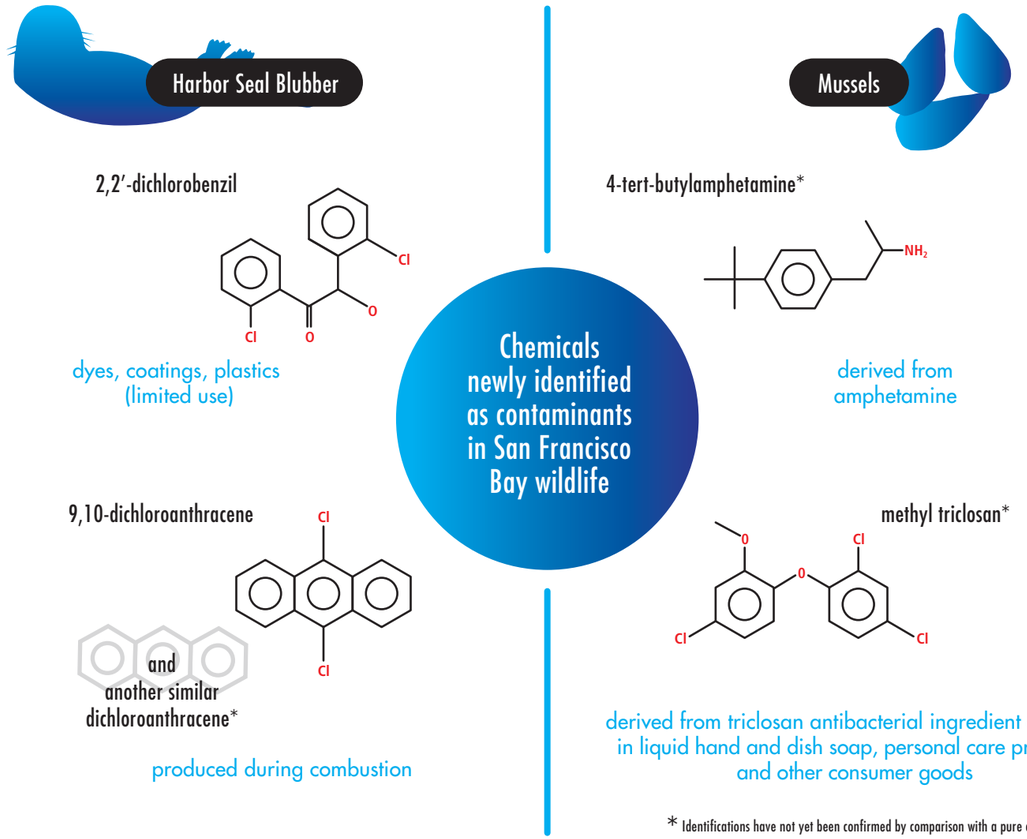
NIST
National Institute of Standards and Technology

NIST's mission is to promote U.S. innovation and industrial competitiveness by advancing measurement science, standards, and technology in ways that enhance economic security and improve our quality of life.

FEW UNEXPECTED CONTAMINANTS DETECTED IN THE BAY

The non-targeted analysis revealed good news:

- Most of the compounds identified in Bay harbor seals and mussels were well-known, "legacy" pollutants, including PCBs, organochlorine pesticides, and chemicals that form when these pollutants break down in the environment. Both seals and mussels also contained some unusual compounds that are related to DDT.
- In seals, this non-targeted approach identified three new contaminants (right). To confirm the identities, pure forms of the chemicals were subjected to the same analytical method. These newly identified compounds were found at very low levels relative to legacy pollutants.
- New contaminants found in Bay mussels include compounds likely derived from the antibacterial ingredient triclosan, as well as amphetamine drugs (right). These identities have not yet been confirmed using pure compounds. These contaminants were also found at very low levels relative to legacy pollutants.
- Naturally-forming, brominated compounds such as "Q1" (2,3,3',4,4',5,5'-heptachloro-1'-methyl-1,2'-bipyrrole) were detected in both seals and mussels, and were most abundant in mussels in less-polluted Bodega Bay. While these natural compounds have been detected worldwide in ocean food webs, little is known about their toxicity.



* Identifications have not yet been confirmed by comparison with a pure compound

It is possible that this non-targeted analysis may have missed other unexpected Bay contaminants. Some may be identifiable but not present in the NIST Mass Spectral Library, while others may provide a signal (chemical mass spectrum or "fingerprint") that cannot be identified. Some contaminants may also build up in Bay species other than the ones examined here.

The detection of these compounds suggests that the original or "parent" contaminants may not always be the most important chemical to monitor in wildlife. The RMP has found the parent amphetamine compound previously, but has not targeted 4-tert-butylamphetamine for analysis. Similarly, while a few studies have characterized triclosan contamination in the Bay, relatively little information exists for methyl triclosan (Klosterhaus et al. 2013). The chemicals identified in this study have been the subject of little or no targeted tissue monitoring elsewhere in the world, and have not been identified in non-targeted studies of wildlife in other areas (e.g., Hoh et al. 2012; Shaul et al. 2015), with the exception of dichloroanthracenes observed in freshwater species exposed to combustion byproducts (Myers et al. 2014). The potential for these newly identified compounds to cause health impacts at current levels is unknown.

