INNOVATION IN THE ASSESSMENT OF RISKS OF PBTs AND POPs

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Introduction

Global and regional chemical regulations have identified a limited number of substances which are considered to have properties requiring specific attention in managing their risks, so-called PBTs and POPs. Some regulators consider these substances so inherently dangerous that it becomes difficult if not impossible to assess their risks. For example the REACH Regulation (Registration, Evaluation, Authorisation and Restriction of Chemicals) covers nearly all industrial chemicals, requires the assessment of their risks, the identification of appropriate risk management measures and their safe uses. Under this regime unsafe uses are unregistered and therefore the substance is not allowed on the market for this use. Nevertheless, for SVHCs (Substances of Very High Concern), including PBTs and POPs, an additional regulatory approach has been developed with specific provisions. These restriction and authorisation approaches follow mainly a hazard-based rather than a risk-based assessment.

Other legislation, such as the Stockholm Convention, requires an assessment of the risks of POPs. For example the risk profile (Annex E) of this Convention requires an evaluation of substances to be identified as POP, underpinning that the substance is ‘likely, as a result of its long-range environmental transport, to lead to significant adverse human health and environmental effects’. This is clearly a requirement to evaluate the risks, but in practice often a precautionary approach mainly focussing on the hazardous properties is followed.

However, from a scientific perspective, there is no reason why the risks of substances with PBT or POP properties could not be assessed and the developments in (eco-)toxicology in recent decades have been significant. Unfortunately, regulations have not kept pace with these developments, and thus risk missing opportunities for improving efficacy of managing risks of chemicals. Such risk assessments are likely to be more complicated as compared to substances not having these properties and therefore will require more data. This paper recommends to adapt current regulations on PBTs and POPs to include the latest scientific developments, in order to come to a more effective and innovative evaluation of the risks of such substances. The developments in environmental sciences have enabled new methodologies and provided knowledge around two main issues: (1) the identification of PBTs or POPs and (2) their risk assessment[1]. The usefulness and applicability of these new approaches will be illustrated using the case of chlorinated paraffins, in particular short-chain chlorinated paraffins (SCCP).

Results and discussion:

Chlorinated paraffins are a class of substances consisting of a saturated alkane chain where some of the hydrogen atoms are replaced by chlorine. They are produced by the reaction of saturated alkanes with chlorine and result in the generated substance being a complex mixture of individual species. Three different feedstocks, varying by chain length are used in the manufacture of CPs. This results in three classes of substance: long-chain chlorinated paraffins (LCCPs) with a carbon chain length more than 17, medium-chain chlorinated paraffins (MCCPs) with a carbon chain length of 14 to 17 and short-chain chlorinated paraffins with a carbon chain length of between 10 and 13. Additionally the substances are characterised by degree of chlorination, expressed as percentage by weight of chlorine. Thus SCCPs 50% are a mixture of alkanes with a chain length of 10-13 chlorinated to 50% by weight chlorine, which for C_{13} means an average molar ratio of 2.6:1 for C:Cl and an average empirical formula of $C_{13}H_{23}Cl_5$. Chlorinated paraffins have several uses, mostly as plasticizers and flame-retardants in PVC and rubber in heavy-duty applications, such as in mine conveyor belts. Typical commercially available SCCP products are chlorinated in the range of 45 to 70%. They have been used for over fifty years in specialised industries due to the inertness of the substance and the flame-retardant properties.

The European Union has identified short-chain chlorinated paraffins as having PBT properties based on measured data and combined with modelling. The measured $\log K_{ow}$ varies with chlorination level, but between chlorination levels of 49-71% the $logK_{ow}$ ranged from 4.39 to 5.37 based on limited data. Studies have shown that the substances will tend to persist in the environment, though results depend heavily on the degree of chlorination. SCCPs with higher levels of chlorination tend to show far higher levels of persistence than SCCPs of lower chlorination. Additionally, for bioaccumulation, using the measured $logK_{ow}$ values, a BAF fish model showed BAF of over 5000 for all possible congeners, indicating that the substance initially meets the criterion for bioaccumulation. Thus SCCPs meet the criteria for PBT and vPvB under REACH. They have been identified as POPs under the UN-ECE POP protocol, but the Stockholm Convention applying a more rigorous scientific evaluation has repeatedly failed to identify SCCPs as POPs. The current risk profile does not demonstrate that the substance is likely to pose a risk of causing adverse affects to human health and the environment. In addition, more recent work has challenged the persistence data on SCCP 50% chlorination using an enhanced OECD301 closed bottle test. Earlier tests had difficulty in finding a method appropriate to the hydrophobicity of the substance, and therefore gave conservative results. The results of the ready biodegradation test with a river water inoculate are shown in Figure1.

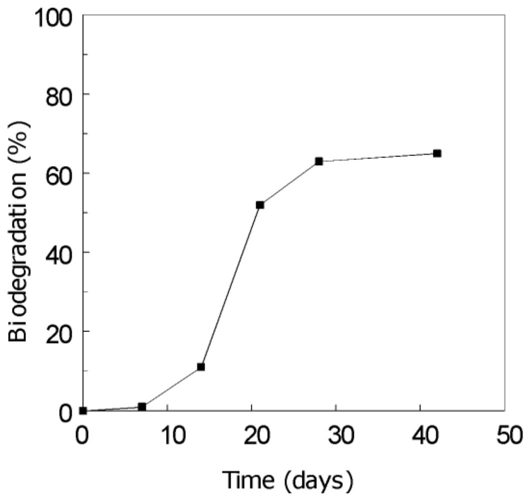

Figure 1. Biodegradation of SCCP 50% chlorination in an enhanced OECD301 closed bottle test.

