

Environmental fate and impact of chlorinated solvents

Introduction

Over many decades, certain chlorinated hydrocarbons have proven their value as high-performance, cost-effective solvents in a wide variety of industrial, commercial and consumer applications. Their main uses include metal degreasing, dry-cleaning, paint stripping, polyurethane foam blowing, the manufacture of pharmaceuticals, the processing of foodstuffs and the production of electronic circuits.

The four chlorine compounds in common use today for such applications are methylene chloride (DCM - also known as dichloromethane [CH_2Cl_2]), trichloroethylene (TRI - trichloroethene [C_2HCl_3]) and perchloroethylene (PER - tetrachloroethene [C_2Cl_4]), and to a lesser extent, chloroform (TCM - trichloromethane [CHCl_3]).

This paper reviews the main features of the environmental fate and impact of these solvents.

Environmental emissions and partitioning

The quantities of MC, TRI and PER produced for solvent applications and the ensuing emissions to the environment have been declining since the latter part of the twentieth century. This fall in consumption is largely due to the introduction of more efficient cleaning and degreasing equipment that uses and releases smaller quantities of solvent per unit volume of material treated, through better emissions control and improved recycling.

Audited surveys commissioned by the principal producers worldwide show the following reductions in global solvents sales between 1988 and 2002 (in thousands of tonnes per year): DCM from 564 to 439 (-22 %), TRI from 249 to 147 (-41 %) and PER from 414 to 203 (-51 %) ^[1]. Emissions of these compounds from their use as

solvents are practically equal to the amounts sold, since consumption essentially compensates for losses; however, some amounts are destroyed by waste or off-gas incineration rather than released ^[2,3].

About 97 % of the TCM produced is used as a feedstock for manufacturing chlorodifluoromethane ^[36]. The estimated emissions from solvent use (about 10 kt/year) are six times smaller than those arising from pulp and paper manufacturing and water treatment ^[4]. Furthermore, it is believed that there are very large natural emissions from the oceans and land, probably totalling several hundred thousand tonnes per year ^[5,5a].

Oceanic sources may well exist also for DCM, TRI and PER ^[5,6], but their magnitude is still a matter of debate ^[7,8].

The chlorinated solvents are volatile compounds, sparingly soluble in water. Any material lost from

processing equipment therefore tends to be emitted directly to the atmosphere and has only limited affinity for other environmental compartments. Even if traces of solvents are initially present in aqueous waste streams, they volatilise from rivers and lakes with a half-life of about a month or shorter^[9], unless they are trapped in groundwater.

Atmospheric degradation and impact

Persistency in air

The chlorinated solvents degrade quite easily in the atmosphere. DCM, TCM and PER have mean half-lives of 3.2, 3.4 and 2.3 months, respectively^[10]. They are therefore persistent enough to undergo long-range transport within the hemisphere in which they are emitted. However, transfer between hemispheres is limited. Since emissions of DCM, TRI and PER occur mainly in the northern hemisphere^[2], their background concentrations are higher north of the equator than at southerly latitudes. TRI is even more reactive than the other solvents: its half-life of about three days is nevertheless long enough for transboundary or even intercontinental transport to occur.

The degradation of all four solvents is however rapid enough to preclude significant vertical transport to the stratosphere^[10].

Ozone depletion

The latest scientific assessment carried out in the framework of the Montreal Protocol on Ozone Depleting Substances^[10] concludes that “it is unlikely that very short-lived chlorine compounds [including DCM, TCM, TRI and PER] will make a significant contribution to the chlorine budget” (and hence to stratospheric ozone depletion). The chlorinated solvents considered here are therefore not regulated under the Montreal Protocol.

Global warming

The Global Warming Potentials (GWPs) of DCM and TCM are greater by factors of 10 and 30,

respectively, than that of carbon dioxide (CO₂)^[11,12]. However, since the global emissions of DCM and TCM are about 50,000 times smaller than those of CO₂, it is clear that their contribution to global warming is negligible. Full data are lacking for TRI and PER, but their GWPs are expected to be either comparable to that of DCM (for PER), or considerably lower (for TRI). The GWP values are hence similar to those of hydrocarbon solvents and several orders of magnitude lower than for chlorofluorocarbons^[12].

