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.
**Few unexpected contaminants detected in the Bay**

- 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 conform 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.

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-butylnaphthylamine 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, Shaoul 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.

**REFERENCES**


**AUTHORS:**

Rebecca Sutton, Ph.D., SFEI, rebeccas@sfei.org | John Kucklick, Ph.D., NIST