Chemosphere 91 (2013) 838–843

Contents lists available at SciVerse ScienceDirect

Chemosphere

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

Dioxins and furans releases in Iranian mineral industries

E. Rezaei [a], A. Farahani [a], A. Buekens [b], T. Chen [b], S.Y. Lu [b,*], M. Habibinejad [a], F. Damercheli [a], S.H. Andalib Moghadam [a], M. Gandomkar [a], A. Bahmani [a]

[a] Department of Environment, Iran Mineral Processing Research Center, Karaj, Iran
[b] State Key Laboratory of Clean Energy Utilization, Zhejiang University, Hangzhou 310027, China

HIGHLIGHTS

- Emissions of PCDD/Fs of Iranian mineral industries were investigated and estimated.
- PCDD/Fs emissions from eight major metallurgical and cement plants were estimated.
- Samples from steel plant and cement plant were analysed for PCDD/Fs.
- The dioxins loads of the tested samples are unusually low.
- The result can confirm the necessity and feasibility of sampling gaseous effluents.

ARTICLE INFO

Article history:
Received 6 June 2012
Received in revised form 20 December 2012
Accepted 16 January 2013
Available online 13 March 2013

Keywords:
Cement
Dioxins
Direct reduction
Integrated iron & steel production
Primary aluminium and copper production
UNEP Toolkit

ABSTRACT

In this project, emissions of Poly-Chlorinated Dibenzo-p-Dioxins and Dibenzo-Furans (PCDD/Fs) were investigated and estimated for selected Iranian mining and ore processing industries, such as integrated iron & steel plant, primary production of aluminium and copper metal, and the production of cement. As a first step of this study the annual emission of PCDD/Fs was estimated at 120 g TEQ annum^{-1} on the base of the UNEP standardised Toolkit for identification and quantification of dioxin and furan releases. Steel and cement were identified as major emission sources and earmarked for further scrutiny. For that reason, filter dust arising in these plants was sampled and analysed, as well as all raw materials employed. After extraction and clean-up according to standard methods, the resulting liquid samples were analysed and quantified by HRGC–HRMS. Complementary analyses using methods such as XRF, TGA/DTA were performed and the emission results statistically evaluated, in order to put PCDD/F emissions in perspective. It is concluded that the dioxins load of cement dust is unusually low, following the low carbon in raw materials, the use of natural gas as a fuel and the absence of waste incineration. Also the production of iron by direct reduction of ore is a low dioxins process; dioxin loads in dust are as usual – correlated with the presence of catalytic metals. Loss on ignition and chlorine are anti-correlated with the main earth elements and with sulphur oxides.

1. Introduction

Poly-Chlorinated Dibenzo-p-Dioxins and Dibenzo-Furans (PCDD/Fs), in brief dioxins, form a generic group of 75 PCDD congeners and 135 PCDF congeners (chlorination level $P = 1–8$). Congeners containing up to three chlorine atoms are considered of little toxicological significance. Congeners with chlorine atoms substituted in the lateral 2, 3, 7 and 8 positions of the aromatic rings, however, create substantial health and environmental hazards. Increasing the substitution level from four to eight chlorine atoms markedly decreases dioxins potency, as expressed in Toxicological Equivalence or TEQ units (WHO, 1998).

Dioxins show low vapour pressure, very low water solubility, high octanol/water partition coefficients; they adsorb strongly to particles and surfaces and are resistant to degradation under environmental conditions. Their inherent stability, persistence in the environment and high fat solubility results in lipophilic bio-concentration and accumulation in the food chain. Almost all individual PCDD and PCDF congeners have been identified in emissions from thermal and industrial processes and as a consequence are found in environmental matrices such as soil, sediment, plants, air and water, although their low aqueous solubility also means that they are largely immobile in soils and can hardly be detected in water. Dioxins are trace contaminants in a number of chemical products, e.g. those derived from chlorophenols. They are unintentionally formed in most thermal, metallurgical and combustion processes, mainly between 250 and 450 °C.

* Corresponding author. Tel.: +86 571 87952628; fax: +86 571 87952438.
E-mail address: lushy@zju.edu.cn (S.Y. Lu).

0045-6535/$ - see front matter © 2013 Elsevier Ltd. All rights reserved.
http://dx.doi.org/10.1016/j.chemosphere.2013.01.064

In this study, information from selected industrial Iranian plants is presented and analysed to investigate both the necessity and feasibility of further sampling the actual gaseous effluents. The project is conducted within the frame of the Stockholm Convention on Principal Organic Pollutants (POPs) to which Iran has subscribed; the results from this study can be evaluated against those of the National Inventory (UNEP, 2008).

2. Materials and methods

2.1. Paper study

This study was accomplished in two parts:

(1) Applying the UNEP standardised Toolkit for identification and quantification of dioxin and furan releases to estimate the annual emissions of PCDD/Fs from Iranian mining industries.
(2) Next, the flow sheet of all plants was studied, dust samples were taken at appropriate locations of selected plants, and analysis of tetra-to octa-chlorinated dioxins and furans was performed on the most relevant samples from cement and steel plant by HRGC/HRMS. Dust analysis alone is insufficient to characterise these outputs (the finest dust, eluding collection, might carry a higher load), but the values given in Table 1 already allow appreciating the gravity of emissions and the location of the most important sources of dioxins, further treated anonymously.

