EMISSION OF PCDD/Fs FROM STEEL MAKING, WASTE INCINERATION, CEMENT KILN AND PAPER PRODUCTION IN VIETNAM

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Introduction

The issue of dioxin contamination from Agent Orange in Vietnam has long been well known and received considerable attention during the past decades. Polychlorinated dibenzo-p-dioxins and polychlorinated dibenzofurans (PCDD/Fs) unintentionally released from thermal processes of various industries have recently been of great concern due to their long term adverse effects to human health and the environment. Over the last decade, many industrial sources of unintentional PCDD/Fs have been reported in national inventories as required to the signatories of the Stockholm Convention on Persistent Organic Pollutants (POPs)[1]. While PCDD/Fs emission from industry based on actual sampling and chemical measurement has been extensively studied in developed countries, very limited information is available in developing countries including Vietnam.

This paper presents results of the BAT/BEP Project to quantify PCDD/Fs emissions from some selected industrial sectors in Vietnam, which is supported by the Global Environment Facility (GEF) through United Nations Industrial Development Organization (UNIDO). Residue concentrations of PCDD/Fs in different industrial samples such as stack gas, ash and dust were examined to understand levels and emission characteristics of PCDD/Fs unintentionally releases from 04 sectors, steel making, waste incineration, cement kiln co-firing hazardous wastes and paper production.

Materials and methods

Stack gas and fly ash samples were collected from an electric arc furace (EAF) steel-making plant, 02 industrial waste incinerators, a cement kiln co-firing hazardous wastes and a paper production plant. Dust were collected only at cement kiln. The stack gas (both particulate and gas phases) in each plant was sampled using isokinetic Method 23 of the United States Environment Protection Agency (U.S EPA)[2]. Stack gas samples were taken using the ESC C5000 sampling train (Environment Supply Company, USA). Particulate phase was collected on a quartz fiber filter (QFF, Pall Corporation, USA). Semi-volatile organic compounds (SVOCs) including PCDD/Fs in gas phase was pumped through a condenser and trapped in a chamber containing XAD2 resin. The isokinetic percent for stack gas samplings conducted in this study were ranged from 95 to 103 %, which were in acceptable range of US EPA method 23 (90-110 %). In order to control cross contaminations, travel blank and field blank samples were taken during each sampling survey.

Fly ash samples were taken from hoppers under the air pollution control devices (APCD) in which simultaneous sampling of stack gas samples to obtain representative samples from very large dusts. All samples were kept at 4^0C until chemical analysis.

PCDD/Fs concentrations were analyzed according to the Method 23 with some modifications. Samples (XAD2 resin and quartz fiver filter for stack gas samples) were Soxhlet extraced using toluen for 24 hours, The extracts were concentrated and treated by sulfuric acid (98%). Clean-up and fractionation steps were performed using pre-packed silica column, alumina column, and activated carbon column. Quantification of seventeen 2,3,7,8-substituted PCDD/Fs congeners were carried out by isotope dilution method using high-resolution gas chromatography coupled with high-resolution mass spectrometry (HRGC–HRMS) based on method 23 (U.S EPA, 1998) and method 1613B (U.S EPA, 1994). In this study, quantification was conducted using Micromass Autospec Ultima system (Waters, UK) with GC Agilent 7890A and DB-5MS capillary column (60 m x 250 µm i.d x 0.25 µm film thickness, J&W Scientific Inc., Folsom, CA). The average recovery value of ^{13}C-PCDD/Fs internal standards for stack gas and fly ash samples were ranged from 70 to 120 %. For stack gas samples, the method detection limits were 1.00 and 2.00 pg/Nm^3 for tetra-CDD/Fs and penta- to octa-CDD/F congeners, respectively. The detection limits of method for fly ash samples were 0.1, 0.5 and 1.0 ng/kg for tetra-CDD/Fs, penta- to hepta-CDD/Fs and octa-CDD/Fs congeners, respectively.

