Chemosphere 111 (2014) 157–163

Contents lists available at ScienceDirect

Chemosphere

journal homepage: www.elsevier.com/locate/chemosphere

2,4,6,8-Tetrachlorodibenzothiophene in the Newark Bay Estuary: The likely source and reaction pathways

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HIGHLIGHTS

- 2,4,6,8-Tetrachlorodibenzothiophene (2,4,6,8-TCDT) is a contaminant in Newark Bay.
- The previously proposed sources for 2,4,6,8-TCDT are unlikely.
- Thiophenol is an impurity in phenol produced via the sulfonation method.
- Thiophenol can be transformed to 2,4,6,8-TCDT in the production of 2,4-D.
- Production quantities of 2,4-D in the estuary can account for 2,4,6,8-TCDT.

ARTICLE INFO

Article history:
Received 4 November 2013
Received in revised form 28 March 2014
Accepted 30 March 2014

Handling Editor: J. de Boer

Keywords:
Tetrachlorodibenzothiophene (TCDT)
Tetrachlorodibenzodioxin (TCDD)
2,4-Dichlorophenoxyacetic acid (2,4-D)
Thiophenol
Passaic River
Newark Bay

ABSTRACT

Historic industrial activity along the Newark Bay Estuary has resulted in pollution from a number of contaminants; one of which is 2,4,6,8-tetrachlorodibenzothiophene (2,4,6,8-TCDT), a unique chemical contaminant whose origins have not been adequately explained. This research demonstrates that the probable source of 2,4,6,8-TCDT was the chlorination of phenol produced via the sulfonation method. Thiophenol, the major impurity in this type of phenol, was likely converted to 2,4,6,8-TCDT through one or more pathways during the production of 2,4-dichlorophenol, 2,4-dichlorophenoxyacetic acid (2,4-D), or 2,4,6-trichlorophenol. From a mass balance standpoint, production of these chemicals at an industrial plant along the Passaic River could account for the 2,4,6,8-TCDT in the Newark Bay Estuary.

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1. Introduction

Historically, the Passaic River and Newark Bay have been heavily industrialized waterways, and as a result have been polluted by a wide range of contaminants. From an environmental forensics perspective, perhaps the most interesting of the contaminants identified in the Passaic River and Newark Bay Estuary is 2,4,6,8-tetrachlorodibenzothiophene (2,4,6,8-TCDT), as the origins of this unique compound have remained elusive for over twenty years.

2,4,6,8-TCDT was detected in marine organisms and sediment of the Passaic River/Newark Bay Estuary in the 1980s, but was initially misidentified as 1,2,8,9-TCDD as it eluted close to 1,2,8,9-TCDD in GC/MS analysis (Rappe et al., 1991; Wenning et al., 1992; Pruell et al., 1993). A number of subsequent studies confirmed the presence of 2,4,6,8-TCDT in the Newark Bay Estuary (Buser and Rappe, 1991; Cai et al., 1994; Pruell et al., 2000). In surficial sediment from the Passaic River, a 2,4,6,8-TCDT to 2,3,7,8-TCDD ratio of approximately 6:1 was found (Pruell et al., 1993, 2000). In crab tissues from Newark Bay and Raritan Bay, the concentration of 2,4,6,8-TCDT was five to ten times greater than the concentration of 2,3,7,8-TCDD (Buser and Rappe, 1991; Cai et al., 1994). The similarity between these ratios in sediments and marine life is not surprising given that the accumulation factor for 2,4,6,8-TCDT in sandworms, clams, and shrimp was similar to the accumulation factor for 2,3,7,8-TCDD in these same organisms (Pruell et al., 1993).

