Journal of Hazardous Materials 215–216 (2012) 259–265

Contents lists available at SciVerse ScienceDirect

Journal of Hazardous Materials

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

A preliminary investigation of unintentional POP emissions from thermal wire reclamation at industrial scrap metal recycling parks in China

Zhiqiang Nie, Minghui Zheng*, Guorui Liu, Wenbin Liu, Pu Lv, Bing Zhang, Guijin Su, Lirong Gao, Ke Xiao

State Key Laboratory of Environmental Chemistry and Ecotoxicology, Research Center for Eco-Environmental Sciences, Chinese Academy of Sciences, P.O. Box 2871, Beijing 100085, China

ARTICLE INFO

Article history:
Received 26 September 2011
Received in revised form 23 February 2012
Accepted 24 February 2012
Available online 3 March 2012

Keywords:
Unintentional POPs
Thermal wire reclamation
Emission source
Scrap metal

ABSTRACT

Thermal wire reclamation is considered to be a potential source of unintentional persistent organic pollutants (unintentional POPs). In this study, unintentional POP concentrations, including PCDD/Fs, dioxin like PCBs (dl-PCBs), polychlorinated naphthalenes (PCNs), hexachlorobenzene (HxCBz) and pentachlorobenzene (PeCBz), were quantified in flue gas and residual ash emissions from thermal wire reclamation at scrap metal dismantling parks in Zhejiang Province, China. The total average TEQ emissions of the investigated unintentional POPs from flue gas and residual ash in two typical scrap metal recycling plants ranged from 13.1 to 48.3 ng TEQ N m^{-3} and 0.08 to 2.8 ng TEQ g^{-1}, respectively. The dominant PCDD/F congeners were OCDD, 1,2,3,4,6,7,8-HpCDD, OCDF and 1,2,3,4,6,7,8-HpCDF, while PCB-126 and PCB-169 were the main contributors to the toxicity of the dl-PCBs. There were clear differences in the distribution dl-PCBs congeners contributing to the TEQ concentrations in the flue gas samples from the two plants. The PCN TEQs were dominated by PCN-66/67 and PCN-73. Although thermal wire reclamation in incinerators has been proposed as an alternative to open burning, there are still considerable environmental risks associated with regulated incinerators, and unintentional POP emissions from thermal wire reclamation sites need to be controlled by local government agencies.

1. Introduction

Unintentional persistent organic pollutants (unintentional POPs), such as polychlorinated dibenzo-p-dioxins and dibenzofurans (PCDD/Fs), polychlorinated biphenyls (PCBs), polychlorinated naphthalenes (PCNs), hexachlorobenzene (HxCBz) and pentachlorobenzene (PeCBz) are damaging to human health and the environment because of their toxicological and ecotoxicological effects [1,2]. Once released into various environmental compartments such as air, water, soil, sediment and food, they can be dispersed on global scale and pose serious health and environmental risks [3,4]. Thus, issues associated with unintentional POP formation, emission, transport, abatement, and environmental risk assessment have been intensively investigated [5–9]. Over the past decade, many sources of PCDD/Fs have been documented in national inventories, as required of signatories to the Stockholm Convention on Persistent Organic Pollutants [10]. In 2007, China established a National Implementation Plan (NIP) for the implementation of the Stockholm Convention. The report identifies that the major potential sources of PCDD/F releases to the air are ferrous and non-ferrous metal production (2486.2 g TEQ yr^{-1}), power and heat generation (1304.4 g TEQ yr^{-1}) and waste incineration (610.5 g TEQ yr^{-1}) [11]. Investigations have also been conducted on various anthropogenic combustion and thermal related sources, which are widely recognized as the major PCDD/Fs formation and emission pathway. However, there are still large uncertainties with regard to the environmental fluxes of PCDD/Fs for sources such as thermal wire reclamation and open burning processes. The open burning of waste wire for metal reclamation has been very common in recent decades in China. Strict environmental protection laws and regulations have now been implemented in China, and the open burning of waste wire is forbidden. Thermal wire reclamation in incinerators has been proposed as an alternative to open burning, but the environmental risks associated with this technique have not been evaluated.

There are various techniques used for thermal wire reclamation in different countries. Currently, there is little information on PCDD/F emissions from commercial scrap wire recovery facilities in developed countries [12–15], and studies on environmental releases of PCDD/Fs from thermal wire reclamation developing countries are also scarce. Additionally, there is almost no information available on emissions to the air of dioxin like PCBs (dl-PCBs), PCNs, PeCBz and HxCBz from thermal wire reclamation. Thus, the development of unintentional POP inventories from thermal

* Corresponding author. Tel.: +86 10 62849172; fax: +86 10 62923563.
E-mail address: zhengmh@rcees.ac.cn (M. Zheng).

0304-3894/$ – see front matter © 2012 Elsevier B.V. All rights reserved.
doi:10.1016/j.jhazmat.2012.02.062

wire reclamation is crucial for the evaluation of unintentional POP releases from scrap metal dismantling and recycling industries.

