EMISSIONS OF PCDD/ Fs FROM MEDICAL INCINERATORS IN HO CHI MINH CITY, VIETNAM

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Introduction

PCDD/F emissions from medical incinerators (MIs) can make a big concern for the health of local residents due to its toxic and deposition. Stack gas, bottom and fly ash, waste water, sludge emission from the main MIs in Ho Chi Minh City were investigated. The obtained result showed that there were the relative high PCDD/Fs concentration of congener in our samples. The evaluation of results based on the environmental impact of hazardous waste incinerators and hold to identify and quantify contaminant sources of PCDD/PCDF. The emission from incinerators has been treated by a wet and dry filter system which mainly focuses to CO, SO_2, NO_x, not yet considering to the toxic parameters such as PCDD/Fs. As resulted, the solid waste from the gas treatment system also contains PCDD/Fs. Thus this waste is a considerable source of PCDD/Fs and it is needed a strict regulation to manage and control it.

Materials and methods

*** Sample collection:** Exhaust samples were collected under US EPA method 23, Keika Ventures (US) sampling instruments, sampling speed class. PCDD/PCDF were adsorbed on the XAD-2 filter and internal standard solution containing 17 isomers of $^{13}C_{12}$ with the concentration of 50pg/μl of noname is added to XAD-2 before collecting samples. Wastewater samples (before undergoing wastewater treatment system) that were contained in glass bottles with sample volume: 2 liter, preserved with 1 mL of concentrated HCl for 1 liter of sample. Sludge samples (of wastewater treatment system) were weighed about 1 to 2 kgs. Samples were dried on aluminum foil in the laboratory from 5 to 10 days. Chemical ash samples: bags of exhaust treatment system were taken back. Bottom ash: Ash storage chambers were taken back. About 2 kgs of ash/kind/incinerator were taken under regulations on solid waste sampling of the Ministry of Natural Resources and Environment.

*** Sample extraction and analysis**

- Extraction:

Sludge samples (from wastewater treatment system): 2 grams of sludge were accurately weighed and mixed with 10 grams of anhydrous Na_2SO_4, 10 grams of Cu powder and internal standard substance ^{13}C. Soxhlet was extracted to 350 ml of Toluene in 24 hours. The extraction was concentrated by the evaporator (40^0C, 100mBar) until nearly dry, 20 ml of n-hexane was added and it was concentrated to approximately 2 ml. And then it was cleaned through three chromatographic columns: silica gel, florisil and alumina.

Wastewater samples: If there is too many residues which are visible in samples, use vacuum filter funnel to filter residues and dry samples in 60^0C in an hour and extract Soxhlet with 350 ml of dichloromethane in eight hours. Pour 1 liter of samples into extraction flask (or purified water stated above), perform three times of extraction (60 ml x 3 times) into 180 ml of dichloromethane. Add internal standard substance. Make samples anhydrous with Na_2SO_4 and coat them with dichloromethane. Wash samples with concentrated H_2SO_4 (1 to 3 times), and then NaCl, KOH and NaCl, put in the evaporator, turn into n-hexan solvent and then it was cleaned through three chromatographic columns: silica gel, florisil and alumina.

Stack gas samples: solid part: Filter paper + XAD-2 adsorbent, then added internal standard substance ^{13}C. Soxhlet was extracted to 350 ml of Toluene in 16 hours. Liquid part: HPLC distilled water solution + MeOH (used to coat the system) extracted with 50ml of Toluene, extracted 2 times. Include all the extracted solvent to put into the evaporator until the volume is 2 ml. The extraction was cleaned through three chromatographic columns: silica gel, florisil and alumina.

Ash samples: 20 gram of ash was accurately weighed and added internal standard substance ^{13}C. Let it stand in approximately in the dark. Add 300 ml of 3M HCl. Stir in three hours away from light, and then filter (including liquid part and solid part + filter paper). Liquid portion was liquid extracted in three times with 30 ml of dichloromethane. Continue to extract with 40 ml of n-hexane. Evaporate the solution to 2 ml in a round-bottomed flask and the flask was used for extracting Soxhlet and solid part with filter paper. Solid part + filter paper were dried at 105^0C in eight hours. Dried solid part + filter paper were mixed with 20 gram of anhydrous Na_2SO_4 + 10 gram of Cu powder. Use round-bottomed flask to extract such liquid solution + solid part: extracted

Soxhlet with 200 ml of toluene/ethanol (90/10) in eight hours and avoid sunlight. The extraction was cleaned through three chromatographic columns: silica gel, florisil and alumina.

