Optimising analytical methods for chlorinated paraffins to evaluate their levels in Australia

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Abstract

Chlorinated paraffins (CPs) are polychlorinated *n*-alkanes typically with a chlorine content between 30 and 70% (w/w). They are used in many applications such as flame retardants or lubricants in plastics, paints, sealants and metal cutting fluids. Based on their carbon chain length, they are categorised into three groups: short-chain (C_{10-13}, SCCPs), medium-chain (C_{14-17}, MCCPs) and long-chain CPs ($C_{>17}$, LCCPs). This current work was initiated in response to rising concerns (i.e. increasing production, use and consequent potential hazard to the environment and human health), lack of data (e.g. no peer-reviewed data on their environmental levels in the Southern Hemisphere) and the challenges that arise with their determination. Hence, this thesis aimed to advance the capabilities for analysis of CPs to allow a preliminary evaluation of their levels in Australia.

The results of the first literature review confirmed that CPs are high production volume chemicals (1 million tonnes/yr in China alone), with persistent, bioaccumulative, long-range transport and toxic potential but for which accurate, reliable information on their environmental levels, fate and effects is scarce. Studies have mainly focused on SCCPs, with few also including MCCPs and LCCPs. The results of the second review confirmed that analysis is still challenging, primarily because of the lack of suitable standards, their low response in various detection systems and highly complex nature (>10,000 congeners), resulting in chromatographic separation difficulties between CPs and also from other organohalogen compounds. Concentrations are typically reported per CP group (i.e. ΣSCCPs, ΣMCCP and ΣLCCPs). Different analytical methods have been developed, with varying success, and no standardised method is available. Large differences in results between laboratories were found in four interlaboratory studies (ILS), although this difference decreased in the 2016 ILS.

A comprehensive two-dimensional GC with a micro-electron capture detector (GC×GC-μECD) technique was developed and combined with a quantification method that utilizes the linear relationship between the response and chlorine content. Despite the use of GC×GC, seperation of congeners was largely not achieved, although differentiation was observed for some lower individual chlorinated CPs. In addition, an existing chlorine-enhanced atmospheric pressure chemical ionisation time-of-flight (ToF) MS technique was adapted and also combined with the same quantification method. The latter technique was found most suitable as it produced satisfactory results in several ILS rounds, can detect all three CP groups, and achieves the MS resolution needed for differentiation between congener groups (21,000 resolution).

This technique allowed a quantification and evaluation of CPs levels in Australia. More specifically, in samples with potentially increasing complexity, including sewage sludge from 15 waste water treatment plants, extracts of passive air samplers deployed for one year at 15 sites covering different land-use, and stratified pooled serum samples from

the Australian Human Biomonitoring Program covering different collection period and age groups.

LCCPs were only found in detectable levels in sewage sludge (<MDL-960 ng/g dry weight, dw). This sludge also contained MCCPs at levels up to 3 times those of SCCPs (both <MDL-low µg/g dw). Estimated concentrations in air (primarily as vapour phase) were of the order of low ng/m^3 for SCCPs and MCCPs, with highest concentrations found around metropolitan areas. SCCPs and MCCPs were also detected in pooled serum samples from the general Australian population (<MDL-910 ng/g lipid weight), with an increasing trend of MCCPs between 2007 and 2015. While no relationship with age groups was identified, highest levels were found in the oldest (46-60 years) and youngest cohorts (<4 years).

Overall, these preliminary data on CPs from sewage sludge, air and serum suggest that concentrations are similar to those in the few reported studies from Europe and North America but lower than data from China, the world's largest CP producer. Considering their main applications in indoor materials in Australia, and their increasing levels over recent years in humans, future studies should aim to further improve analytical capabilities so that more accurate data can be produced. Improvements may include the availability of more standards together with better separation and analysis of carbon chain length and chlorine content or congener groups rather than based on groups. Current rapid developments in instrumental techniques (e.g. HRMS Orbitrap and ToF, possibly in combination with GC×GC etc.) bring a standardised, specific analytical method within reach, and more improvements are expected. With these continued developments, studies of uptake, distribution, degradation and elimination potential in humans and wildlife become feasible.