Occupational exposure to PCDD/PCDF from industrial boilers at a whisky factory and vegetable oil factory in Samutsakorn Province, Thailand

S. Pongpiachan¹, T. Wiriwutikorn², C. Rungruang², K. Yodden², A. Sbrilli³, M. Gobbi³ & C. Centeno³

¹NIDA Centre for Research and Development on Disaster Prevention and Management, School of Social and Environmental Development, National Institute of Development Administration, Thailand ²Hazardous Substance Division, Waste and Hazardous Substance Management Bureau, Pollution Control Department (PCD), Bangkok, Thailand ³Stockholm Convention Unit, Environmental Management Branch,

Vienna, Austria

Abstract

It is well known that polychlorinated dibenzo-p-dioxins (PCDDs) and dibenzofurans (PCDFs) are carcinogens and mutagens, which are mainly released from industrial sectors. Fossil fuel fired utilities and industrial boilers are considered as two main sources responsible for the emissions of dioxins. As a consequence, the regional project "Demonstration of BAT and BEP in the Fossil Fuel-fired Utilities and Industrial Boilers in response to the Stockholm Convention on POPs", officially approved for full implementation by the Global Environmental Facility (GEF) in April 2010 in order to investigate the emissions of dioxins from various types of industrial sectors in ESEA (East and South East Asia) countries. This study aims to quantify the emissions of dioxins from industrial boilers at a whisky factory and vegetable oil factory in Samutsakorn Province, Thailand.

Keywords: PCDD/PCDF, mercury, dioxins, industrial boilers.



WIT Transactions on The Built Environment, Vol 134, © 2013 WIT Press www.witpress.com, ISSN 1743-3509 (on-line) doi:10.2495/SAFE130701

1 Introduction

Polychlorinated dibenzo-p-dioxins (PCDDs) and dibenzofurans (PCDFs) are ubiquitous environmental pollutants and classified as persistent organic pollutants (POPs) that are mostly of industrial origin. These compounds are generally acknowledged as dioxin-like compounds, or more basically 'dioxins.' Once dioxins released into the atmosphere as air pollutants, it can be directly transmitted to human body through inhalation and distributed across various environmental media such as marine, riverine and lake sediments, terrestrial soils, vegetation, water, biota, etc. Therefore, all human tissues have had measurable levels of dioxin congeners as detected by the most accurate methods. Tetrachlorodibenzo-p-dioxin (TCDD), the most toxic dioxin has an estimated half-life of 7-11 years in humans. Recent studies reveal the adverse health effects of dioxins which responsible for an enhancement in cancers, liver damage, endocrine disruption, neurotoxicity, reproductive disorders and various immune system alterations. According to our best knowledge, there is no known method to reduce an elevated dioxin human body burden. International publications of dioxin emission levels and its adverse health impacts are few in number and strictly limited to certain countries. The majority of studies have been focused in the US [1, 2], Denmark [3, 4], UK [5, 6], Italy [7, 8], Japan [9, 10] and China [11, 12] and other geographical regions. As a part of UNIDO (United Nation Industrial Development Organization)'s primary objective, which believes that competitive and environmentally sustainable industry has a crucial role to play in accelerating economic growth, reducing poverty and achieving the Millennium Development Goals, several attempts have been made in order to reduce dioxins' emissions from fossil fuel-fired utilities and industrial boilers particularly in developing countries.

With reference to the Stockholm Convention, the ESEA (East and South East Asia) countries are committed to reduce/eliminate UP-POPs emission releases. Formally launched on October 5, 2007, the ESEA Forum is a programmatic regional initiative of UNIDO on the introduction of the BAT/BEP measures on priority sectors defined by participating countries. The main objective of the Forum is to serve as a platform for information dissemination and exchange of experiences between countries in the region on different aspects of implementation of BAT/BEP and provide regular reporting on the impact of these in the industrial sectors cited in Annex C of the Convention. Countries have been grouped based on their priority sectors of interest, as mentioned in annex C of article 5 of the Stockholm Convention.