Results and discussion

PCDD/Fs levels and patterns in 04 industrial plants

Concentrations of PCDD/Fs in stack gas of waste incinerators showed the highest levels, followed in samples from paper production, steel making plant and cement kiln (Figure 1). Relatively high levels were found in waste incineration facilities, ranged from 0.383 - 9.8 ng TEQ/Nm^3, in which PCDD/Fs concentrations in some stack gas samples exceeded the international and Vietnam standard level of 0.6 ng TEQ/Nm^3. On the other hand, PCDD/Fs emission from EAF steel making, cement kiln and paper production showed apparently lower levels than those in waste incinerators. TEQ concentrations in stack gases from steel making plant, cement kiln and paper production ranged from 0.016 - 0.046 ng TEQ/Nm^3, 0.012 - 0.056 ng TEQ/Nm^3 and 0.043 - 0.161 ng TEQ/Nm^3, respectively. In waste incineration, factors such as composition of combustion wastes, temperature of secondary combustion chamber, and quality of air pollution control device, are considered to be important factors for the formation and releases of PCDD/Fs. Elevated concentrations of dioxins in waste incineration suggest improper operation and control of incinerators, and this fact deserves further monitoring measurement. Relatively lower levels found in steel making fuel gas samples could be due to the feeding material of the plant is mainly liquid cast iron, not scrap. Best practice measures within national cleaner production program have also been implemented during recent few years in the plant. PCDD/Fs emissions from steel making plant in Vietnam were comparable to those reported in a plant in Korea[3], but lower than those in Taiwan[4,5] and Germany[6]. As for waste incineration, it should be noted that PCDD/Fs residues in fuel gases from industrial waste incinerators monitored in this study were in the range from those reported in some municipal and industrial waste incinerators in industrialized countries in Europe[7] and Korea[8]. Best available techniques (BAT) and best environmental practices (BAT) measures are therefore particularly needed to introduce and replicate in waste incineration sector in an effort to gradually reduce unintentionally produced PCDD/Fs in Vietnam.

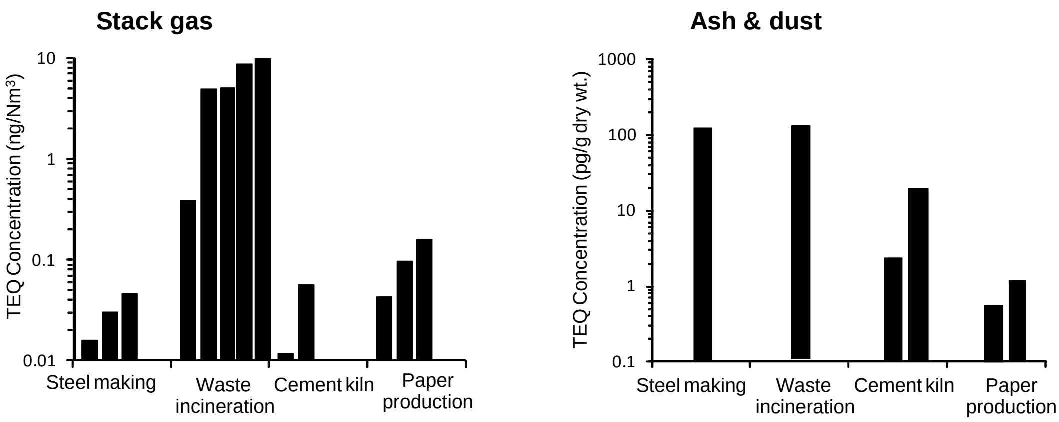

Fig. 1. TEQ concentrations of PCDD/Fs in stack gas, ash and dust from steel making, waste incineration, cement kiln and paper production plants in Vietnam

For ash and dust samples, residue concentrations remain relatively high in waste incineration and in steel making (Fig. 1). Fly and bottom ash samples from steel making and waste incinerators showed higher dioxin levels than those found in Taiwan. Despite lower levels in fuel gas, high residues found in ash samples from EAF steel plant suggest continuous monitoring measurement of dioxin emission in steel making industry in Vietnam.

