EMISSIONS OF CHLORINATED PARAFFINS IN STOCKHOLM: A CHEMICAL FLOW ANALYSIS STUDY

Ulrika Fridén[1], Louise Sörme[2] and Michael S. McLachlan[1]
[1]ITM, Stockholm University, SE-10691 Stockholm, Sweden; [2]City of Stockholm Environment and Health Administration, PO Box 8136, SE-104 20 Stockholm, Sweden

Abstract
Chlorinated paraffins are currently under consideration for classification as POPs. They have been used for many decades, particularly in industrial lubricants and different building materials, but there is very little information available on their inventories in the technosphere and their emissions to the environment. In this study a chemical flow analysis was conducted for the city of Stockholm with the goals of estimating the current emissions of CPs to different environmental media. The results indicate that approximately 0.5 tonnes of CP are released to air and water in Stockholm annually, with paints and sealants being the major sources. The vast majority of the CPs are expected to end as solid waste, but there are uncertainties regarding their ongoing leakage into the environment.

Introduction
Chorinated paraffins (CPs, also called polychlorinated *n*-alkanes or PCAs) are complex mixtures containing thousands of different isomers. The commercial mixtures are classified according to their carbon chain length into short chain CPs (SCCPs, C_{10}-C_{13}), medium chain CPs (MCCPs, C_{14}-C_{17}) and long chain CPs (LCCPs, C_{18}-C_{30}). These mixtures, in particular SCCPs, have attracted increasing interest among European regulators within the last 10 years. SCCPs have been the subject of a detailed risk assessment, while an evaluation of MCCPs is in progress. Both SCCPs and MCCPs have been found to be persistent and to bioaccumulate. CPs have a low acute toxicity, but SCCPs are classified as toxic to aquatic organisms.[1] Furthermore, carcinogenic effects in rats and mice have been observed.[2, 3] Currently, CPs are under consideration as a "new" persistent organic pollutant (POP). They have been recently included in the regulatory programme of the European Community, and they have been proposed for inclusion as a new POP in the UNECE Convention on Long-range Transboundary Air Pollution (CLRTAP).

Despite the progressed state of regulation of CPs, there is very little information available on their sources to the environment. Without this information, it will be difficult to reduce the environmental levels of CPs, even if they are designated as POPs. In this study we did a chemical flow analysis study of CPs in the city of Stockholm with the aims of identifying the most important sources of CPs to the environment and evaluating the consistency of estimates of CP release compared to measurements of CP levels in sewage sludge and ambient air.

Methods
The use of CPs within the city of Stockholm was estimated based on information on chemical usage in Sweden extracted from the Product Registry of the Swedish National Chemical Inspectorate.[4-8] The use information was sorted according to the product classes / uses: paints; sealants; plastics and rubber; lubricants; other. The uses for each product class for Sweden were scaled by population to estimate the use in Stockholm. For each of these product classes emissions factors describing the fraction of the product usage that is released to different environmental media (air, water) in the city were taken from European risk assessment documents.[2,3] Multiplying the usage by the emissions factor gave an estimate of the releases of CPs to air and to water in Stockholm. The remaining CPs used in building materials were assumed to have an average lifetime of 20 years before being transferred to waste sites.

An independent estimate of the release of CPs to air and water was obtained from data on CP levels in sewage sludge, ambient air, and waste.[9-11] Assuming that all of the CPs released to water reach the STP, and that they are completely retained in the sewage sludge without degradation, the release to water was estimated by multiplying the CP concentration in sewage sludge by the annual production of sewage sludge in the city. CP concentrations in air were available for two stations, one in the city centre, and one at a remote location 100 km south of the city, for a period of one year with monthly resolution. The CP emission from Stockholm were estimated by

scaling the difference between the ambient air levels at the two sites with a factor derived from the difference in NO_x levels at the two sites and knowledge of NO_x emissions in the city and the surrounding area. The CP flux to waste was estimated from measurements of CP levels in household waste from the nearby city of Uppsala. The calculations were done for the sum of the SCCPs, MCCPs, and LCCPs for air and household waste and for SCCPs for sewage sludge.