Sample clean phase for all sample patterns: Column 1: mixture of silica gel (in order from bottom to top: 1 gram of activated silica, 2 gram of basic silica, 1 gram activated silica, 4 gram of silica acid, 1 gram of activated silica) and 2 gram anhydrous Na_2SO_4 at the top. Make desorption at column (1) with 90 ml of hexane. Column (2) with florisil (6 gram) was directly connected with a mixture of silica gel column. Column 2 was made desorption with 50 ml of dichloromethane/n-hexane (2:98), 150 ml of dichloromethane. Divide dichloromethane segment of column 2 to column 3: Column of basic alumina (4 gram of basic alumina Super I), 2 gram of anhydrous sodium sulfate. Fractionate with: a/ 10 ml of n-hexane, b/ 10 ml of n-hexane dichloromethane (92:8), c/ 15 ml of dichloromethane/n-hexane (3:2), d/ 20 ml of dichloromethane. Last phases c and d containing PCDD/PCDF were recovered and evaporated with liquid nitrogen to the volume of 200 μL. Transfer samples into glass insert and completely dry with liquid nitrogen at room temperature. Immediately dissolve 50μL of iso – octane solution containing internal standard substance. Measure samples on High Performance Gas Chromatography HRGC/HRMS.

*** Assay**

PCDD/PCDF compounds were identified and quantified by High Performance Gas Chromatography HRGC/HRMS (Micromass, UK). BPX-5 column (60m x 0,25mm x 0,25 μm). Temperature program was as follows: 140^{o}C/(4min)→220^{o}C/(8^{o}C/min)→260^o/(1,4^{o}C/min)→310^{o}C/(3^{o}C/min)/5min.

Using EI-SIM mode. Ion source temperature of 250^{o}C; electron energy 35eV; trap current 650μA; interface temperature is 260^{o}C.

Concentration of PCDD/PCDF was converted to the toxic equivalent I-TEQ coefficient according to toxicity i-TEF. TEQ concentration was calculated as total of 17 toxic isomers which were assigned as highly toxic. Corresponding factors (TEF) was according to WHO (2005).

***Quality control and quality assurance of testing results**

Test the quality of methods by EDF-2513, CRM 529 standard samples (for the sludge). Concentration of PCDD/PCDF obtained when analyzing standard samples is similar to that of the supplier. The accuracy of 2,3,7,8-TCDD in the standard methods used for the analysis was compared with NIST SRM 1614. The accuracy of 2,3,7,8 isomers which were PCDD and PCDF substituent was checked in comparison with reference method by inter-laboratory testing (Quebec-Canada) in water sample analysis with the code of CAL-76, 0531-2009 DMR, DMR 07,032,010 program for both soil and water patterns. The result was assessed as passed for all 17 isomers in soil and water patterns. The recovery rate of exhaust sampling standard is 78 to 92%. The recovery efficiency of sample patterns is 87 to 100%. Repeatability, reproducibility, uncertainty of measurement, detection limit, and quantification limit are also evaluated.

2.4 Research location

There are only two main locations managed by Ho Chi Minh City Environment Company(CITENCO) , to gather and treat medical wastes in the Ho Chi Minh City.

a/ Binh Hung Hoa Incinerator - capacity of 7 ton / day, Binh Tan District: This is an incinerator produced by Germany and it has multi-stage thermal degradation technology. It was designed to operate 7 ton/day in the form of batch and semi-continuous operation. The plant has had high quality technical systems and pollution control. The used energy is gas. The exhaust has been cooled by heat exchanger (water). Primary chamber's temperature is less than 1050^{o}C; secondary chamber's temperature is from 1050 to 1225^{o}C, and the exhaust's temperature is less than 180^{o}C. Pollution control and treatment system has used a filter bag, dry filter, activated carbon and $NaHCO_3$, and 15m chimney without caps. The incinerator is located far away from residential area.

