CHEM 6001: MSc Departmental Seminar

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Title:
Comprehensive screening of persistent organic pollutants in industrial wastewater using GC and LC cyclic ion mobility-high resolution mass spectrometry

Abstract:
Industrial chemicals play an important role in all facets of modern society; from flame retardants in electronics and furniture to non-stick coatings in cookware and food packaging. However, despite their extensive applications and many desired benefits, chemicals are sometimes released during their lifecycle resulting in deleterious ecological and human health effects. Industrial wastewater effluents are rich in chemical pollutants, both known and unknown as well as legacy and emerging. In this study, a combination of targeted, suspect and non-targeted methods was used to analyze industrial wastewater samples from over 10 sectors in Ontario for halogenated persistent organic pollutants (POPs). Samples were characterized with both gas chromatographic and liquid chromatographic cyclic ion mobility mass spectrometry (GC/LC-cIM-MS) methods.

A novel non-target technique utilizing GC-cIM-MS, capable of isolating unknown per- and polyfluoroalkyl substances (PFAS) and other halogenated compounds based on the ratio of their mass and collision cross section (CCS) values, was recently developed in our group. When the combined dataset from GC-cIM-MS analysis of the wastewater samples was subjected to this novel filtering strategy, c. 344 potentially brominated, chlorinated or fluorinated chemical species were identified from the ~27,000 initially present. Following the application of a previously developed script tool (R code) and manual investigation, 44% of these ions were confirmed to be halogenated. Five compounds belonging to frequently detected classes were identified by suspect screening (e.g. brominated diphenyl ethers; BDEs, polychlorinated biphenyls; PCBs, organophosphate flame retardants; OPFRs and perfluorosulfonamides; PFSMs). Confirmed suspects represented a mere 14% of the halogenated ions (9% intensity) indicating that 86-91% of the halogenated content is truly “unknown”. A more in-depth look at these unknown ions revealed 19 suspected PFAS including 2 classes that were detected in the environment for the first time. Targeted analyses showed
that legacy pollutants such as BDEs, PCBs, polychlorinated naphthalenes (PCNs) and organochlorine pesticides (OCPs) were either not detected or present at low levels.

For characterization via LC-cIM-MS, wastewater samples were extracted using a tandem solid phase extraction (SPE) technique with weak anion exchange (WAX) and weak cation exchange (WCX) cartridges. LC-cIM-MS experiments revealed the presence of ~50000 chemical species across all samples and filtering based on CCS and m/z yielded 937 likely brominated, chlorinated or fluorinated compounds. Further data reduction and mass defect analysis led to the discovery of almost 300 potential PFAS by NTS. Only half of them were matched to a suspect screening database implying that the chemical identities of several PFAS in the Ontario environment are unknown. Multiply charged ions formed during electrospray ionization were found to be non-problematic when filtering data using CCS and m/z. As such, this novel way of data prioritization is a promising approach for PFAS discovery in complex samples when analyzed by LC-ESI-IM-MS. GC-APCI-IM-MS was also found to be a complementary technique for PFAS discovery since comparable numbers were identified using the same workflow.