Emerging Contaminants 2 (2016) 166–172

Contents lists available at ScienceDirect

Emerging Contaminants

journal homepage: http://www.keaipublishing.com/en/journals/emerging-contaminants/

Environmental levels and toxicological potencies of a novel mixed halogenated carbazole

Miren Pena-Abaurrea [a, b, c, d, *], Matthew Robson [e, c], Sri Chaudhuri [d], Nicole Riddell [f], Robert McCrindle [f, g], Brock Chittim [f], Robert Parette [h], Un-Ho Jin [i], Stephen Safe [i], David Poirier [c], Ralph Ruffolo [c], Richard Dyer [j], Rachael Fletcher [c], Paul A. Helm [c, k], Eric J. Reiner [b, c]

[a] Department of Analysis, CEPSA Research Center, Alcala de Henares, 28805, Spain
[b] Department of Chemistry, University of Toronto, Toronto, ON, M5S 3H6, Canada
[c] Ontario Ministry of the Environment and Climate Change, Toronto, ON, M9P 3V6, Canada
[d] Conservation Ontario, Newmarket, ON, L3Y 2P5, Canada
[e] Department of Chemistry, Brock University, St. Catharines, ON, L2S 3A1, Canada
[f] Wellington Laboratories Inc., Guelph, ON, N1G 3M5, Canada
[g] Department of Chemistry, University of Guelph, Guelph, ON, N1G 2W1, Canada
[h] Matson & Associates, Inc., State College, PA, 16801, USA
[i] Veterinary Medicine & Biomedical Sciences, Texas A&M University, Texas, TX, 77843–4461, USA
[j] Ministry of Northern Development and Mines, Sudbury, ON, P3E 6B5, Canada
[k] School of the Environment, University of Toronto, ON, M5S 3EB, Canada

ARTICLE INFO

Article history:
Received 2 July 2016
Received in revised form
23 July 2016
Accepted 25 July 2016
Available online 8 August 2016

Keywords:
Halogenated carbazoles
Levels
GC×GC
REP
TEQ
Dioxin-like
Risk assessment
Regulation

ABSTRACT

The present work involves an extensive analytical and toxicological description of a recently identified mixed halogenated carbazole found in sediment samples, 1,8-dibromo-3,6-dichloro-9H-carbazole (BCCZ). Concentrations and the relative effect potency (REP) were calculated for the target BCCZ in a set of stream sediments collected in 2008 in Ontario, Canada. The levels calculated for BCCZ as compared to those previously assessed for legacy persistent organic pollutants (POPs) in the same samples revealed a significant contribution of BCCZ to the total organic chemical contamination (<1%–95%; average 37%). The corresponding dioxin toxic equivalencies (TEQs) of BCCZ in the sediment extracts were estimated from experimental REP data. The experimental data presented supports the classification of this emerging halogenated chemical as a contaminant of emerging environmental concern. Although potential emission sources could not be identified, this study highlights the importance of on-going research for complete characterization of halogenated carbazoles and related compounds.

1. Introduction

Non-target investigation to identify contaminants that may be of concern is one of the most challenging topics that have emerged in the field of environmental research [1–3]. Contaminants of emerging environmental concern (CoEECs) include known chemicals with increasing environmental levels, substances with newly-reported toxic effects and, occasionally, newly discovered compounds. Novel compounds can encompass substances such as anthropogenic industrial additives (e.g. novel halogenated flame retardants) [4–6], personal care products (e.g. pharmaceuticals) and by-products [7–9], as well as metabolites and degradation products of currently regulated pollutants [10,11]. Ultra-high resolution mass spectrometric and high resolution chromatographic approaches have facilitated the elucidation of substances present in

* Corresponding author. Department of Analysis, CEPSA research center, Avda Punto Com 1, Alcala de Henares, 28805, Spain.
E-mail address: miren.pena@cepsa.com (M. Pena-Abaurrea).
Peer review under responsibility of KeAi Communications Co., Ltd.

http://dx.doi.org/10.1016/j.emcon.2016.07.002

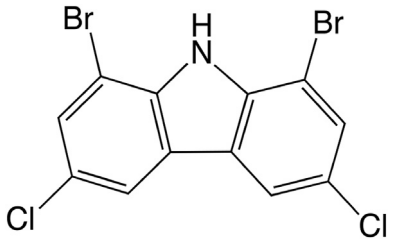

Fig. 1. Structure of 1,8-dibromo-3,6-dichlorocarbazole.

environmental media which have properties that render them possible CoEECs. Indeed, multitudes of halogenated substances that have the potential to persist, bioaccumulate, and be toxic in the environment still need to be identified [12–15].