b/ Dong Thanh incinerator site, Hoc Mon District: This is a closed incinerator produced by Swiss and it has multi-stage thermal degradation technology and rotary kiln. It was designed to operate 21 ton/day in the form of batch and continuous operation. The plant has had high quality technical systems and pollution control. The used energy is gas. The exhaust has been cooled by heat exchanger (water). Primary chamber's temperature is less than 1000^{o}C; secondary chamber's temperature is from 1030 to 1250^{o}C, and the exhaust's temperature is from 100 to 120^{o}C. Pollution control and treatment system has used a filter bag, dry filter, activated carbon and $NaHCO_3$, 20m chimneys. The incinerator is located far away from residential area.

c/ Input waste component to both incinerators: Since CITENCO has managed both Binh Hung Hoa and Dong Thanh incinerators, input wastes are all hazardous medical wastes after being collected and classified; medical wastes input which are identical and distributed daily depends on the capacity of each incinerator. General composition of solid medical wastes in the Binh Hung Hoa incinerator: 8% of organic waste, 21.5% of cotton tape, 1.5% of paper, 9.5% of glass, 30.5% of plastic, 3.5% of metal, 21.5% of rubber, and 4% of water [1].

Result and discussion

*** Research on exhaust samples**

To compare the emission of PCDD/PCDF from hazardous waste and medical waste incinerators, we conducted the sampling of the emission of other hazardous waste incinerators in Nha Be and Ba Ria – Vung Tau. In 26 samples of emission, i-TEQ value of emission sample in Ba Ria – Vung Tau was higher than the threshold of US-EPA standard (i-TEQ $_{limit:}$ 600pg/Nm^3) and Vietnam's standard (i-TEQ $_{limit:}$2300pg/Nm$^{3)}$ with a level of 1.85 times; the reason is that the component of hazardous waste contains pesticides. Compared with the EU and Singapore's standards (i-TEQ $_{limit:}$ 100pg/Nm^3), incinerators in Nha Be and Ba Ria – Vung Tau exceeded the threshold with the level of 2.69 ÷ 42.69 times. i-TEQ values of remaining incinerators were below regulated thresholds. In addition, according to a detailed assessment: There were TCDD compounds appearing in the research samples with the concentration ranging from 0.2971 ÷ 229.4395 pg/Nm^3 in medical incinerators of Nha Be < Ba Ria – Vung Tau; and there were TCDF compounds appearing in the analysis samples with the concentration ranging from 0.05 ÷ 335 pg/Nm^3 in medical incinerators of Nha Be < Ba Ria – Vung Tau. The impact of these hazardous compounds from waste incinerators is significant, because of pesticides contained in the burned wastes . There were PCDD/PCDF appearing in the research samples, in which: 2,3,4,7,8-PeCDF had the highest concentration of PCDF group. The ratio between PeCDF and PeCDD for all samples is higher1, which implies pollutants derived from synthetic substances were always more superior [2]. Findings of Dong Thanh incinerator showed the levels of PCDD/PCDF through years were lower the threshold of QCVN02: 2012/BTNMT. Value for inorganic parameters in the exhaust such as CO, SO_2, NO_2, O_2, HCl was very low for both medical incinerators. Moreover, Cd, Hg and Pb were found in the exhaust from both medical incinerators. We has studied further of total of PCB and we did not find total of PCB in the exhaust from both medical incinerators in Ho Chi Minh City.