The biodegradability of MCCPs has recently been investigated more extensively, confirming the rapid biodegradation in enhanced closed bottle tests and applying other techniques such as chloride mass balance measurements in sequencing batch reactors[2]. Components with higher levels of chlorination also degrade, but gradually at a reduced speed which may be due to the presence of chlorine atoms bound to adjacent carbons on the chain. Results so far suggest that MCCPs at levels of chlorination up to 50% are readily biodegradable.

Due to the PBT properties, SCCPs should be made subject to restrictions under the EU REACH process in order to rigorously control emissions into the environment, in combination with other regional controls. As SCCPs have met the criteria for listing as a PBT substance, a detailed assessment into the risks and exposures posed by the substance should be conducted. At a global level work has been ongoing as part of the Stockholm Convention process under the POP Review Committee process. Table 1 (adapted from the UNEP POP Review Committee draft risk profile)[3] provides the exposure for multiple species at proximate, regional and distant ranges from sources of the substance. As the table shows, the substance is measured in species distant from the source of the substance, due to long-range transport and bioaccumulation. However, the levels at which the substance is measured are one or more orders of magnitude below the relevant toxicity value, except for local pelagic fish. This could trigger local management options, but it also indicates that at present SCCPs are unlikely to lead to significant adverse environmental or human health effects, and justification for global action on this substance is unwarranted.

	Receptor	Exposure concentration	Relevant toxicity value
Local	Fish-eating mammals (otter)	2.63 mg/kg ww	1000 mg/kg food ww
	Pelagic invertebrates	44.8 ng/L	8,900 ng/L
	Pelagic fish	2.63 mg/kg ww	0.79 mg/kg ww
Regional	Pelagic invertebrates	1.19 ng/L	8,900 ng/L
	Pelagic fish	0.123 µg/g ww	0.79 mg/kg ww
	Benthic invertebrates	0.41 mg/kg dw	35.5 mg/kg dw
	Benthic fish	0.037 mg/kg ww	0.79 mg/kg ww
Remote	Benthic invertebrate	0.0176 mg/kg dw	35.5 mg/kg dw
	Arctic ringed seal	0.52 mg/kg ww	100 mg/ kg ww.

Table 1. Measured exposures of various species to SCCPs in sites local, regional and distant from sources of SCCPs[3].

Substances with some PBT and POP properties pose major challenges to identification and to risk assessment methodologies, due to the difficulties in dealing with a variety of substances with different uses and physical characteristics within those definitions. In the case of SCCPs the high hydrophobicity has meant that care must be taken in carrying out and interpreting biodegradation tests, as the OECD tests are primarily designed for water soluble substances. When evaluating risks, secondary poisoning adds a dimension of complexity to many of these substances.

It has been shown in many case studies that the environmental uses of PBTs and POPs can be assessed, though the amount of information required is larger than for non-PBTs. Current knowledge recommends a series of steps to be followed in the risk assessment of PBTs, depending on whether the approach begins from a wide ranging screening process or from potential identification of a single substance. When substances are identified as being a potential PBT, either through screening or through modelling, further information is required to provide a definite answer using a weight of evidence approach. If the PBT status is confirmed, then the potential impact must be examined to assess the likelihood of significant impact on health or the environment. In the case of MCCPs, initial screening flagged components of the substance as possibly PBTs. However, further testing showed that there are no components that meet the PBT criteria.

The results indicate that the level of chlorination is an important factor in the biodegradation of the mixture, with lower chlorinated components biodegrading rapidly and completely, while at higher levels more recalcitrant metabolites will occur. For SCCPs, it has been initially shown that the substance does meet the criteria for listing as a PBT but recent information on SCCPs-50% chlorination may challenge this conclusion. Additionally, recent studies of historical SCCP residues in a natural lake bed may support this, as the older samples show metabolites of higher chlorination, which would be expected if the lower chlorinated components biodegrade rapidly[4]. The risk assessment of SCCPs shows that the effects are most pronounced locally, and that the substance is unlikely to cause adverse effect to the environment and human health. Restriction of the uses to control environmental release and occupational exposure should be considered to control the risk of SCCPs.

Conclusions

The identification of new generation PBTs and POPs is proving to be more difficult than with the first generation 'dirty dozen'. This is because the substances being addressed now are more borderline cases, leading to greater uncertainty in the meeting of specific criteria. SCCPs are an excellent example of the difficulties that arise closer to the borderline. Additionally, the science of risk assessment has made tremendous strides over the past decades, including in the risk assessment of PBTs and POPs, which is often not recognised within the regulatory framework. The identification of PBT/POP substances has benefited from the use of new methodologies, especially with regard to the hydrophobic nature of the substances, including SCCPs. It has been shown that the biodegradation of chlorinated paraffins is a complicated issue that has not been well understood in the past, leading to conservative decision making. New testing indicates that the level of chlorination is critical in the biodegradation of SCCPs, which may lead to further discussion on this issue. New advances in risk assessment show that it is possible to screen for and risk assess PBT and POP substances, while recognising that the process is more difficult than for non-PBT substances and requires a greater level of information and testing.

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