Tracing and apportioning sources of dioxins using multivariate pattern recognition techniques

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Akademisk avhandling

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Abstract
High levels of polychlorinated dibenzo-p-dioxins and polychlorinated dibenzofurans (PCDD/Fs) in edible fish in the Baltic Sea have raised health concerns in the Baltic region and the rest of Europe. Thus, there are urgent needs to characterize sources in order to formulate effective mitigation strategies. The aim of this thesis is to contribute to a better understanding of past and present sources of PCDD/Fs in the Baltic Sea environment by exploring chemical fingerprints in sediments, air, and biota. The spatial and temporal patterns of PCDD/F distributions in the Baltic Sea during the 20th century were studied in Swedish coastal and offshore sediment cores. The results showed that PCDD/F levels peaked in 1975 (± 7 years) in coastal and 1991 (± 5 years) in offshore areas. The time trends of PCDD/Fs in the sediment cores also showed that environmental half-lives of these pollutants have been shorter in coastal than in offshore areas (15 ± 5 and 29 ± 14 years, respectively). Consequently, there have been remarkable recoveries in coastal areas, but slower recovery in offshore areas with 81 ± 12% and 38 ± 11% reductions from peak levels, respectively.

Source-to-receptor multivariate modeling by Positive Matrix Factorization (PMF) showed that six types of PCDD/F sources are and have been important for the Baltic Sea environment: PCDD/Fs related to i) atmospheric background, ii) thermal processes, iii) manufacture and use of tetra-chlorophenol (TCP) and vi) penta-chlorophenol (PCP), iv) industrial use of elementary chlorine and the chloralkali-process (Chl), and vi) hexa-CDD sources. The results showed that diffuse sources (i and ii) have consistently contributed >80% of the total amounts in the Southern Baltic Sea. In the Northern Baltic Sea, where the biota is most heavily contaminated, impacts of local sources (TCP, PCP and Chl) have been higher, contributing ca. 50% of total amounts. Among the six sources, only Thermal and chlorophenols (ii-iv) have had major impacts on biota. The impact of thermal sources has, however, been declining as shown from source apportioned time-trend data of PCDD/Fs in Baltic herring. In contrast, impacts of chlorophenol-associated sources generally increased, remained at steady-state or slowly decreased during 1990-2010, suggesting that these sources have substantially contributed to the persistently high levels of PCDD/Fs in Baltic biota.

Atmospheric sources of PCDD/Fs for the Baltic region (Northern Europe) were also investigated, and specifically whether the inclusion of parallel measurements of metals in the analysis of air would help back-tracking sources. PCDD/Fs and metals in high-volume air samples from a rural field station near the shore of the central Baltic Sea were measured. The study focused on the winter season and air from the S and E sectors, as these samples showed elevated levels of PCDD/Fs, particularly PCDFs. Several metals were found to correlate significantly with the PCDFs. The wide range of candidate metals as source markers for PCDD/F emissions, and the lack of an up-to-date extensive compilation of source characteristics for metal emission from various sources, limited the use of the metals as source markers. The study was not able to pin-point primary PCDD/F sources for Baltic air, but it demonstrated a new promising approach for source tracing of air emissions. The best leads for back-tracking primary sources of atmospheric PCDD/Fs in Baltic air were seasonal trends and PCDD/F congener patterns, pointing at non-industrial related thermal sources related to heating. The non-localized natures of the sources raise challenges for managing the emissions and thus societal efforts are required to better control atmospheric emissions of PCDD/Fs.

Keywords: polychlorinated dibenzo-p-dioxin, polychlorinated dibenzofuran, positive matrix factorization, PMF, principal component analysis, PCA, Baltic Sea, sediment core, PCDD/F, sources, marine, fish, environmental half-live, peak year, peak level, temporal trend, spatial variation, coastal, offshore, chemical fingerprint