***Research on ash samples**

- Fly /Chemical ash samples

In 15 samples of fly/chemical ash, there were TCDD compounds appearing in the fly/chemical ash with the concentration ranging from 10.7128 ÷ 111.3532 ng/kg for Binh Hung Hoa incinerator and 12.0912 ÷ 98.6522 ng/kg for Dong Thanh incinerator. However, compared with national technical regulation QCVN 07:2009/BTNMT (0.1 mg/kg for 2,3,7,8-TCDD), the appearance of TCDD in both incinerators met QCVN. There were 17 PCDD/PCDFs appearing in samples, in which: 2,3,4,7,8-PeCDF; 1,2,3,4,7,8-H_xCDF; 1,2,3,6,7,8-H_xCDF; 2,3,4,6,7,8-H_xCDF; 1,2,3,4,6,7,8-H_pCDF; OCDF had the highest concentration in PCDF group; similarly, 1,2,3,4,6,7,8-H_pCDD and OCDD had the highest concentration in PCDD group. However, chemical ash in all incinerators also contained 1,2,3,7,8,9-H_xCDF; 1,2,3,4,7,8,9-H_pCDF and 1,2,3,6,7,8-H_xCDD. The ratio between the PCDF and PCDD for all samples were higher 1, which implies pollutants derived from synthetic substances are always more superior [Everaert and Baeyens, 2002] [2,6]. According to the figure above, total content of PCDD/PCDF in fly/chemical ash samples of Binh Hung Hoa and Dong Thanh incinerators was lower the threshold compared to QCVN 07:2009/BTNMT (0.3 mg/kg # 300,000 ng/kg). To study and evaluate the toxicity of fly/chemical ash, we also studied heavy metal norms for both incinerators such as Hg, As, Pb, Cd and Zn aerosolized in normal evaporation temperature [3], and Pb result (from 12.3 to 14.9 mg/kg) exceeded three times compared to QCVN 07:2009/BTNMT (4 mg/kg) and PCB was not detected in samples (MLOD: 3 ppb).

-Bottom ash samples

In 15 samples of bottom ash, there were TCDD compounds appearing in the bottom ash with the concentration ranging from 7.0529 ÷ 84.0766 ng/kg for Binh Hung Hoa incinerator and 9.7731 ÷ 91.6350 ng/kg for Dong Thanh incinerator. However, compared with national technical regulation QCVN 07:2009/BTNMT (0.1 mg/kg for 2,3,7,8-TCDD), the appearance of TCDD in both incinerators met QCVN. There were 17 PCDD/PCDFs appearing in bottom ash samples; in which: 2,3,4,7,8-PeCDF; 1,2,3,4,7,8-H_xCDF; 1,2,3,6,7,8-H_xCDF; 2,3,4,6,7,8-H_xCDF; 1,2,3,4,6,7,8-H_pCDF; OCDF had the highest concentration in PCDF group; 1,2,3,4,6,7,8-H_pCDD and OCDD had the highest concentration in PCDD group for both incinerators. The ratio between the PCDF and PCDD for all samples are higher 1, which implies pollutants derived from synthetic substances are always more superior [Everaert and Baeyens, 2002] [2,6]. According to the figure above, total content of PCDD/PCDF in bottom ash samples of Binh Hung Hoa and Dong Thanh incinerators was lower the threshold compared to QCVN 07:2009/BTNMT (0.3 mg/kg # 300,000 ng/kg). To study and evaluate the toxicity of bottom ash [4], we also studied heavy metal norm for both incinerators such as Hg, Pb, Cd, however, such heavy metal and total of PCB were not detected in both incinerators.

-Research on sludge samples (from wastewater treatment system)

Traces of 1,2,3,7,8, 9-H_xCDD; 1,2,3,4,6,7,8-H_pCDD and OCDD were found in the Binh Hung Hoa incinerator's sludge and traces of 2,3,7,8- TCDD; 1,2,3,4,6,7,8-H_pCDD and OCDD were found in the Dong Thanh incinerator's sludge. Heavy metals such as Hg, Pb and Cd were detected to exceed the permitted norm of both incinerators; especially, the concentration of lead (Pb) (375 – 504 mg/kg) was higher QCVN 50:2013/BTNMT (73.4 – 96.2 mg/kg). However, total of PCB was not found.

