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QUANTIFICATION OF SORT-, MEDIUM-, AND LONG-CHAIN CHLORINATED PARAFFINS IN AUSTRALIAN SEWAGE SLUDGE BY APCI-QTOF-HRMS

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Introduction

Chlorinated paraffins (CPs) are complex mixtures of various carbon chain lengths and chlorine atoms and presently produced in high volumes (e.g. up to 1 million tons year−1 in China alone (WCC, 2014). These compounds are persistent in the environment , and have been found in many environmental compartments including remote areas (Reth et al., 2006). In particular CPs with a carbon chain lengths between 10 and 13, so-called short-chained CPs (SCCPs), are under scrutiny, as these compounds have a high bioaccumulation potential (Houde et al., 2008, Stevens et al., 2003) and are highly toxic to aquatic organisms (Shaw et al., 2010). They are, therefore, classified as substances of high concern, listed as key compounds for monitoring in several legislations or guideline and current candidates to be designated as persistent organic pollutants (POPs) under the Stockholm Convention. In case of the longer chained CPs, medium- (C14-C17) and long- (≥C18) chained, relevant information on their presence, concentration and fate in the environment is still insufficient to facilitate classifications. This lack of information due to significant limitations regarding the reliability of analytical methods to identify and quantify these compounds. Reliable CP exposure data is needed, particularly in regions where the CP levels and fate are still unknown. In Australia, for example, limited data on CPs exists and the capability of analyzing CPs is lacking. Australia is among one of few countries that still manufactures M/LCCPs (e.g. Orica, Melbourne) with ongoing investments for expansion of CP manufacturing facilities (Orica, 2015). Major releases of CPs in Australia are thought to be from production, both from spills or facility wash-down, and from industrial usage, either from improper disposal of used metalworking lubricants or carry-off from work pieces (NICNAS, 2004). Such releases can result in accumulation of CPs, either directly or through sewage treatments plants (Zeng et al., 2012). As CPs are emerging POPs, determining the levels of CPs near suspected sources (i.e. sewage treatment plants) would facilitate a first understanding on the release, presence and potential risks of these compounds. Therefore, with this study, CPs were determined in sewage sludge samples from various sewage treatment plants (STPs) in order to allow a first evaluation of CP levels in Australia.

Materials and methods

Samples

Pooled (eight subsamples at each STP) sewage sludge samples were collected in 2014 at fifteen different STPs in Australia. The STPs were located in five of the eight states and territories of Australia, servicing populations of between 25,000 and 600,000 people, representing a combined population of approximately 2.5 million people (over 10% of the Australian population).

Quality control

For quality assurance purposes, two blanks, one duplicate sewage sludge sample and three recovery standards were analysed alongside the 15 sewage sludge samples. Matrix interferences were investigated by spiking four of the analysed sewage sludge samples with environmentally realistic concentrations of three SCCP, three MCCP and two LCCP mixtures in the concentration range of 120 -160 ng absolute. The extracts were analysed before and after spiking, and by subtracting the contractions of the CPs detected in the spiked extracts from the non- spiked extracts the recovery was calculated. Variability of the APCI-qTOF-HRMS was investigated by an 8-fold measurement of one of the cleaned sewage sludge samples. Background interferences were investigated before starting with the sewage sludge samples. All solvents and compounds used for the extraction and cleanup were screened for the presence of CPs.

Calibration dilutions were prepared from the eight CP stock solutions for the SCCPs, MCCPs and LCCPs. The lowest concentration of the calibration curve, 0.1 ng/μL, corresponds to the LOQ (10 times the signal/noise) for the SCCPs and for both the MCCPs and the LCCPs the LOQ could easily be lowered by a factor of 10. However all S/MCCPs levels detected in the sewage sludge samples we above 0.1 ng/μL and above 0.05 ng/μL for the LCCPs.

Measurements of the CPs
Measurements of the CPs in the Australian sewage sludge samples was performed with the slightly adopted analytical method recently developed by Bogdal et al. (2015). Without using an analytical column 10 μl of the cleaned sewage sludge extract was directly injected into the quadrupole time-of-flight high resolution mass spectrometer (qTOF-HRMS) (Triple TOF 5600 AB/Sciex, Concord, Ontario, Canada) running in the negative atmospheric pressure chemical ionization (APCI) mode.

Deconvolution and quantification
Quantification of the S/M/LCCPs was based on a mathematical algorithm recently applied by Bogdal et al., 2015 for the quantification of CPs in various environmental matrices. The CP pattern measured in the analyzed sample was reconstructed into a linear combination of patterns of CPs of the technical mixtures using an deconvolution algorithm. The reconstructed CP pattern was compared to the initial CP pattern of the analyzed sample to determine the goodness of fit (R2)

Results and discussion
An example of the deconvolution whereby the CP pattern measured in the sludge sample was reconstructed into a linear combination of patterns of CPs of the three technical mixtures is given in Figure 1 for the MCCPs in sewage sludge S1.

CP levels in Australian sewage sludge
MCCPs were the dominated CPs and were detected in all sludge samples with levels ranging from 542 to 3449 ng/g dw. In eight of the fifteen samples SCCPs were detected with levels from <60 to 1421 ng/g dw. The LCCPs levels were comparable to the SCCP levels (250-960 ng/g dw). Nine of the fifteen LCCPs levels were reported as tentative values due to a $R2 < 0.5$. The results of the total CP (sum of SCCPs, MCCPs and LCCPs) detected in sewage sludge collected at the various STPs around Australia are illustrated in Figure 2. Highest total CP levels (5880 ng/g dw) were detected in sewage sludge from location S4 in the Northern Territory of Australia. However, elevated levels were also detected in South-East Queensland (location S2; 4416 ng/g dw), South Australia (location S9; 4737 ng/g dw) and Western Australia (location S13; 4567 ng/g dw).

