Chemosphere 88 (2012) 1332–1339

Contents lists available at SciVerse ScienceDirect

Chemosphere

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

Emission profiles of polychlorinated dibenzodioxins, polychlorinated dibenzofurans (PCDD/Fs), dioxin-like PCBs and hexachlorobenzene (HCB) from secondary metallurgy industries in Portugal

Pedro Antunes [a], Paula Viana [a], Tereza Vinhas [a], J. Rivera [b], Elvira M.S.M. Gaspar [c,*]

[a] Reference Laboratory of Environmental Portuguese Agency, Rua da Murgueira, 9/9A, Zambujal 2611-865 Amadora, Portugal
[b] Instituto de Investigaciones Quimicas y Ambientales,CSIC, Departamento de Ecotecnologıas, Laboratorio de Dioxinas, C/Jordi Girona, 18, 08034 Barcelona, Spain
[c] Departamento de Química, CQFB-Requimte, Faculdade de Ciências e Tecnologia, Universidade Nova de Lisboa, Quinta da Torre, 2825-114 Caparica, Portugal

HIGHLIGHTS

- ▶ Atmospheric persistent organic pollutants emissions.
- ▶ Secondary metallurgy industry emissions in Portugal.
- ▶ Study of emission factors and total emission amounts of PCDD/Fs, dioxin-like PCBs and hexachlorobenzene (HCB).
- ▶ Congener patterns were characterized and are discussed.
- ▶ A brief evaluation of Portuguese citizen's exposure.

ARTICLE INFO

Article history:
Received 20 June 2011
Received in revised form 19 April 2012
Accepted 19 May 2012
Available online 15 June 2012

Keywords:
PCDDs
PCDFs
PCBs
Persistent organic pollutants
Emissions
Metallurgy industry

ABSTRACT

This paper reports, for the first time, a study of dioxin emissions from 10 siderurgies and metallurgies, secondary copper, aluminum and lead metallurgies, in Portugal. The study reports the emission factors and total emission amounts of PCDD/Fs, dioxin-like PCBs and hexachlorobenzene (HCB). The congener patterns were characterized and are discussed. The results showed that the total amount of PCDFs is higher than PCDDs in flue gas of each industrial unit. The toxic equivalent emission factors of pollutants emitted are 3098–3338 ng I-TEQ t^{-1} for PCDD/Fs and 597–659 ng I-TEQ t^{-1} for dioxin-like PCBs in siderurgies production (total estimated emission amounts released to atmosphere of 3.9–4.5 g I-TEQ yr^{-1}), 50–152 ng I-TEQ t^{-1} for PCDD/Fs and 24–121 ng I-TEQ t^{-1} for dioxin-like PCBs in ferrous foundries production (total estimated emission amounts released to atmosphere of 0.0010–0.0016 g I-TEQ yr^{-1}) and 5.8–5715 ng I-TEQ t^{-1} for PCDD/Fs and 0.49–259 ng I-TEQ t^{-1} for dioxin-like PCBs in non-ferrous foundries production (total estimated emission amounts released to atmosphere of 0.00014–0.12 g I-TEQ yr^{-1}). The HCB emission from siderurgies production is 0.94–3.2 mg t^{-1} (total estimated emission amounts released 0.94–3.8 g yr^{-1}), being much smaller, residual, in the emissions of the other types of plants (0.0012–0.026 mg t^{-1} production and total estimated emission amounts released to atmosphere of 0.013–1.7 mg yr^{-1}).

1. Introduction

The Stockholm Convention on Persistent Organic Pollutants (POPs) (Stockholm Convention, 2003) was adopted in 2001 to protect human and environment against POPs. Under the Stockholm Convention release inventory of unintentional POPs have to be established and maintained in order to be possible the release reduction. The EU created, the "Seveso Directive" (Fiedler, 2007; Ba et al., 2009) and other Directives (Directive 82/501/CEE, Directive 96/82/EC and Directive 96/56/EC), to minimize the production of these substances.

The EU has also adopted in 2003 an "Environment and Health" strategy (Environment and Health strategy, 2003) in order to foster effective policy making regarding environment and health issues. The objectives of the proposed strategy are: (1) to reduce the disease burden caused by environmental factors in the EU; (2) to identify and to prevent new health areas threats caused by environmental factors; (3) to strengthen EU capacity for policy making in this area. Organohalogens have been integrated in this strategy.

A number of countries have already developed national inventories of polychlorinated dibenzo-*p*-dioxin (PCDD) and polychlorinated dibenzofuran (PCDF) emissions to atmosphere (Eduljee and

* Corresponding author. Tel.: +351 212949649; fax: +351 212948550.
E-mail address: elvira.gaspar@fct.unl.pt (E.M.S.M. Gaspar).