An increasing number of recent publications have reported the presence of a series of mono- and polyhalogenated carbazoles, which have been mainly found in sediment and soil samples [16–20]. The majority have been unexpectedly identified during targeted analyses for organic pollutants including brominated flame retardants [16,19] and organochlorine pesticides [21], or during subsequent non-targeted analyses of samples previously analyzed for other potential contaminants such as polycyclic aromatic hydrocarbons (PAHs), polychlorinated dioxins and furans (PCDD/Fs), and polychlorinated biphenyls (PCBs) [18,20,22]. One of the earliest reports on the occurrence of a chlorinated carbazole in sediments obtained in the Great Lakes region was in the early 1980s. A site was contaminated by dye industry waste in the Buffalo River, Buffalo, New York [23] Three decades after, an increase interest for monitoring this potential group of CoEECs is observed. halogenated carbazoles have already been reported in soils and sediments in Germany [19,21], marine sediments in Greece [22], and freshwater lake and stream sediments in the Great Lakes region of North America [16–18,24].

Extensive characterization of these emerging compounds, including potential sources and toxicity, has been rarely described in the literature. Different hypotheses have been proposed regarding sources of halogenated carbazoles including: (i) natural synthesis, specifically through halide catalysis with peroxidase enzymes [25], (ii) as by-products from the dye industry [23], more specifically indigo dyes [26], and (iii) production as a by-product of the combustion of tribromoaniline [27]. Due to their conformation and planarity, halogenated carbazoles are likely to have biological activity similar to dioxin-like compounds, and this has now been demonstrated for the 3,6-dichlorocarbazole [21,28] and more recently for a series of mono-to tetra-halogenated carbazoles [29,30]. More importantly, Fang et al. recently demonstrated, for

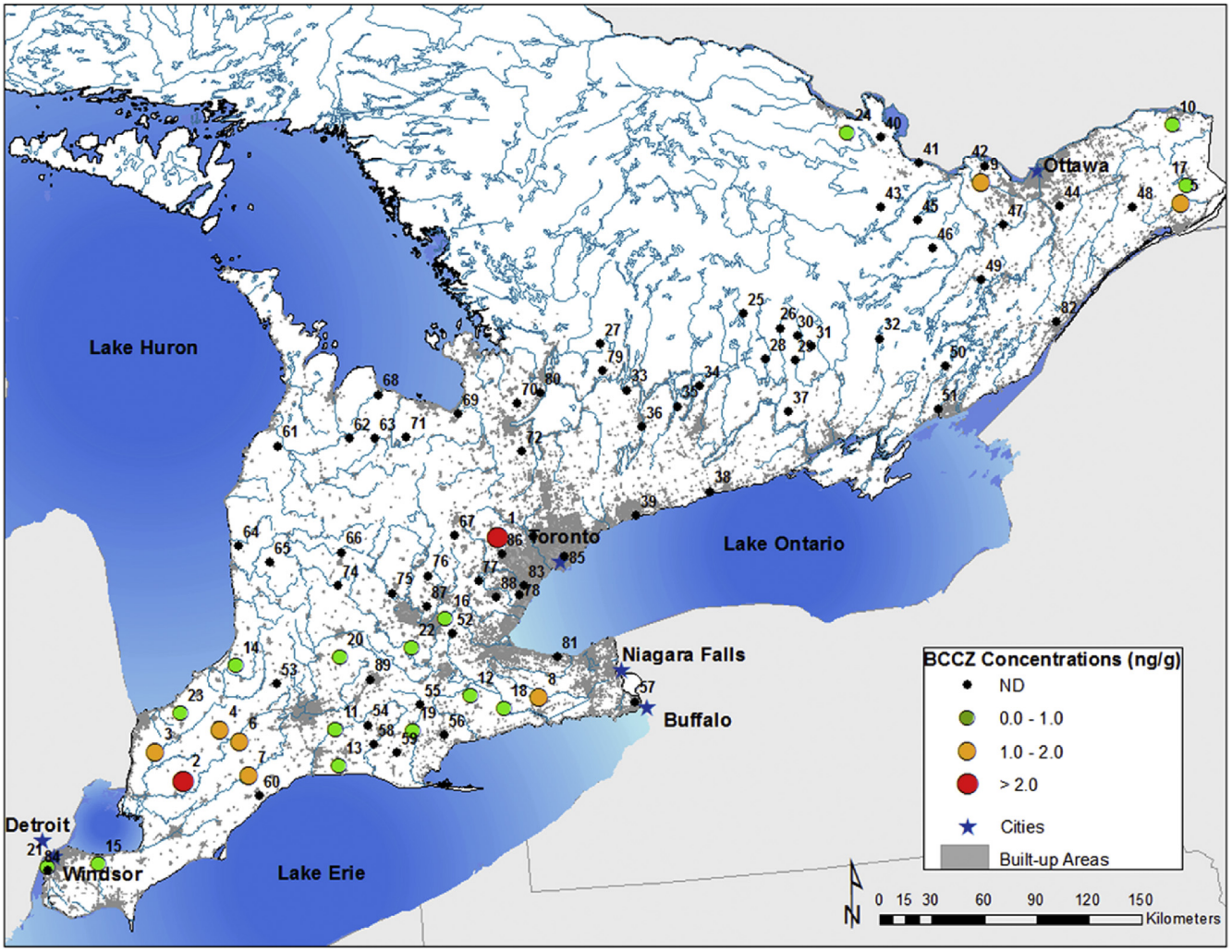

Fig. 2. Graphic map of sampling locations and BCCZ hit locations.