Utilizing estimated releases of 2,3,7,8-TCDD to the Passaic River and Newark Bay can help to provide an estimate of the 2,4,6,8-TCDT release. The deposition of 2,3,7,8-TCDD in Newark Bay has been estimated at 4–8 kg (Bopp et al., 1991) and it has been suggested that up to 50 kg of 2,3,7,8-TCDD is contained in the

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http://dx.doi.org/10.1016/j.chemosphere.2014.03.076
0045-6535/© 2014 Published by Elsevier Ltd.

sediment of the Passaic River (Chant et al., 2011). If a 6:1 ratio of 2,4,6,8-TCDT to 2,3,7,8-TCDD is utilized, the 2,4,6,8-TCDT release to the Newark Bay Estuary may have been as high as 350 kg assuming the depth profile of 2,4,6,8-TCDT is similar to that of 2,3,7,8-TCDD and assuming similar environmental half-lives. The literature provides 2,4,6,8-TCDT concentration data for only surficial sediment samples in the Passaic River. 2,3,7,8-TCDD concentrations are significantly greater at depth than at the surface (Bopp et al., 1991; Chant et al., 2011).

Despite the relative low toxicity in comparison to 2,3,7,8-TCDD (Kopponen et al., 1994), 2,4,6,8-TCDT may serve as a useful contaminant marker in the Passaic River/Newark Bay estuary. The concentration of 2,4,6,8-TCDT in aquatic organisms of Newark Bay suggests that 2,4,6,8-TCDT comprises approximately 95% of the total TCDT in the Passaic River (Buser and Rappe, 1991). The disproportionally high concentration of 2,4,6,8-TCDT relative to other TCDT congeners strongly suggests a chemical process-specific point source (Buser et al., 1991; Huntley et al., 1994). Therefore, understanding the source of 2,4,6,8-TCDT may help to understand the movement of other contaminants in the Newark Bay Estuary.

The objective of this research was to utilize the scientific literature to determine whether the previously proposed potential sources of 2,4,6,8-TCDT were plausible explanations for its presence in the Newark Bay Estuary; and if not, to utilize the scientific literature and other available resources to determine the probable source or sources of 2,4,6,8-TCDT in the estuary.

2. Results and discussion

2.1. Review of the suggested sources for 2,4,6,8-TCDT

It has been suggested that PCBs from Monsanto Chemical Company (Pennsylvania Avenue, Kearny, NJ) are the most plausible source of the 2,4,6,8-TCDT in the Newark Bay Estuary (Huntley et al., 1994). The thermal reaction of 2,2′,3,3′,5,5′-hexachlorobiphenyl (PCB-133) with sulfur has been shown to produce 2,4,6,8-TCDT (Buser and Rappe, 1991). However, PCB-133 was only an extremely minor constituent of commercial PCB formulations (Ballschmiter and Zell, 1980; Frame et al., 1996), and PCB-133 would theoretically be the only congener of the 209 PCB congeners which would predominantly form 2,4,6,8-TCDT upon reaction with sulfur (Buser and Rappe, 1991; Huntley et al., 1994). Furthermore, when Aroclor 1254, a commercial PCB formulation produced by Monsanto, reacted with sulfur, 2,4,6,8-TCDT comprised only 1% of the overall TCDT profile (Huntley et al., 1994).

A number of studies have also examined the presence of individual PCB congeners in the Passaic River (Pruell et al., 1993, 2000; Iannuzzi et al., 1995; Huntley et al., 1997; Su et al., 2002). PCB-133 was either not detected, or not analyzed for in these studies. While 3,3′,5,5′-tetrachlorobiphenyl (PCB-80) and 2,3,3′,5,5′-pentachlorobiphenyl (PCB-111) also have chlorine atoms in positions that could theoretically lead to the formation of 2,4,6,8-TCDT via other mechanisms, these PCB congeners comprised less than 0.01% of Aroclor products (Frame et al., 1996). Thus, the scientific literature does not support the basis that PCBs are the source of the high levels of 2,4,6,8-TCDT in the Passaic River.

Other known sources of TCDTs also contain low percentages of 2,4,6,8-TCDT, rendering them unlikely sources of the 2,4,6,8-TCDT in the Newark Bay Estuary. For example, 2,4,6,8-TCDT comprised 12% of the total TCDTs produced from the thermal reaction of hexachlorobenzene with sulfur, 13% of the total TCDTs produced from the direct chlorination of dibenzothiophene, 0–13% of the total TCDTs in municipal solid waste incinerator fly ash samples, and up to 16% of the total TCDTs in pulp and paper mill effluent (Huntley et al., 1994). TCDTs from a metal reclamation process were not speciated, though the chromatographs demonstrated that the TCDT profile is a mixture of TCDTs, with no one individual TCDT congener dominating (Sinkkonen et al., 1994).