Results

Use and Emissions estimated from the Product Registry

The total use of CPs in Stockholm for 2004 was estimated to be 16 tonnes: 4.9 in paints, 3 in sealants, 7.7 in plastics and rubber, and <0.2 for other uses. Although the calculation indicated that lubricants were also a major usage of CPs in Stockholm, this result was discarded as an artifact of the population scaling procedure, since there are no known industrial users of lubricants containing CPs in Stockholm.

Of the 16 tonnes of use, 0.58 tonnes (3.8 %) was estimated to be released to the environment, whereby approximately equal parts were released to air and water (0.25 and 0.33 tonnes, respectively). The sources of the emissions to air and water are shown in Figures 1. For air, paints were responsible for ~60 % of the emissions, whereas for water, sealants were responsible for ~75 %.

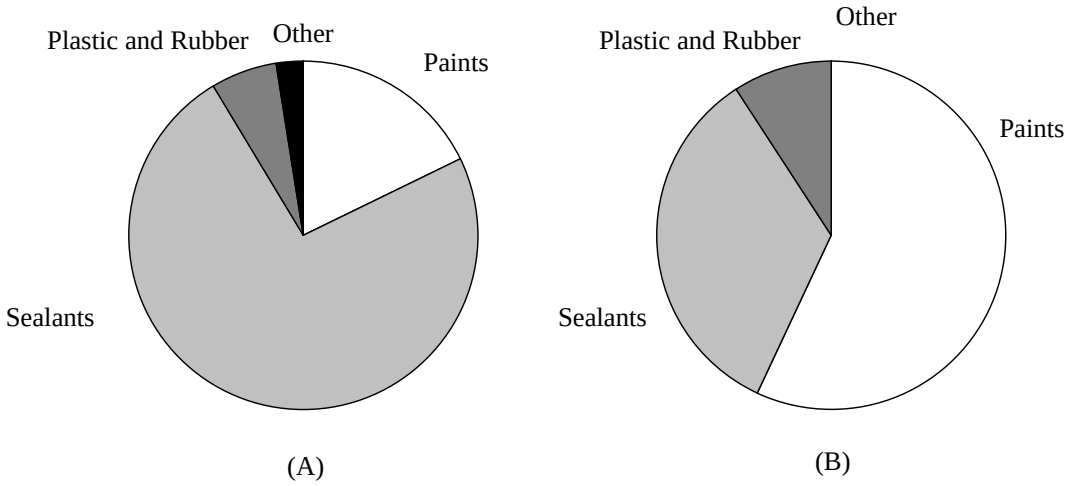

Figure 1: Sources of the CP emissions to the city of Stockholm in 2004 as estimated from CP usage
A: to air (total emissions = 0.33 tonnes/year); B: to water (total emissions = 0.33 tonnes/year)

Of the remaining CP use (i.e. 96 %), the majority is expected to land in waste sites as the building materials or the buildings are replaced. The flux of CPs to landfills in Stockholm in 2004 was estimated to be equal to the use of CPs in 1995. Although detailed historical use data are not available, the use in 1995 was thought to be an intermediate value of the use of CPs over the last 20 years. This yielded an estimated flux of CPs to landfills of 80 tonnes in 2004.

Emissions estimated from Measurements

The estimated emissions to air in 2003 based on the measured gradient in CP concentrations in ambient air between the inner city and the remote station was 0.75 tonnes/year. This is three times greater than the emissions to air estimated on the basis of CP use above. Considering the uncertainty in both methods of estimation, this is reasonable agreement. There is some indication that the CP usage or the emissions factors could be underestimated. Alternatively, past uses of CPs could play a significant role in current emissions.