Degradation products

The degradation of all four chlorinated solvents in the lower atmosphere is initiated by reaction with the hydroxyl radical. Complex sequences of reactions then lead to the formation of products that include hydrogen chloride (HCl), phosgene (COCl₂) and formyl chloride (HCOCl)^[13]. Cloud and rain water scavenges these compounds from the air and hydrolyses COCl₂ and HCOCl to carbon dioxide and hydrochloric and formic acids, the latter being deposited from the atmosphere in rain and snow. Nevertheless, the acids resulting from the degradation of chlorinated solvents have an insignificant impact on “acid rain” on a global scale, the main contributors being oxides of sulphur and nitrogen, arising largely from the combustion of fossil fuels^[14].

In the particular case of PER, a degradation sequence initiated by chlorine atoms – occurring in parallel with the one mediated by hydroxyl radicals – can lead to the formation of trichloroacetic acid (TCA) as a minor product^[13]. The environmental impact of TCA will be examined separately below.

Ozone creation

The potential for organic compounds to enhance the formation of atmospheric ozone and related oxidants – and hence contribute to “photochemical smog” – increases with their atmospheric reactivity. Indices such as Photochemical Ozone Creation Potentials (POCPs) are used for comparing the smog-forming capabilities of different substances. The values of these indices vary greatly for a given

compound depending on the calculation procedure and modelling assumptions. Published POCP values for the chlorinated solvents lie within the following ranges, relative to a benchmark of 100 for ethylene^[16-18]: DCM 1.6-6.8, TCM 2.3, TRI 7.5-32.5 and PER 1.0-3.5. These values are clearly lower than those of many other commonly used solvents, for example methyl ethyl ketone (37-51) and xylene (83-109)^[16,18]. DCM and PER have been exempted by the United States Environmental Protection Agency from control as smog-forming “volatile organic compounds”^[19] on the basis of their “negligible reactivity”^[20].

Effects on plants

The concentrations of PER in the background atmosphere are too low for this compound to affect plants. This has been demonstrated in a study in which a range of plant species were exposed for long periods to various levels of PER in air. The No Observed Effect Concentration (NOEC) for the most sensitive species was $46 \mu\text{g}/\text{m}^3$ ^[21], while observed levels of PER are lower by a factor of 1000 or more^[22] in truly remote air and they generally do not exceed one tenth of the NOEC even in more populated areas^[23].

Fate and impact in water and soil

Bioaccumulation potential

The bioaccumulation potential of these solvents is generally considered to be low. Investigations have shown that the octanol-water partition coefficients (K_{ow}) of the chlorinated solvents are: DCM 18-20, TCM 79-100, TRI 195-954 and PER 339-2500^[24,25,26] and the bioconcentration factors (BCFs) are: DCM 5-40, TCM 1.6-13, TRI 17-39, PER 49-226^[25,26,27]. These two sets of values lie below the thresholds of 10,000-100,000 (for K_{ow}) and 500-5000 (for BCF) above which certain authorities consider that substances are liable to bioaccumulate in the food chain^[28].

Mobility in soil

Due to their substance properties, chlorinated

solvents are quite mobile in soil. The coefficients for partitioning from water to organic carbon in soil (K_{oc}) increase with K_{ow} . Measured coefficients are as follows: DCM 47, TCM 77, TRI 137 and PER 359^[24]. All are low enough to explain a relatively high mobility in soil for these substances^[29].