The regional project "Demonstration of BAT and BEP in the Fossil fuel-fired Utilities and Industrial Boilers in response to the Stockholm Convention on POPs", officially approved for full implementation by the Global Environmental Facility (GEF) in April 2010, is the first integral sectoral project of the ESEA BAT/BEP FORUM. In accordance with the relevant resolutions of the third session of the Conference of the Parties (COP3) of the Stockholm Convention (SC), the overall objective of the regional project aims at reducing and, where feasible, eliminating unintentionally produced POPs (UP-POPs) releases (in



particular, PCDDs – polychlorinated-dibenzo-para-dioxins and PCDFspolychlorinated-dibenzofurans) by enhancing guidelines and guidance on best available techniques and best environmental practices (BAT/BEP) for fossil fuelfired utilities and industrial boilers through addressing specific features of industry, common practices in the region and related socio-economic considerations. In addition, the project also targets the identification of possible options for the simultaneous reduction of PCDD/PCDFs and CO₂ from fossil fuel-fired utilities and industrial boilers in response to the Stockholm Convention and climate change requirements. While it focuses on the introduction of BAT/BEP measures, it also considers increasing energy efficiency, as required in Annex C Part V B (a)(iv) of the convention. The evaluation of the mercury emissions by specific monitoring programs has been added afterwards according to the raising concerns on these pollutants.

In particular, in Thailand two boilers in a whisky factory and vegetable oil factory have been selected as potential pilot facilities to implement the above indicated project activities. Industrial boiler selection criteria and BAT/BEP implementation program were discussed with company managers. It was agreed that the activities for BAT/BEP implementation will mainly focus on boiler modifications and efficiency improvement, as mean to simultaneously reduce the emissions of PCDD/PCDFs, mercury and CO₂. Sampling campaigns were carried out before the implementation of the related interventions in order to measure the background of pollutant releases.

2 Methodology

2.1 Dioxin

Undertake sampling and chemical determination of PCDD/PCDFs in the flue gases emitted by the stack of the boiler in the two factories and in samples of ashes released by the multicyclone and in samples of bottom ashes of the burning chamber

Solid residues were collected as follows:

- 1 sample representing 3 mixture samples taken from ashes of the multicyclone (morning, midday, and at the end of the sampling day).
- 1 sample representing 3 mixture samples taken from bottom ashes of the burning chamber.

Flue gas samples were collected as follows:

• 3 samples at the stack (one per day).

For the sampling of flue gases, the USEPA Method 23/23A, European Method EN 1948-1 were applied. For PCDDs/PCDFs analysis, the USEPA Method 1613B, USEPA Method 8290 or European Method EN 1948 2-3 were applied. All chemical analyses were conducted at SGS laboratories.



2.2 Trace gaseous species

During the sampling activity at the stacks, the relevant operational parameters in the sampled flue gases needed for normalization of data were measured and registered by manual methods or portable detectors. The parameters requested are:

• Temperature, pressure, gas velocity, gas flow rate, oxygen, H₂O content (humidity), CO and CO₂, SO_x, NO_x by portable detectors

Table 1:	Boiler information	at the whisky factory,	, Samutsakorn, Thailand.
----------	--------------------	------------------------	--------------------------

Information	Unit	Detail
Stack		
1.Height	m	~22
2.Diameter	m	0.8
Boiler	•	•
1.Fuel used	-	Fuel Oil
2.Fuel feeding rate	liters/hr.	- 329.5 (Date 15/08/2012)
		- 398.3 (Date 16/08/2012)
		- 385.4 (Date 17/08/2012)
3.Production rate of Ash	Kg/day.	- Fly ashes 8 kg/d
		 Bottom ashes 3 kg/d

Table 2:Boiler information at the vegetable oil factory, Samutsakorn,
Thailand.

Information	Unit	Detail
Stack		
1.Height	m	~25
2.Diameter	m	0.64
Boiler	I	
1.Fuel used	-	Coal
2.Fuel feeding rate	Kg/hr.	1,601.3
3.Capacity of boiler	Ton	16
4.Production rate of Ash	g/hr.	77

2.3 Quality control and quality assurance (QA/QC)

All SGS environmental laboratories have ISO 17025 accreditations and demonstrate the effectiveness to properly execute testing methods practices, inspection routines, data validation and employee competences. ISO 17025 is an



Traverse	(Fraction of Stat	cks Diameter fro	om Inside Wall t	o Traverse Poin	t)
Point		Num	nber of Traverse	Point on a Diar	neter	
Number	2	4	6	8	10	12
1	.146	.674	.044	.032	.026	.021
2	.854	.250	.146	.105	.082	.067
3		.750	.296	.194	.146	.118
4		.933	.704	.323	.226	.177
5			.854	.677	.342	.250
6			.956	.806	.658	.356
7				.895	.774	.644
8				.968	.854	.750
9					.918	.823
10					.974	.882
11						.933
12						.979