-Research on wastewater samples

Binh Hung Hoa incinerator has quiet thermal degradation technology and high moisture waste, so the garbage should be pressed to reduce its moisture before being burned. Though garbage juice was not much, pollution level of BOD_5, COD and total N were very high [5], which should be strictly treated and managed. Traces of 2,3,4,7,8-PeCDF; 1,2,3,4,7,8-H_xCDF; 1,2,3,6,7,8-H_xCDF; 2,3,4,6,7,8-H_xCDF; 1,2,3,4,6,7,8-H_pCDF; OCDF; 1,2,3,4,6,7,8-H_pCDD and OCDD were found in both incinerators. In addition, results of waste water from exhaust treatment system showed that total of BOD_5, COD and N were higher QCVN 40: 2011/BTNMT Column B, which shows that organic components were not completely burnt. However, waste water from garbage juice and gas treatment system have been treated by wastewater treatment system of both plants.

-Results of the research on the exhaust showed that the content of PCDD/ PCDF through years is lower QCVN standard, and value parameters in inorganic gases such as CO, SO_2, NO_2, O_2 were low. Low concentration of HCl and the technology with 2 levels of incinerators met QCVN standard, which showed that the exhaust from medical waste incinerators of two medical waste incinerators of Ho Chi Minh City have been controlled. However, further research should be conducted on incinerator technology to meet higher standards on environmental protection. The distribution of PCDD/PCDF showed that OCDF; OCDD; 1,2,3,4,6,7,8-H_pCDF; 1,2,3,4,6,7,8-H_pCDD; 2,3,4,7,8-PeCDF; 2,3,4,6,7,8-H_xCDF had the highest concentration and contributed the most toxicity of i-TEQ of PCDD/PCDF for medical waste incinerators. Meanwhile, in hazardous waste incinerators, 2,3,4,7,8-PeCDF had the highest concentration in PCDF group. The ratio between the PCDF and PCDD for all samples were higher 1, which implies pollutants derived from synthetic substances are always more superior. Besides, other norms such as heavy metals, BOD, COD, total N and PCB were also studied to evaluate the toxicity of pollutants. Also, the research found out that garbage juice contained harmful substances, and sewage sludge contained relatively high amounts of metal, which shows the need to have appropriate treatment measures for each emission source. Incinerators meeting QCVN 02:2010/BTNMT on the design, operation process and thorough pollution treatment measures would ensure not to release the toxin into the environment. Chemical ash and bottom ash samples contained PCDD/PCDF lower the threshold, while heavy metal Pb content was 3 times higher QCVN 07:2009/BTNMT. Such ashes were pollution sources from medical waste incinerators, and we should have appropriate management plan to protect the environment.

Table: The results of TCDD of stack gas, chemical ash and bottom ash

Stack gas	Chemical ash	Bottom ash
0.2971 ÷ 229.4395 pg/Nm^3 in incinerators of Nha Be < Ba Ria – Vung Tau	10.7128 ÷ 111.3532 ng/kg for Binh Hung Hoa incinerator. 12.0912 ÷ 98.6522 ng/kg for Dong Thanh incinerator.	7.0529 ÷ 84.0766 ng/kg for Binh Hung Hoa incinerator 9.7731 ÷ 91.6350 ng/kg for Dong Thanh incinerator.

References

[1] Vietnam Institute for Tropical Technology and Environmental Protection (2002). *Survey to assess the effectiveness of medical waste incinerators in southern region.*

[2] Jindfich Petrlik et al (2005). *After Incineration: The toxic ash problem.* The International POP's Elimination Network's (IPEN) report.

[3] M.Cobo et al. (2009). *Characterization of fly ash from a hazardous waste Incinerator in Medellin*. Journal of Hazardous Materials 168 (2009) 1223-1232.

[4] Evanelos Gidarakos et al (2009). *Characterization and hazard evaluation of bottom ash Incinerator Produced from hospital waste*. Journal of Hazardous Materials 172 935-942.

[5] National Science Council and the Environmental Protection Administration, Executive Yuan, air pollution control fees science project report (Project number: NSC 88-EPA-Z- 008-002), (2002). *Evaluation of Dioxins Concentration Measurement and Removing Efficient in Waste Incinerator"s Exhaust.*

[6] Pai-Sheng Cheng, Ming-Sheng Hsu et al et al (2003). *Levels of PCDD/Fs in ambient air and soil in the vicinity of a municipal solid waste incinerator in Hsinchu.* Chemosphere 52 1389-1396.