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PBT screening profile of chemical warfare agents (CWAs)

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Abstract

Chemical warfare agents (CWAs) have been used and disposed of in various fashions over the past decades. Significant amounts have been dumped in the Baltic Sea following the disarmament of Germany after World War II causing environmental concerns. There is a data gap pertaining to chemical warfare agents, environmental properties not the least their aquatic toxicities. Given this gap and the security limitations relating to working with these agents we applied Quantitative Structure–Activity Relationship ((Q)SAR) models in accordance with the European Technical Guidance Document (2003) to 22 parent CWA compounds and 27 known hydrolysis products. It was concluded that conservative use of EPI Suite (Q)SAR models can generate reliable and conservative estimations of chemical warfare agents acute aquatic toxicity. From an environmental screening point of view the organoarsenic chemical warfare agents Clark I and Adamsite comprise the most problematic of the screened CWA compounds warranting further investigation in relation to a site specific environmental risk assessment. The mustard gas agents (sulphur and nitrogen) and the organophosphorous CWAs (in particular Sarin and Soman) are a secondary category of concern based upon their toxicity alone. The undertaken approach generates reliable and conservative estimations for most of the studied chemicals but with some exceptions (e.g. the organophosphates).

Keywords: Chemical weapon agents; (Q)SAR; Environmental toxicity; EU TGD; Marine toxicity

1. Introduction

Chemical warfare agents (CWAs) cover, among other, nerve-gases, blistering agents, pulmonary, blood agents and vomiting agents [1]. CWAs have been used in several armed conflicts worldwide, starting with German attacks during World War I [2]. As a result of the disarmament of Germany following the Second World War, and subsequent general disarmament with respect to CWAs globally 10,000s tonnes of CWA have dumped at sea in the years following 1945 [2–4], e.g. more than 30,000 tonnes in the Baltic Sea alone [2]. In 1999, 126 countries ratified the Chemical Weapons Convention (CWC) [5,6] mandating that all CWAs should be disposed of by April 2007. Until recently disposing of CWAs was achieved in part by dumping at sea without sound knowledge of the environmental consequences, however, nowadays most of the disposing is done by incineration or by conversion to peaceful purposes/products by the chemical industry [3,7].

There is evidence of both accidental human exposure, primarily fishermen [8], as well as environmental exposures due to releases from corroding and leaking containers at sea [2,4]. These documented releases have renewed concerns over the human and environmental risks associated with CWAs dumped at sea. There are very few baseline environmental toxicity and physio-chemical property data available in the open literature [1,9] to help guide site specific risk assessments and prioritize remediation initiatives, and provide scientific support in prevention of munition dumping at sea. The relative datagap with regard to CWAs compared to many other compounds in the open literature is expected due to the elevated individual and societal security precautions needed to perform laboratory work on CWAs. In this added security context application of predictive tools such as Quantitative Structure–Activity Relationships ((Q)SARs) for screening level assessment of environmental properties is prudent [10].

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The European Technical Guidance Document (EU TGD) in support of Commission Directive 93/67/EEC on Risk Assessment for new notified substances, Commission Regulation (EC) No. 1488/94 on Risk Assessment for existing substances and Directive 98/8/EC of the European Parliament and of the Council concerning the placing of biocidal products on the market, includes a chapter on marine risk assessment, which states that using (Q)SARs and freshwater species toxicity data *in lieu* of absent specific marine data on chemicals persistence, bioconcentration, toxicity (PBT) properties may be required [11].

In light of the imminent potential environmental hazards posed by CWAs, the lack of comprehensive environmental property and toxicity data for CWAs as well as their hydrolysis products. Hence, the aim of this paper is to; provide a compilation of predicted environmental toxicity data of parent and hydrolysis products of CWAs; evaluated the conservatism of (Q)SAR predictions with regards to CWAs acute aquatic toxicity; and finally, briefly touch upon their persistence and bioconcentration potential. In other words, to present the predicted environmental PBT profile of CWAs according to EU TGD approaches.

2. Materials and methods

2.1. Compounds

The majority of CWAs mentioned in the CWC and their known major degradation products [1], primarily hydrolysis products [12], are covered in the analysis, in total 49 compounds, see Table 1.