Table 3:	Location	of transverse	point in	circular	stacks.



international standard, which sets the general requirements for the competence of testing and calibration laboratories. In addition, QA/QC for emission air measurements are as follows:

- The isokinetic rate must be conducted and the result must be between 90 and 110%.
- Conduct sampling equipment leak check and equipment calibration.
- Conduct sample control using Chain of custody (COC) form for the sample delivery and controlling to laboratory.
- Conduct field blank to check about any contamination.

3 Results

3.1 Vegetable oil factory

The emission air quality of stack was monitored during July 31 and August 3, 2012, at the beginning and at the end of the PCDD/PCDF sampling and calculated at the temperature of 0° C, 11% oxygen pressure of 1 atm or 760 mm.Hg., dry basis, temperature of 25°C, 11% oxygen pressure of 1 atm





Table 4: Flow chart of dioxins analysis.

or 760 mm.Hg., dry basis and the temperature of 20°C, 7% oxygen pressure of 1 atm or 760 mm.Hg., dry basis.

At the temperature of 0°C, 11% oxygen pressure of 1 atm or 760 mm.Hg., dry basis, the total suspended particulate (TSP), SO₂, NO_x (as NO₂) and CO was calculated. TSP ranged from 165–463 mg/m³, SO₂ was 127–328 mg/m³, NO_x was 95–251 mg/m³ and CO was 1,241–2,759 mg/m³. The dioxins and furans (TEQ) were 0.0038–0.0089 ng 1-TEQ/m³. For stack condition measurement, the percent of O₂ was 14.73–16.08% (see Table 5).





Figure 1: Emission air sampling of stacks at the whisky factory at Samutprakarn Province, Thailand.





Figure 2: Ash sampling with wet cyclone at the whisky factory, Samutprakarn Province, Thailand.





Figure 3: Emission air sampling of stacks at the vegetable oil factory at Samutprakarn Province, Thailand.



Dioxin emissions from stacks at a vegetable oil factory at the temperature of 0°C, 11% oxygen pressure of 1 atm or 760 mm.Hg., dry basis.

						Sampling date				
			31/07/12			01/08/12			02/08/12	
Parameters	₽		at actual O ₂	at 0°C		at actual O ₂	at 0°C		at actual O2	at 0°C
		ng/Nm³	(0.C)	and 11% O ₂	ng/Nm³	(0°C)	and $11\% O_2$	ng/Nm³	(0°C)	and $11\% 0_2$
			(ng I-TEQ/Nm ³)	(ng I-TEQ /Nm ³)		(ng I-TEQ/Nm ³)	(ng I-TEQ /Nm ³)		(ng LTEQ/Nm ³)	(ng I-TEQ /Nm ³)
Determination of PCDD/PCDFs										
1.3 Total I-TEQ										
1) 2,3,7,-8TCDD	-	0.0007	0.0007	0.0011	0.0010	0.0010	0.0018	0.0005	0.0005	0.0010
2) 1,2,3,7,8-PeCDD	0.5	0.0024	0.0012	0.0019	0.0022	0.0011	0.0020	0.0021	0.0010	0.0021
 1,2,3,4,7,8-HxCDD 	0.1	0.0018	0.0002	0.0003	0.0015	0.0001	0:0003	0.0012	0.0001	0.0003
4) 1,2,3,6,7,8-HxCDD	0.1	0.0031	0.0003	0.0005	0.0034	0.0003	0.0006	0.0033	0.0003	0.0007
5) 1,2,3,7,8,9-HxCDD	0.1	0.0044	0.0004	0.0007	0.0036	0.0004	0.0007	0.0041	0.0004	0.0008
6) 1,2,3,4,6,7,8-HpCDD	0.01	0.0131	0.0001	0.0002	0.0088	0.0001	0.0002	0.0093	0.0001	0.0002
7) OCDD	0.001	0.0181	0.00002	0.00003	<0.0175	<0.00002	<0.00003	<0.0178	<0.00002	<0.00004
8) 2,3,7,8-TCDF	0.1	0.0010	0.0001	0.0002	0.0047	5000:0	6000'0	0.0049	0.0005	0.0010
 1,2,3,7,8-PeCDF 	0.05	0.0013	0.0001	0.0001	0.0019	0.0001	0.0002	0.0013	0.0001	0.0001
10) 2,3,4,7,8-PeCDF	0.5	6000.0	0.0005	0.0007	0.0012	0.0006	0.0011	0.0018	6000.0	0.0018
11) 1,2,3,4,7,8-HxCDF	0.1	0.0014	0.0001	0.0002	0.0016	0.0002	0.0003	0.0018	0.0002	0.0004
12) 1,2,3,6,7,8-HxCDF	0.1	6000:0>	60000.0>	<0.00014	0.0011	1000.0	0.0002	0.0016	0.0002	0.0003
13) 2,3,4,6,7,8-HxCDF	0.1	6000:0>	60000:0⊳	<0.00014	<0.008	60000:0>	<0.0002	60000⊳	60000.0>	<0.0002
14) 1,2,3,7,8,9-HxCDF	0.1	<0:000	6000000⊳	<0.00014	<0.008	60000.0>	<0.0002	60000⊳	60000.0>	<0.0002
15) 1,2,3,4,6,7,8-HpCDF	0.01	0.0042	0.00004	0.0001	0:0050	0.00005	0.0001	0.0048	0.00005	0.0001
16) 1,2,3,4,7,8,9-HpCDF	0.01	<0.0035	<0.00003	<0.00006	<0.0034	<0.00003	1000.0>	<0.0034	<0.00003	<0.0001
17) 0CDF	0.001	<0.0181	<0.00002	<0.00003	<0.0175	<0.00002	<0.00003	<0.0178	<0.00002	<0.00004
PCDD/PCDFs-TEQ			0.0038	0.0060		0.0045	0.0083		0.0043	0.0089
Remarks: - Nm ³ = Normal cu.	Dic meter fo	or gas condition me	ans at temperature	of 0 °C, pressure of	1 atm and dry bas	is. (European Union)				