To our knowledge this is the first time that CPs were detected in Australian sewage sludge. The SCCP and MCCP levels observed in the Australian sewage sludge were comparable with the SCCP and MCCP levels observed in Swedish sewage sludge collected between 2004 and 2010 (median SCCPs; 1100 ng/g dw, median MCCPs; 3800 ng/g dw) (Olofsson et al., 2012), and Swiss sewage sludge collected in 2007 around Zürich (SCCP; 135-581 ng/g dw, MCCPs; 1070-8960 ng/g dw) (Bogdal et al., 2015). Maulshagen et al. (2003) measured only SCCPs (75-859 ng/g dw) in sewage sludge from Germany collected in the early 2000s, which were also comparable with the SCCP levels observed in our study. Higher SCCP levels were found in municipal and industrial sewage sludge in China with levels from 0.80 to 52.7 ug/g dw (Zeng et al., 2012). The highest CP levels were found in municipal and industrial sewage sludge from the UK (Stevens el al., 2003) with SCCP levels ranging from 6.9-200 μg/g dw, MCCPs levels from 30-9700 ng/g and by Nicholls et al., (2001) with sum SCCP and MCCPs levels ranging from 1.8 to 93.1 μg/g dw. These levels were up to 200-fold higher than those reported in our study. In two studies (Stevens et al., 2003 and Zeng et al., 2012) no correlation was observed between the CP concentration and the STP location, treatment capacity and serving population.

Carbon and chlorine homologue groups of CPs in sewage sludge
The carbon and chlorine homologue groups for the SCCPs, MCCPs and LCCPs in the Australian sewage sludge are calculated an example for the MCCPs. Between the sewage sludge samples collected at different locations in Australia similar carbon and chlorine homologue patterns were observed for the SCCPs, MCCPs and LCCPs. The calculated chlorination degree for the sewage sludge ranged 58-63% for the SCCPs, from 54-58% for the MCCPs and from 40-48% for the LCCPs. This finding was consistent with the study of Zeng et al. (2012) who studied the SCCP composition in various sewage

sludge samples from China and observed similar carbon and chlorine homologue among different STPs. However, the SCCP homologue pattern observed in the sewage sludge from China was different than the pattern observed in the Australian sewage sludge. In the Chinese sludge the SCCP homologue groups were dominated by C11 (37%) followed by C10 (27%) and C12 (23%) with Cl7 (37%) and Cl8 (29%), whereas in our study the SCCP homologue groups were dominated by C13 (51%) followed by C12 (24%) and C11 (18%) with Cl7 (37%) and Cl6 (26%). Zeng et al. (2012) only detected some MCCPs in sewage sludge from China at low levels, which is in contrast with our study were MCCPs were dominant. These findings indicate that the CP composition of the technical SCCP mixtures used in China are different than used in Australia, and MCCPs are probably used in less amounts in China compared to Australia. The carbon homologue group pattern for the SCCPs and MCCPs in the Australian sewage sludge were more comparable with the pattern found in sewage sludge from the UK and Switzerland (Stevens et al., 2003, Bogdal et al., 2015), which were also dominated by C11-C13 for the SCCPs and C13-C14 for the MCCPs.

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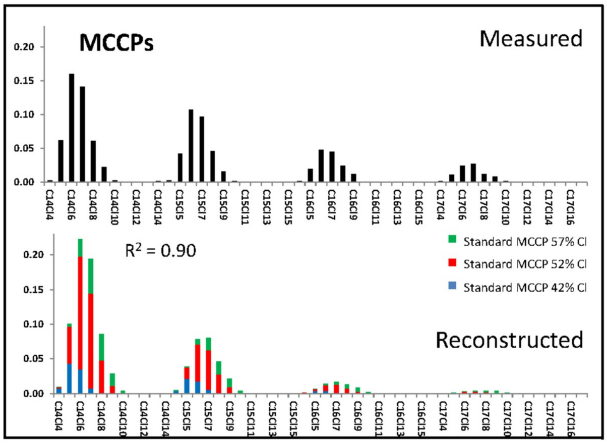

Figure 1.Example of the measured and deconvoluted congener pattern of MCCPs in the sewage sludge sample S2. CP levels in Australian sewage sludge.

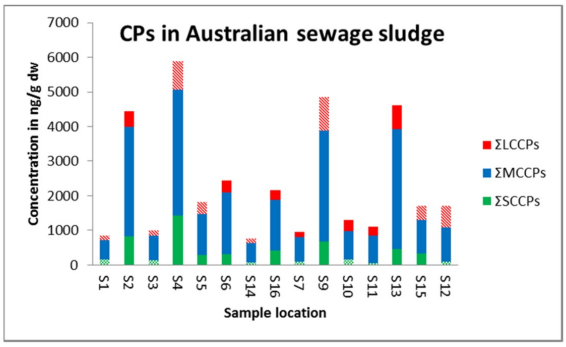

Figure 2. Total CP concentrations in ng/g dry weight measured in the sewage sludge samples from Australia. Red stripes are semi-quantitative values of LCCPs. SCCP values <LOD are marked with striped green blocks.