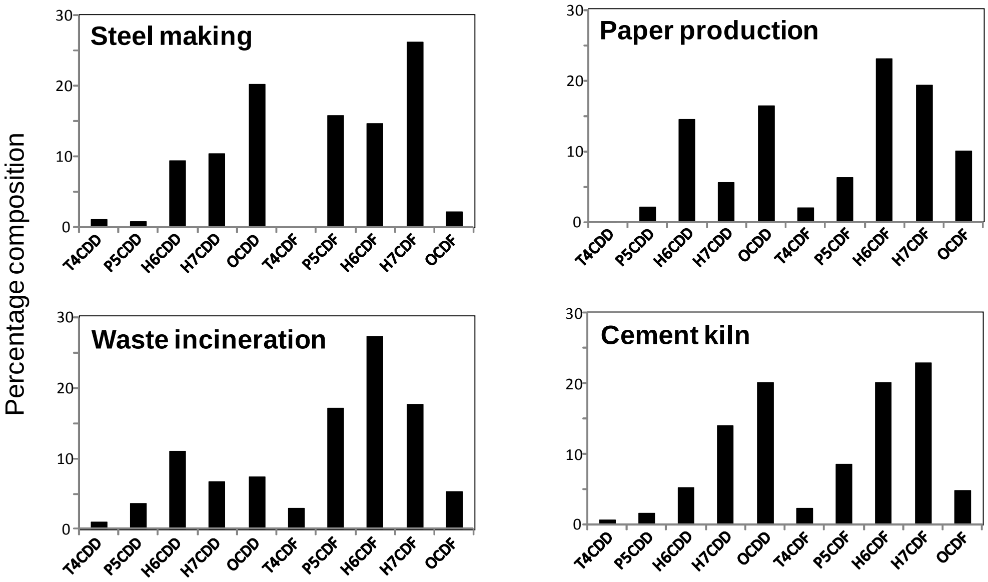

Fig. 2. Homolog profile PCDD/Fs in different industrial sources in Vietnam. Vertical bars represent the percentage of each homolog to total PCDD/Fs concentrations.

Congener profile in stack gas samples revealed relatively similar pattern among 04 industrial plants (Fig. 2). This is different to that found in our previous investigation in solid samples collected from various industrial sectors in Bien Hoa, south Vietnam[9]. Profile of fuel gas samples probably reflects more practical and recent emission status of PCDD/Fs as compared to those of solid samples such as ash, dust and soil. Congener profiles of fuel gas samples in all investigated industrial sites exhibited pattern of emission sources which are predominated by PCDF congeners. OCDD congener showed higher proportion in stack gases from steel and cement making plant, which is similar to those representing lower emission and background pattern. In general, PCDD/F profile in stack gas of waste incineration reflects high emission sources dominated by higher chlorinated dibenzofuran congeners than those in other industrial sites.

PCDD/Fs Emission factor of steel making plant

Based on the information on the operation and control of EAF steel making plant and TEQ concentration in fuel gases, emission factor of PCDD/Fs from steel making plant was estimated. The emission factors were calculated based on average flow rates of stack gas and the operating time per year of the plant. The emission factor of PCDD/Fs in EAF plant was estimated to be 0.93 µg TEQ/ton. This result was similar to that reported in China in 2012[10], but lower than in Taiwan[11], which is in the range of 1.84-2.44 µg I-TEQ/ton EAF steel. The PCDD/Fs emission factor in China in 2002 was 0.2 to 20 µg I-TEQ/ton for electric arc furnaces[12]. Iron and steel production plants have been identified as the sub-categories in ferrous and non-ferrous categories of UNEP Toolkit[13]. In this toolkit, emission factor of seventeen 2,3,7,8-substituted PCDD/Fs to the air of EAF using clean scrap were 3 µg TEQ/ton liquid steel. The emission factor of EAF plant investigated in this study (0.93 µg TEQ/ton) was lower than the value calculated by the toolkit.

This is among the first studies to report baseline information on the levels and patterns of PCDD/Fs emissions in different industrial sources from Vietnam. Our result suggest that waste incineration and steel making are potential source categories for PCDD/Fs releases. In response to the Stockholm Convention, comprehensive studies are currently implemented to measure PCDD/Fs emission and provide more in-depth characterization of the unintentionally produced PCDD/Fs from industry in Vietnam

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