7 7



Table 5:

- At the temperature of 25°C, 11% oxygen pressure of 1 atm or 760 mm.Hg., dry basis, the total suspended particulate (TSP), SO₂, NOx (as NO₂) and CO was calculated. TSP ranged from 154–424 mg/Nm³, SO₂ was 116–300 mg/Nm³, NOx was 87–230 mg/m³ and CO was 1,137–2,527 mg/m³. The dioxins and furans (TEQ) were 0.0034–0.0081 ng 1-TEQ/m³. For stack condition measurement, the percent of O2 was 14.73–16.08% (see Table 6).
- At the temperature of 20°C, 7% oxygen pressure of 1 atm or 760 mm.Hg., dry basis, the total suspended particulate (TSP), SO₂, NOx (as NO₂) and CO was calculated. TSP ranged from 153–605 mg/m³, SO₂ was 118–428 mg/Nm³, NOx was 88–328 mg/m³ and CO was 1,156–3609 mg/m³. The dioxins and furans (TEQ) were 0.0040–0.0116 ng 1-TEQ/m³. For stack condition measurement, the percent of O2 was 14.73–16.08%.
- Soil residues and ashes from the multicyclone and bottom ashes from the burning chamber. The soil residues of stack were monitored during July 31–August 3, 2012. TEQ of dioxins and furans in ashes of the multicyclone ranged from 0.0024 (OCDF) to 11 (TCDDs) ng l-TEQ/kg. On the other hand, the result of dioxins and furans (TEQ) in bottom ashes of the burning chamber show the minimum value at 0.0024 ng l-TEQ/kg and the maximum value at 29 for OCDF and TCDDs respectively.

3.2 Whisky factory

The emission air quality of stack were monitored during August 15–17, 2012, at the beginning and at the end of the PCDD/PCDF sampling and calculated at the temperature of 0°C, 11% oxygen pressure of 1 atm or 760 mm.Hg., dry basis, temperature of 25°C, 11% oxygen pressure of 1 atm or 760 mm.Hg., dry basis and the temperature of 20°C, 7% oxygen pressure of 1 atm or 760 mm.Hg., dry basis.

