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Editorial

A new focus on legacy pollutants: Chlorinated Paraffins (CPs) and Polychlorinated Naphthalenes (PCNs)

With volume production spanning almost a century, chlorinated paraffins (CPs) are industrial chemicals that are of increasing concern to the environment and to human health. Polychlorinated naphthalenes (PCNs) are legacy contaminants that occur in the environment, food chains and human tissues and contribute to the burden of dioxin-like effects such as carcinogenicity, hepatotoxicity, teratogenicity, embryotoxicity, etc. In recognition of these concerns, and following structured risk assessments, short-chain CPs (SCCPs, C_{10}-C_{13}) and PCNs have recently been listed for elimination, in Annex A of the Stockholm Convention. This followed an earlier listing for SCCPs as a priority hazardous substance for control under the European Union (EU) Water Framework Directive. The importance of these developments has not been lost on scientists who have researched an increased volume of new information in these fields. The Dioxin 2018 symposium in Krakow devoted a full day to the dissemination of the latest findings, with 18 oral presentations and 8 posters covering analytical aspects, occurrence in the environment, materials and food, and the toxicological effects of these pollutants.

Chemically, CP products are complex isomeric mixtures of several thousands of individual compounds having carbon chain lengths ranging from C_{10} to C_{28}. Reliable analytical determination is one of the most intractable barriers to the accurate measurement of CP occurrence, a recognised drawback that was illustrated in the inter-laboratory studies by Krätschmer and Schächtele (*Chemosphere* 234, 252-259). The issue is compounded by the ambiguity in defining CP analytes – a necessary first step in reliable analytical determination.

The Stockholm convention lists SCCPs in its annex, but this relates to commercial products. An innumerable selection of different "SCCP" products of varying compositions were manufactured globally, and the environmental legacy of widespread historical usage that is observed in environmental media is a complex integral of these mixtures. This integral is further modified by transformative processes such as modification during usage, selective rates of evaporation, photochemical and microbial degradation (Heeb et al. *Chemosphere* 226, 744-754), etc. Reported occurrences in food of animal origin (Krätschmer et al., *Chemosphere* 227, 630-637; Labadie et al., *Chemosphere* 223, 232-239; Jiang et al., *Chemosphere* 229, 358-365) imply additional transformation through metabolic processes which further enhance the complexity of the observed profiles. It is therefore unsurprising that the profiles for SCCPs (and other CPs) observed during analysis do not correspond to individual commercial products, and perhaps more relevantly, to analytical standards.

In general, early insights into the toxicological effects of CPs were based on the use of standard mixtures that reflected the commercial products. As CP residues in real foods and animal tissues have never been completely characterised (but are clearly modified integrals of different mixtures), it would prove difficult for a human exposure based risk assessment to correlate occurrences to the reported effects. Another pressing issue is that of current CP manufacture and use. The most recent literature suggests that shining a regulatory spotlight on SCCPs, has resulted in a shift to the use of medium- (MCCPs, C_{14}-C_{17}) and long-chain CP (LCCPs, > C_{18}) mixtures. Despite some investigations on MCCPs within the EU and North America there is still a lower level of knowledge on the toxicity of these products, particularly the LCCPs. In the long term, regulation of SCCPs on their own is unlikely to address potential risks arising from these other mixtures and their breakdown products. Further, CP mixtures are known to contain other chlorinated contaminants as by-products, such as polychlorinated biphenyls (PCBs), PCNs and chlorinated dioxins and furans (PCDD/Fs), and may also give

rise to these as by-products during combustion (Matsukami and Kajiwara *Chemosphere* 230, 164-172). Clarification is required as to whether the toxicological effects that have been reported were directly attributable to CPs, and were not influenced, at least in part, by the presence in the test mixtures of such by-products which show more sensitive toxicological endpoints than CPs.