2.2. Models

The Estimation Program Interface modules (EPI Suite v. 3.12) used in this assessment is developed by the Syracuse Research Corporation on behalf of the United States Environmental Protection Agency (USEPA) and comprises a suite of regression based (Q)SAR models with Log Kow as one of the most significant descriptors. ECOSAR is based on approximately 150 (Q)SARs for 50 different compound structure/classes (e.g. neutral organics, aliphatic amines, esters, etc.) (http://www.epa.gov/oppt/exposure/docs/episuitedl.htm). The models are widely used and accepted for screening chemicals from a broad spectrum of the chemical universe [13]. Carlsen [14,15] have previously applied the EPI Suite models to nerve agents, and Munro et al. [1] reported data generated by EPI Suite for nitrogen mustard gas, and Tørnes et al. [2] used the models on organoarsenic CWAs and nerve gases. Finally, the models have been widely used by the US National Institute of Health (NIH) in assessing the physio-chemical and fate properties of CWAs [10]. In this study, we applied the BIOWIN v.2.15 model to assess the biodegradation, PCKOCWIN v.1.66 for Koc values, BCFWIN v.4.02 for bioconcentration factor values, and ECOSAR for the environmental toxicity predictions. The EPI Suite program and associated information regarding the models may be downloaded of the USEPA website: http://www.epa.gov/oppt/exposure/docs/episuitedl.htm.

3. Results

3.1. Persistence

The EU TGD [11] recommends using the BIOWIN model from the EPI Suite for assessment of persistence. It is recommended to use BIOWIN models 2, 3 and 5, with the following default benchmark values (non-linear model (<0.5 biodegradation probability = persistent)); or MITI non-linear model (<0.5) and ultimate biodegradation ≥ months, respectively). If the compound fulfils these requirements an "open-ended" categorization as being potentially persistent (P) can serve as an indicator for the need for further experimental evaluation. Based on this approach the following CWAs are potentially persistent compounds: Adamsite; Lewisite; the three Nitrogen mustards; Sulphur mustard, Yperite; HT; VX; VG; VM; Cyclosarin; Soman; Chloropicrin (PS) and Diphosgene (DP).

In relation to marine risk assessments under the EU TDG [11], it is moreover noted that one needs to conservatively consider site specific parameters such as: temperature; frequent anaerobic conditions below the top 5 mm of the sediment; salinity; alkalinity; the less favourable conditions for microbial communities to degrade xenobiotics (less exposure and adaptation, e.g. due to increased drift and flux) and general physio-chemical conditions governing the persistence of chemicals in marine environments. Generic site specific parameters in the EU TGD [11], suggests that degradation in estuaries are approximately four times lower than in freshwater environments and even lower further away from land. For the predicted persistent CWAs it would be recommended to use default marine mineralization half-lives of >150 days [11], see Table 1.

3.2. Bioconcentration

None of the agents are predicted to bioconcentrate significantly (BCF < 2000). Clark I and Adamsite have the highest BCF = 600 (Log Kow = 4.52) and 262 (Log Kow = 4.05), respectively. The remaining CWAs had BCFs < 70. The geometric mean BCF value for the parent compounds = 8.1. For the hydrolysis products the BCF were, as expected, lower with a geometric mean of 3.9, with the VX hydrolysis product (MPA) CAS# 2387-23-7, as the outlier at BCF = 206. It should also be noted that the solubility of a contaminant is normally reduced in saline waters, typically by a factor of 1.36 [11]. The resulting biomagnification factor (BMF) for all the CWAs covered in this assessment is thus predicted to be insignificant (=1) according to EU TGD [11], see Table 1.

3.3. Acute aquatic toxicity

Table 1 summarizes the predicted LC50 values (mg l^{-1}) for the parent compound and know major hydrolysis products. The relative predicted species sensitivity frequency rank based in their geometric mean LC50 for the parent compounds is thus; algae 4.6 > daphnid 16.8 > fish 24.1 (mg l^{-1}). For the hydrolysis products the rank is; algae 43.4 > daphind 101 > fish 426 (mg l^{-1}). All the parent compounds were more toxic than the