0045-6535/$ - see front matter © 2012 Elsevier Ltd. All rights reserved.
http://dx.doi.org/10.1016/j.chemosphere.2012.05.032

Dyke, 1996; Buckley-Golder, 1999; Chen, 2004; Cleverly, 2005; Yu et al., 2006; Lin et al., 2007). The reason is the toxicity of them – they are considered one of the most toxic pollutants known to human, and have acute and chronic effects including carcinogenicity, immunotoxicity, teratogenicity, reproductive and neuroendocrine effects (Yu et al., 2006; Kodavanti and Curras-Collazo, 2010). Studies have shown that secondary metallurgy industry is considered as an important source of PCDD/Fs. The reason is derived from incomplete combustion of organic material that happens during incineration processes which is used in metallurgy industries (Ba et al., 2009; Stieglitz et al., 1997).

In Portugal the limit value is established by Decree-Law No. 85/2005, of April 28, for the emission of PCDD/Fs, but it is only applicable to the waste incineration plants and waste co-incineration plants. The value, 0.1 ng TEQ N m^{-3}, is the limit value of dioxins and furans emission, calculated taking into accounts the 17 congeners (applying the I-TEF – International Equivalence Factors). For the other sectors of industry, like siderurgies and metallurgies, secondary copper, aluminum and lead metallurgies, there is no legal limit of emission established. Nevertheless the Environmental Portuguese Agency (APA – Agência Portuguesa do Ambiente) requires the characterization of emissions of stationary sources from those industries two times a year. The total number of siderurgies, non-ferrous foundries and ferrous foundries existent in Portugal are 141 (5 siderurgies and 136 ferrous and non-ferrous foundries).

This paper reports, for the first time, the study of the emissions from 10 of the biggest siderurgies and metallurgies, secondary copper and aluminum metallurgies, in Portugal. The study reports the emission factors and total emission amounts of PCDD/Fs, dioxin-like PCBs and hexachlorobenzene (HCB). All the plants of this study belong to category 2 (Production and processing of metals) of the European Directive No. 2008/1/EC of the European Parliament and of the Council, of 15 January 2008, concerning integrated pollution prevention and control (IPPC): two belong to category 2.2 (Installations for the production of pig iron or steel – primary or secondary fusion – including continuous casting, with a capacity exceeding 2.5 tonnes per hour), another two belong to category 2.4 (ferrous metal foundries with a production capacity exceeding 20 tonnes per day) and the last six belong to category 2.5B (for the smelting, including the alloyage, of non-ferrous metals, including recovered products, (refining, foundry casting, etc., with a melting capacity exceeding 4 tonnes per day for lead and cadmium or 20 tonnes per day for all other metals). The congener patterns were characterized and are discussed. It will contribute to a better evaluation of the quality of atmosphere and because these compounds are highly persistent, bio accumulative and cause adverse effects the study will also contribute to the evaluation of Portuguese citizen's exposure to them.

2. Materials and methods

The analytical methodology used in this study was based on EN 1948 (NP), parts I, II, III (for PCDD/Fs determination), on the USEPA Method 1668 (for dioxin-Like PCBs determination), and on internal method (for HCB determination). The study was divided in two different stages; the first begun with the implementation and validation of the analytical method and the second refers to the measure of emissions in different plants of Portugal (Fig. 1) making use of the tools developed in the initial stage (siderurgies, ferrous foundries and non-ferrous foundries).

2.1. Standards and reagents

PCDD/Fs native standards for the recovery tests (EPA 1613PAR), PCDD/Fs internal standards for sampling (EN 1948SS), PCDD/Fs internal standards for extraction (EN 1948ES), PCDD/Fs internal standards for injection (EN 1948IS) and PCDD/Fs calibration standards (EN 1948 CS2–CS5), all in nonane solution, were purchased from Wellington Laboratories (Ont., Canada). Dioxin-like PCBs native standards for the recovery tests (WP-STK), dioxin-like PCBs internal extraction standards (WP–LCS), dioxin-like PCBs internal injection standards (WP–ISS) and dioxin-like PCBs calibration standards (WP CS1–CS7), all in nonane solution, were also purchased from Wellington Laboratories (Ont., Canada). All internal standards are $^{13}C_{12}$-labelled compounds with exception of the EPA 1613PAR and the WP-STK used in the recovery test for native compounds. HCB internal standard for injection (PCB IUPAC #198) and HCB calibration standards (HCB in powder with 99.5% of purity) were purchase from Dr. Ehrenstorfer. All used solvents are from Merck (pesticide grade; Darmstad, Germany). Power-prep columns are from Power Prep (Fluid Management System, Waltham, MA, USA); silica (19 cm), basic alumina (11 g, 19 cm) and carbon/celite (0.34 g, 4 cm) column were used.

Fig. 1. Location of siderurgies (E1 and E2), ferrous foundries (E3 and E4) and non-ferrous foundries (E5–E10).

2.2. Method validation

For validation of the method, clean adsorbents (polyurethane foam – PUF and glass fibber filter) were fortified with a known