First eight major industrial plants were selected within our scope of mining related industries and then the Toolkit questionnaires were prepared and dispatched to the plant operators. The plants were categorised in two major groups of the UNEP Toolkit, i.e. as primary production (a) of ferrous and nonferrous metals, and (b) of cement (natural gas-fired, no waste co-firing). Then, according to the criteria presented in the Toolkit and detailed information gathered from aforementioned questionnaires, subcategories as well as applicable PCDD/Fs emission factors were chosen for different compartments (i.e., air, water, land, products, and residues) (EN 1948-2, 1997).

2.2. Experimental work

2.2.1. Sampling

In this study dust samples were seized after selecting suitable sampling locations, identified after analysis of flow-sheets related to the relevant production and off-gas cleaning plant. The partitioning of dioxins between gas phase and particulates is still unknown. Still, it is plausible that low dust load corresponds with low gas load; thus, the level of dioxins concentration is used as criterion for identifying the locations that need further scrutiny.

2.2.2. Sample pre-treatment, clean-up and analysis

All sample bottles were cleaned thoroughly before using and prepared according to standard method EN-1948. Samples were put in cleaned amber glass bottles, then closed using PTFE-lined screw-caps seals and transferred to the laboratory and stored at sub-ambient temperature (<4 °C)(Kudlak et al., 2007) to avoid losses or prevent contamination.

Sample extraction allows transferring the analytes (PCDD/F or PCB) into the solvent and removing the bulk of sample matrices. The extraction procedure follows Method 1613 (US EPA, 1994a, 1994b). The analysis was conducted by HRGC/HRMS on a 6890 Series gas chromatograph (Agilent, USA) and coupled to a JMS-800D mass spectrometer (JEOL, Japan).

Table 1
PCDD/Fs distribution (% of total TEQ) and total concentration (pg I-TEQ g^{-1} dust) in direct reduction steel plant samples.

Congeners	A	B	C	D
2,3,7,8-TCDD	N.D.	N.D.	5.5	N.D.
1,2,3,7,8-PeCDD	N.D.	N.D.	11.7	N.D.
1,2,3,4,7,8-HxCDD	N.D.	N.D.	2.6	0.4
1,2,3,6,7,8-HxCDD	N.D.	6.5	8.3	1.0
1,2,3,7,8,9-HxCDD	4.5	7.3	5.9	1.0
1,2,3,4,6,7,8-HpCDD	1.9	3.3	5.2	0.4
OCDD	0.6	N.D.	0.7	0.1
2,3,7,8-TCDF	6.5	5.7	4.2	9.4
1,2,3,7,8-PeCDF	5.2	4.9	2.6	3.0
2,3,4,7,8-PeCDF	50.0	43.1	48.8	62.2
1,2,3,4,7,8-HxCDF	9.1	9.8	10.1	7.3
1,2,3,6,7,8-HxCDF	7.1	9.8	7.1	7.0
1,2,3,7,8,9-HxCDF	3.9	4.1	1.1	1.4
2,3,4,6,7,8-HxCDF	9.1	9.8	10.8	6.7
1,2,3,4,6,7,8-HpCDF	1.9	2.4	2.9	1.3
1,2,3,4,7,8,9-HpCDF	0.6	0.8	0.4	0.3
OCDF	0.6	N.D.	0.1	0.1
Sum I-TEQ, % TEQ	100	100	100	100
Total I-TEQ, pg g^{-1}	1.54	1.23	53.5	15.8

N.D. = below the detection limit (estimated at 0.5 pg g^{-1}).

2.2.3. Other characterisation methods

Different methods such as XRF (PhilipsAnalytical V.B., Netherland) and TGA/DTA (STA 409 PC, Netzsch, Germany) were used to characterise the crude samples and investigate the influence of composition and thermal treatment on the selected samples. The results will be interpreted in a dedicated paper.

3. Results and discussions

3.1. First evaluation by using the UNEP Toolkit

The scope of activities of the Iran Mineral Processing Research Center comprehends: integrated iron & steel plant, production of cement, metallurgical cokes, primary aluminium and primary copper metal (no scrap feeding). Some of these activities are unique; others are distributed over several sites. Further analysis leads to (production capacities supplied from the answers to our detailed questionnaires):

(A) Cement industry is classified here as category 4, class 3, subcategory a of the UNEP Toolkit, i.e. Rotary Kiln clinker production, flue gas treatment with Electrostatic Precipitator (ESP) or fabric filter (FF) operating at a temperature above 200 °C. Therefore, the annual release of dioxins and furans from this type of plant (annual production capacity of 1,050,000 tonnes of clinker) was estimated at 0.63 g TEQ $annum^{-1}$ (for the air compartment) based on equations proposed in the Toolkit.
(B) In an integrated iron & steel company the following operations have been identified: primary iron & steel production, foundries, lime production, and continuous steel coil galvanization. Thus, the following plant classes and subcategories were identified:
  - (B1) Steel production, 4.8 M tons of steel per year, subcategory 2-c, Class 1, (due to the additionas coolant to the charge of scrap, possibly contaminated with chlorides);
  - (B2) lime production, 270,000 tons of lime per year, subcategory 4-b, Class 2, (application of fabric filter); and
  - (B3) Continuous coil galvanization plant, 200,000 t/a, subcategory 2-c (Galvanization part), Class 1, (no air pollution control systems).