2,4,6-trichlorobenzenesulfonic acid is a specific chemical that has been suggested as another potential source of 2,4,6,8-TCDT as its chlorines and sulfur molecules are oriented in positions to allow for the theoretical production of 2,4,6,8-TCDT (Huntley et al., 1994). However, a search of several databases yielded only a few papers where this chemical was utilized or studied in any capacity. In addition, no industrial process or other significant usage of 2,4,6-trichlorobenzenesulfonic acid could be identified in any application, eliminating this chemical as a likely source of the 2,4,6,8-TCDT in the Newark Bay Estuary.

The site of a former 2,4,5-T manufacturing facility located along the Passaic River on Lister Avenue in Newark, NJ, has also been suggested as the likely source of the 2,4,6,8-TCDT. Phenoxy herbicides were produced at the site from the 1940s through the mid-1970s (Diamond Shamrock Chemicals Company, 1985; U.S. Tariff Commission, 1941–1978). For much of this time period, 2,4,5-trichlorophenol (2,4,5-TCP) was produced on-site and further converted to the herbicide 2,4,5-trichlorophenoxyacetic acid (2,4,5-T). In the production of 2,4,5-TCP, the highly toxic 2,3,7,8-TCDD was produced as an unwanted by-product. It has been suggested that this facility is a major source of 2,3,7,8-TCDD to the estuary (Tong et al., 1990; Bopp et al., 1991; Cai et al., 1996; Barabas et al., 2004; Hansen, 2006).

Based on a correlation between 2,4,6,8-TCDT and 2,3,7,8-TCDD concentrations in crabs from Newark Bay and Raritan Bay ($r^2 = 0.98$), it was suggested that 2,4,6,8-TCDT originated from the same site as 2,3,7,8-TCDD (Cai et al., 1994). However, the position of the chlorine atoms in 2,4,5-TCP would favor the predominant formation of 2,3,7,8-substituted tricyclic compounds (Huntley et al., 1994) and 2,3,7,8-TCDT was not observed in Newark Bay samples (Buser et al., 1991). Cai et al. (1994) indicated that 2,4,6,8-TCDT could be a by-product of other chemical synthesis at the Lister Avenue site or a result of environmental processing of plant discharges; however, no mechanism to explain the formation of 2,4,6,8-TCDT at this site was offered.

2.2. The 2,4-dichlorophenoxyacetic acid (2,4-D) process

Though it can be reasonably concluded that 2,4,6,8-TCDT in the Newark Bay Estuary is not a result of 2,4,5-TCP or 2,4,5-T manufacture, the production of other chemicals at the Lister Avenue site has been largely ignored due to their lack of association with 2,3,7,8-TCDD. One such chemical is 2,4-D, produced at the site primarily from 1946 to 1969 (U.S. Tariff Commission, 1941–1978). An estimated 38.5 million kg of 2,4-D was produced at this site, more than three times the amount of 2,4,5-T (Diamond Shamrock Chemicals Company, 1985). Ostensibly, there does not seem to be a potential connection between 2,4-D and 2,4,6,8-TCDT as a source of sulfur would be required. To produce 2,4-D, phenol is chlorinated under conditions to produce a product comprised predominantly of 2,4-dichlorophenol (2,4-DCP). 2,4-DCP is reacted with monochloroacetic acid (MCA) in the presence of sodium hydroxide (NaOH) and water under reflux conditions (~110 °C) for several hours. The sodium salt of 2,4-D is then converted to its acid form with hydrochloric or sulfuric acid (Faith et al., 1965).

2.2.1. Phenol as the source of sulfur

To determine whether 2,4,6,8-TCDT could be associated with 2,4-D production, the process was examined beginning with phenol, the primary raw material. Historically, five processes have been employed commercially to produce phenol in the U.S: sulfonation, chlorobenzene, regenerative, cumene, and toluene oxidation methods (Collins and Richey, 1992; Faith et al., 1965).

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