The estimates of emissions to water were based on two sets of data on CP concentrations in Stockholm sewage sludge generated by two different laboratories. The estimated annual fluxes to water were 0.004 tonnes of total CP per year in one case, and 0.036 tonnes of SCCP in the second. If one considers that current CP use in Stockholm is dominated by the MCCPs, then the second value of 0.036 tonnes of SCCPs is reasonably

consistent with the of 0.33 tonnes of total CPs that were estimated to be released to water on the basis of CP usage (above). However, the large differences between the CP levels measured in the sewage sludge illustrates the limitations of current analytical methods and the difficulty in using measured data to estimate CP fluxes. The CP flux to household waste disposal sites was 0.5 tonnes per year, based on the measurements of CP concentrations in household waste. This is much less than the 80 tonnes per year that was estimated from the CP usage to go to solid waste sites. This discrepancy is to some extent due to the fact that much of the CP is likely not in household waste, but rather in construction and building demolition waste.

Discussion

The chemical flow analysis indicates that CP emissions to air and water in Stockholm are of the order of 0.5 tonnes/year, whereby paints and sealants are the major sources. The current flux to solid waste is some two orders of magnitude greater. Major uncertainties in the chemical flow analysis include the effectiveness of the sequestration of the CPs in solid waste. It is possible that some fraction of the CPs in solid waste is not effectively transported to and isolated in solid waste disposal sites. If a relatively small fraction remains in the environment, it could contribute significantly to the overall emissions.

Assembling a chemical flow analysis for CPs was limited by the inconsistencies in the CP use information available from the Swedish Product Registry, by the paucity of measured data for CP levels in relevant matrices, and by the inconsistencies in the available data. Further progress in this area requires improvements in the quality of CP analytical methods and more effort to measure CP levels in important chemical flow streams such as sewage sludge, (indoor) air, urban soil, waste, and waste site leachate.

Acknowledgements

This study was financially supported by the City of Stockholm Environment and Health Administration and Stockholm Water Company.

References

1. Muir, D. C. G.; Stern, G. A., et al. In: *The handbook of environmental chemistry*, Paasivirta, J. (Ed.), Springer-Verlag: Heidelberg, 2000; Vol. 3 Part K, pp 203-236.
2. United Kingdom Report: *European Unions Risk Assessment Report. Alkanes, C14-17, chloro (MCCP)*, 2005. European Communities.
3. European Commission Report: *EUR 190010: European Union Risk Assessment Report: Alkanes, C10-13, chloro*. 2000, European Communities.
4. Swedish National Chemical Inspectorate. Uttag ur KemIs produktregister. 2007.
5. Swedish National Chemical Inspectorate. *Kemstat*. http://www.kemi.se. 2006. Swedish National Chemicals Inspectorate (KemI), Sweden.
6. Swedish National Chemical Inspectorate. *Klorparaffiner, Kortstatistik 1997*. http://www.kemi.se. 2006. Swedish National Chemicals Inspectorate (KemI), Sweden.
7. Swedish National Chemical Inspectorate. *Klorparaffiner, Flödet i Sverige i kemiska produkter 1995*. http://www.kemi.se. 2006 Swedish National Chemicals Inspectorate (KemI), Sweden.
8. Swedish National Chemical Inspectorate. *Klorparaffiner, Flödet i Sverige i kemiska produkter 2004*. http://www.kemi.se. 2006. Swedish National Chemicals Inspectorate (KemI), Sweden.
9. Järnberg, Ulf, Fridén, Ulrika, Haglund, Malin, Johansson, Carina, and Nilsson, M-L. *Screening av klorparaffiner i den Svenska miljön*. 2005. Swedish Environmental Protection Agency, Sweden.
10. Sternbeck, John, Brorström-Lundén, Eva, Remberger, Mikael, Kaj, Lennart, Palm, Anna, Junedahl, Erika, and Cato, Ingemar. *WFD Priority substances in sediments from Stockholm and the Svealand coastal region*, 2003. IVL Swedish Environmental Research Institute, Sweden.
11. Nilsson, M-L. *Occurrence and Fate of Organic Contaminants in Wastes*. 2000. Department of Environmental Assessment, Swedish University of Agricultural Sciences, Uppsala