In recent years, the importation, disassembly and processing of scrap metal in China has developed rapidly, with millions of tons of copper, steel and aluminum recovered each year by dismantling and recycling waste electric motors, waste wire and cables, and waste hardware. In general, the waste is shipped from developed countries such as Japan, USA, the EU and Australia to mainland China, and scrap metal imports play an important role in the Chinese metal recycling industry. The scrap metal recycling industry has lead to significant social and economic benefits due to increased revenue and local employment. However, years of open burning of scrap metal and the dumping of processed materials has released huge amounts of contaminants into the environment. To regulate scrap metal dismantling activities and control pollutant emissions, two main industrial scrap metal dismantling and recycling parks in Zhejiang Province were established by the local government. Factories with disassembly licenses were moved into the industrial parks. The waste is dismantled as follows: first, most of the waste hardware and cables are dismantled using mechanical tools to recycle steel, copper, aluminum and plastic; second, the difficult to disassemble scrap metal, such as enameled wires and electronic motors, are burned in furnaces to facilitate metal recovery. It is the second step, the disassembly and incineration of enamel wires and electronic motors that can lead to unintentional POP releases with serious risks to human health and the environment. During this process, all the ingredients for unintentional POP formation are present, including carbon (in the wire sheaths), chlorine (PVC) and catalysts (Cu or Zn). Consequently, investigations into the concentrations and profiles of unintentional POPs from the incinerators at thermal wire reclamation factories would be very helpful in understanding the sources and exposure risks associated with these compounds.

The objective of this study was to provide a preliminary characterization of the emission concentrations of unintentional POPs and their toxic equivalents to improve understanding of the level of unintentional POP emissions from thermal wire reclamation in China. A further objective was to present and discuss the unintentional POP emissions profiles, which may provide useful information for establishing POP inventories for the thermal wire reclamation industry. After considerable investigation, two typical scrap metal dismantling factories were selected in the secondary resources industrial recycling parks in Zhejiang Province, China. These plants varied in scale, technological level and raw materials, allowing us to obtain credible and representative data.

2. Experimental

2.1. Sample collection

Zhejiang Province is a major scrap metal dismantling and processing area in China and has been for several decades. There are two secondary resource importing and processing parks with scrap metal import licenses issued by the Ministry of Environmental Protection (MEP) in China. After considerable investigation, combustion of scrap metal consists of smoldering and cracking in a furnace fitted with afterburners. In this study, five flue gas and two mixed residual ash samples were collected from two typical metal scrap dismantling plants: one plant burns waste electronic motors in Ningbo City (P1); and the other burns waste enameled wires in Taizhou City (P2). The approximate composition and content of waste electric motors and enameled wires from the two plants are provided in Table S1. The details schematic diagram of the incinerator and disposal procedure of thermal wire reclamation are given and supplemented in Fig. A and Supplementary Information, respectively. In P1, the waste electric motors were combusted in a cracking furnace. The furnace was equipped with two subsidiary combustion burners including a primary combustion chamber (PCC) and a secondary combustion chamber (SCC). Following the SCC was a flue gas cleaning system consisting of an afterburner and water-cooling equipment. The temperature of the flue gas was higher than 1000 °C in the afterburner and the temperature of the flue gas at the sampling point, after water-cooling, was lower than 100 °C. In P2, mostly waste enameled wires and a few waste rotors were burned in an incinerator. The generated flue gas from the SCC in the plant, however, was directly emitted to the atmosphere through an exhaust funnel with a 10-m stack. The temperature of the flue gas at the sampling point was higher than 500 °C. The collected flue gas samples passed through the whole combustion process in each plant. In each of the two plants, one composite residual ash sample was collected. The ash samples were collected from areas with different burning conditions and raw materials within the plants are detailed in Table 1.

Table 1
Basic operating conditions at the scrap metal disassembly and processing plants.

Denotation	P1	P2
Operating mode	Batch	Batch
Air pollution control device (APCD)	Water-cooling	No
Feeding materials	Electric motors	Enamel wires
Run time (h/batch)	5	3
Capacity (tons batch^{-1})	19	30
Auxiliary fuel	Heavy oil	Heavy oil
Flue gas temperature of sampling point (°C)	60.3	506.8
Temperature of PCC[a] (°C)	205–658	220–560
Temperature of SCC[b] (°C)	680–1025	310–720
O_2 content of flue gas in PCC (%)	5	8
O_2 content of flue gas in SCC (%)	12	10
Average flue gas flow (N m^3/h)	5954	4927
O_2 content in flue gas of sampling point (%)	16.8	14
CO_2 content in flue gas of sampling point (%)	2.4	4
Moisture content in flue gas of sampling point (%)	8.4	2.8
The volume of flue gas samples (N m^3)	1.9–2.6	1.9–2.4

[a] Primary combustion chamber.
[b] Secondary combustion chamber.

The flue gas samples were collected with an automatic isokinetic sampling system (Isostack Basic, TECORA, Italy). The selected sampling points at each plant were located downstream of the secondary combustion chamber or water-cooling device. Prior to collection, the O_2 and CO_2 contents, and flue gas temperature at the sampling points were measured using a Testo 355 flue gas analyzer (Testo, Germany). The sampling system consisted of a filter (25 mm i.d., 90 mm length, silica glass microfiber thimble, Whatman, UK), a condensing system, and an adsorbing resin (Amberlite XAD-2, Supleco, USA). The resin was spiked with a $^{13}C_{12}$-labeled PCDD/Fs internal standard before sampling was initiated. The residual ash samples were collected from the bottom of the furnaces after combustion.

2.2. Sample extraction and analysis

The samples were analyzed for PCDD/Fs and dl-PCBs in accordance with US EPA Methods 23 and 1668A. The flue gas and about 2–3 g of residual ash samples were pretreated and analyzed for specific PCDD/F and dl-PCB congeners. The samples were spiked with known amounts of $^{13}C_{12}$-labeled internal standards before extraction. The sample extraction, cleanup and instrumental analysis for PCDD/Fs and dl-PCBs determination are described in detail by Ba et al. [16]. The extraction and cleanup of PCNs, HxCBz and PeCBz