Non-targeted chemical analysis is a new and rapidly evolving science, and this study may help others to better identify unknown compounds. Some non-targeted methods can detect greater numbers of new compounds by analyzing relatively concentrated samples. We chose instead to analyze samples in a way that allowed simultaneous measurement of new contaminants and established, "legacy" contaminants at higher concentrations, and provided rough estimates of their relative concentrations. Also, even though the NIST Mass Spectral Library contains information on over 200,000 chemicals, some chemicals in our samples might not yet be present in the library, and identifying a matching chemical is very difficult without this reference information.

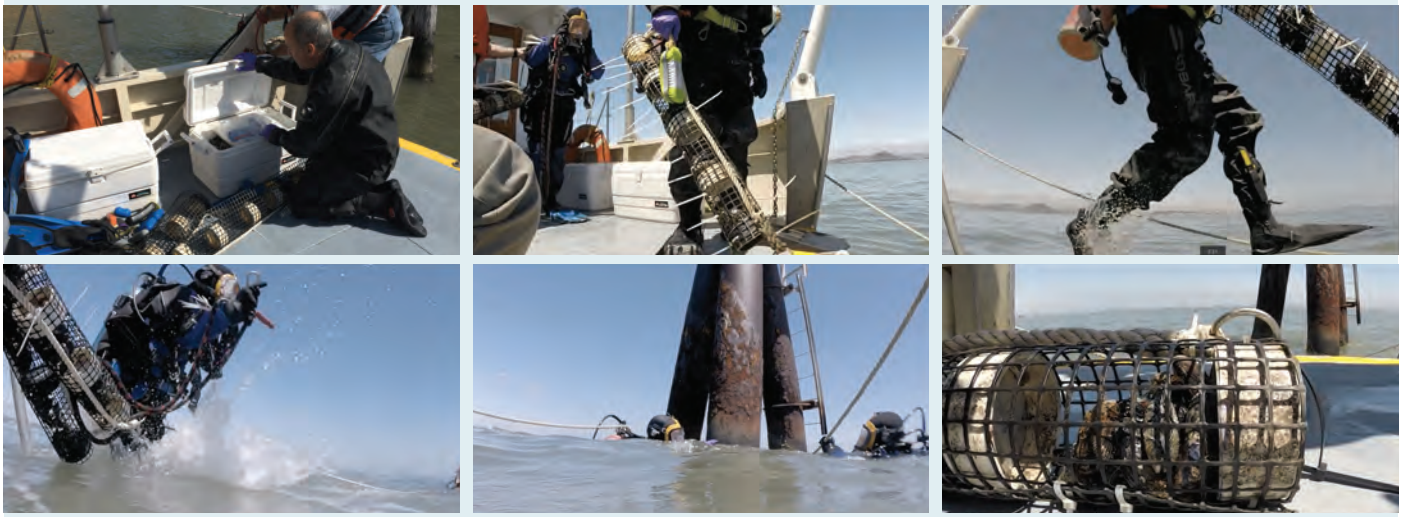
FUTURE INVESTIGATIONS

The RMP's monitoring strategy for contaminants of emerging concern (Sutton et al. 2013) is designed to identify potential threats before they can cause harm to the Bay. This non-targeted investigation of contaminants in two Bay species suggests that many of the highest priority persistent chlorinated and brominated chemicals have already been identified, with key contaminants regularly monitored. According to the RMP's tiered CEC monitoring framework, the five Bay contaminants newly identified via this study may be considered of "possible concern" because more information about toxicity is needed to determine their risk to aquatic life. They may become targets of future monitoring related to specific sources, such as pharmaceuticals and personal care products, or specific pathways, including wastewater and stormwater discharges.

While the analysis described here works well for identifying chemicals with persistent and lipophilic (or "fat-loving") properties, future non-targeted work could also consider techniques that examine water-soluble compounds. Examples include many cleaning and personal care product ingredients, contaminant breakdown products or metabolites, and chemicals that associate with protein-rich tissues like blood rather than fats. Although some of these water-soluble chemicals do not linger long in the environment, they are widely used and may be continuously discharged to the Bay at relatively high levels, potentially leading to prolonged exposure and toxicity to aquatic life.

While the low number and low levels of unexpected contaminants found in this study is good news for the Bay, it is important to consider that we only monitor a small fraction of the multitude of chemicals in commerce today. For many of these chemicals, major information gaps limit the ability to assess their potential risks. The primary challenge for regulators and scientists is managing this ever-growing variety of chemicals to ensure that they do not adversely impact the health of humans and wildlife.

Sampling mussels in South San Francisco Bay, courtesy Paul Salop, Applied Marine Sciences. Images by Tony Hale, SFEI, 2014.



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For more information on Emerging Contaminants in the Bay please visit www.sfei.org and download the RMP's 2013 Pulse of the Bay.

For more information about the RMP please go to www.sfei.org/rmp

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