As the assessment of exposure is an integral component of human health risk assessment, a useful first step would be to characterise the CP profiles observed in foods as these are expected to constitute an important exposure pathway (as observed with other similar halogenated contaminants). This should include food packaging materials which have also been shown to contain CPs (Wang et al., *Chemosphere* 225, 557-564). Recent advances in instrumentation that allow qualitative homologue group characterisation of CP occurrence may prove a useful tool in the identification and mapping of groups that predominate in "typical" profiles for different food types. As many household and workplace materials are known to contain CPs, a similar approach to characterising these occurrences would yield information on other possible exposure pathways.

This characterisation would have two immediate advantages – it would provide a more focussed approach to toxicological studies by allowing the targeting of relevant (occurring) homologue groups and help identify groups that elicited more potent responses, and also provide direction to the analytical effort by indicating a qualitative definition of the analytes. The characterisation would also allow the formulation of more relevant standard CP mixtures that correlate to a greater extent with observed profiles, thus aiding quantitative determination. In this context specific single chain length mixtures are currently being synthesised and characterised (Sprengel et al., *Chemosphere* 228, 762-768). The discrepancies observed in the most recent inter-laboratory comparisons (Krätschmer and Schächtele, *Chemosphere* 234, 252-259) underline the requirement for representative standards, but also

highlight the need for a robust and harmonised approach to the quantitation procedures applied to the identified CP homologue groups. Until there is progress on these issues, the expression of CP concentrations as total CP (either combined, or if analytical advances allow, speciated into short, medium and long chain) would be a sensible interim measure, allowing the generation of much needed occurrence data and laying the groundwork for future control and regulation efforts.

For PCNs, information from emerging research continues to define the issues surrounding these contaminants. An increasing amount of recent literature that speciates PCN occurrences in environmental media and foods, by individual congeners, provides further information on the persistence and fate of these chemicals, decades after production ceased. The historical and continuing human exposure arising from PCN occurrence in foods and dietary supplements (Falandysz et al., *Chemosphere* 231, 240-248; Zhihua et al., *Chemosphere* 230, 559-566) underlines the persistence of PCN congeners and the enduring legacy of this contamination in marine regions from where current fish supplies continue to be sourced. New insights into the environmental behaviour and chemistry of individual congeners help to explain observed patterns in environmental media and the resulting occurrence, particularly in marine products.

Relative to CPs, the analytical determination of PCNs is at an advanced level with reliable measurement of individual congeners allowing behavioural studies of selected compounds. It is particularly encouraging to see new work that adds to the body of toxicological insights into PCN disposition in animal tissues and the effects on reproductive processes (Kilanowicz et al., *Chemosphere* 226, 75-84; Kilanowicz et al., *Chemosphere* 228, 577-585). The dioxin-like behaviour of some PCN congeners has been recognised for several years, but the identification of other toxicological effects such as disruption to haemostasis parameters such

as clot formation and fibrinolysis, adds to the growing evidence of requirement for future regulatory action.

Although the majority of the work presented at Dioxin 2018 included targeted studies with specific outcomes directed to ultimately investigating the environmental, human exposure and health effects of PCNs and CPs, it is important that this collated dissemination is viewed within a wider context. Both of these contaminant classes are mass produced anthropogenic products that have seen, often unrestricted, usage for the best part of a century. However, the volume of pertinent literature is relatively small in comparison to other similar contaminants such as PCBs, PCDDs/Fs and flame retardants. In the case of CPs, the combination of a lack of widespread recognition combined with the real difficulty with analytical access is a clear factor. For PCNs, the similarity of chemical behavior and effects to the more widely produced PCBs has overshadowed the potent toxicological response of these chemicals. However, in the light of the current re-evaluation of PCB toxicity, particularly PCB 126, the contribution of PCNs to the cumulative dioxin-like toxicity could potentially become more significant, engendering more interest in the regulation of these contaminants as well.

The inclusion of both these classes of contaminants within the Stockholm convention listing has been followed by regional interest, e.g. within the EU, which has set up specific working groups to address human exposure through the occurrence of these chemicals in food. Both of these measures, provide direction to the task for scientists to facilitate and generate information that will ensure that the remaining challenges and risks to human health are characterized and are available for policy making.

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