Biodegradation

Any chlorinated solvents trapped in water or soil are likely to be degraded by biotic processes, i.e. by naturally-occurring micro-organisms, rather than by abiotic processes such as hydrolysis. The rate at which natural biotransformation occurs is however highly dependent on local conditions, as well as on the properties of the solvent. For example, local conditions can be either anaerobic (oxygen-poor) or aerobic (oxygen-rich). The more highly chlorinated solvents are susceptible to anaerobic degradation, involving sequential substitution of chlorine atoms with hydrogen atoms. Thus PER can be converted to TRI, which in turn can yield dichloroethylenes (DCEs). This dechlorination process can continue until ethylene is ultimately formed. The lesser chlorinated intermediates (DCEs and vinyl chloride) however, are also susceptible to aerobic degradation. For MC and CF, biotransformation may proceed under either anaerobic or aerobic conditions, but the aerobic pathway is generally predominant for MC and the anaerobic one for CF^[30-32].

Natural degradation of DCM and TCM in soil and groundwater generally occurs on a time-scale of days to weeks. For TRI and PER, the degrading process is much slower, but may be greatly enhanced by the implementation of promising new remediation technologies^[33,37].

Marine risk assessments

Marine risk assessments have been performed for all four solvents^[26]. Literature data were evaluated to determine the sensitivity of living organisms to these substances at three different levels in the marine food chain: aquatic plants (primary producers), invertebrates (primary consumers) and fish (secondary consumers). From these data, a Predicted No-Effect Concentration (PNEC) was

derived. The ratio between the PNEC and the observed concentrations in rivers and estuaries gave a “safety margin”, varying from 6 to 4,000, depending on the solvent and the sampling location [26]. Dilution within the sea would of course increase these margins. Furthermore, levels of chlorinated solvents in surface waters have been steadily declining for many years.

Fate and impact of trichloroacetic acid

As stated above, trichloroacetic acid (TCA) can be formed as a minor product in the atmospheric degradation of PER [13]. TCA has been shown to be broadly distributed in precipitation, surface water and soil on a global scale [34]. Since the observed levels in soil occasionally exceed the proposed PNEC of 2.4 µg/kg for terrestrial organisms, the European Commission instructed PER producers to carry out

extensive studies of the origin and fate of environmental TCA. This project focussed on monitoring TCA in precipitation and soil in mountainous, forested regions, and performing mass balances. It was concluded that the observed TCA levels in soil and their seasonal variation could not be explained by input from precipitation alone, so natural formation and degradation in soil was likely.

Support for this hypothesis was provided by the appearance of isotopically enriched TCA when soil patches were treated with sodium chloride (Na^{37}Cl) [35]. The European Union Risk Assessment on PER concluded that “it is considered unlikely that deposition of TCA from the atmosphere will by itself lead to levels of TCA in soil that pose a risk for terrestrial organisms” [35].

The full set of references can be found on *Chlorine Online* at <http://www.eurochlor.org/science> (FOCS)

The chlorine industry in Europe

Euro Chlor represents chlor-alkali producers in the EU and EFTA regions employing about 39,000 people at 69 manufacturing locations. Almost 2,000,000 jobs in Europe are directly or indirectly related to chlorine and its co-product caustic soda (sodium hydroxide). These two key chemical building blocks underpin 55% of European chemical industry turnover (2009: € 657 billion).

Focus on Chlorine Science

This Focus on Chlorine Science (FOCS) is part of a series of leaflets aiming to clarify and consolidate scientific research in the field of chlorine industry. With the FOCS series, we want to facilitate the knowledge gathering of scientists, regulators and key decision makers. For further Euro chlor science publications, please consult <http://www.eurochlor.org/science>


EURO CHLOR

Euro Chlor provides a focal point for the chlor-alkali industry's drive to achieve a sustainable future through economically and environmentally-sound manufacture and use of its products. Based in Brussels, at the heart of the European Union, the federation works with national, European and international authorities to ensure that legislation affecting the industry is workable, efficient and effective.

Euro Chlor®

Avenue E Van Nieuwenhuysse 4, box 2
B-1160 Brussels
eurochlor@cefic.be

Find out more about
chlorine on Chlorine Online at
www.eurochlor.org

An affiliate of  cefic