- At the temperature of 0°C, 11% oxygen pressure of 1 atm or 760 mm.Hg., dry basis, the total suspended particulate (TSP), SO₂, NOx (as NO₂) and CO was calculated. TSP ranged from 52–159 mg/m³, SO₂ is 310–1,022 mg/m³, NOx was 217–332 mg/m³ and CO was 1.3–3.8 mg/m³. The dioxins and furans (TEQ) were 0.0010–0.0142 ng 1-TEQ/m³. For stack condition measurement, the percent of O₂ was 13.40–15.52% (see Table 7).
- At the temperature of 25°C, 11% oxygen pressure of 1 atm or 760 mm.Hg., dry basis, the total suspended particulate (TSP), SO2, NOx (as NO2) and CO was calculated. TSP ranged from 48–146 mg/Nm₃, SO₂ was 284–936 mg/Nm₃, NOx was 199–304 mg/m³ and CO is 1.1–3.5 mg/m³. The dioxins and furans (TEQ) were 0.0009–0.0130 ng 1-TEQ/m³. For stack condition measurement, the percent of O₂ was 13.77–15.49% (see Table 8).
- At the temperature of 20°C, 7% oxygen pressure of 1 atm or 760 mm.Hg., dry basis, the total suspended particulate (TSP), SO2, NOx (as NO₂) and CO was calculated. TSP ranged from 49–208 mg/m³, SO₂ is 289–1,337 mg/Nm3, NOx was 202–435 mg/m³ and CO was 1.2–5.0 mg/m³. The dioxins and furans (TEQ) were 0.0009–0.0186 ng 1-TEQ/m³. For stack condition measurement, the percent of O₂ was 13.77–14.41%.



Dioxin emissions from stacks at a vegetable oil factory at the temperature of 25°C, 11% oxygen pressure of 1 atm or 760 mm.Hg., dry basis.

						Sampling date				
			31/07/12			01/08/12			02/08/12	
Parameters	ŧ		at actual O ₂	at 25°C		at actual O ₂	at 25°C		at actual O ₂	at 25°C
		ng/Nm³	(25°C)	and $11\% O_2$	ng/Nm³	(25°C)	and $11\% O_2$	ng/Nm³	(25°C)	and $11\% O_2$
			(ng I-TEQ/Rm ³)	(ng I-TEQ/Rm ³)		(ng I-TEQ/Rm ³)	(ng I-TEQ/Rm ³)		(ng I-TEQ/Rm ³)	(ng LTEQ/Rm ³)
Determination of PCDD/PCDFs										
1.3 Total I-TEQ				_						
1) 2,3,7,-8TCDD	1	90000	0.0006	0.0010	6000.0	0.0009	0.0016	0.005	0.0005	0.0010
2) 1,2,3,7,8-PeCDD	0.5	0.0022	0.0011	0.0017	0.0020	0.0010	0.0018	0.0019	6000'0	0.0019
3) 1,2,3,4,7,8-HxCDD	0.1	0.0017	0.0002	0.0003	0.0014	0.0001	0.0002	0.0011	0.001	0.0002
 1,2,3,6,7,8-HxCDD 	0.1	0.0028	0.0003	0.0004	0.0031	0.0003	0.0006	0:0030	0.0003	0.0006
5) 1,2,3,7,8,9-HxCDD	0.1	0.0041	0.0004	0.0007	0.0033	0.0003	0.0006	0.0038	0.0004	0.0008
6) 1,2,3,4,6,7,8-HpCDD	0.01	0.0120	0.0001	0.0002	0:0080	0.0001	0.0001	0.0085	0.0001	0.0002
7) OCDD	0.001	0.0165	0.00002	0.00003	<0.0161	<0.00002	<0.0003	<0.0163	<0.0002	<0.0003
8) 2,3,7,8-TCDF	0.1	6000:0	0.0001	0.0001	0.0043	0.0004	0.0008	0.0045	0:0005	6000:0
 1,2,3,7,8-PeCDF 	0.05	0.0012	0.0001	0.0001	0.0017	0.0001	0.0002	0.0012	0.0001	0.0001
10) 2,3,4,7,8-PeCDF	0.5	0.0008	0.0004	0.0007	0.0011	0.0005	0.0010	0.0016	0.0008	0.0017
11) 1,2,3,4,7,8-HxCDF	0.1	0.0013	0.0001	0.0002	0.0015	0.0001	0.0003	0.0016	0.0002	0.0003
12) 1,2,3,6,7,8-HxCDF	0.1	<0.008	<0.0008	<0.0001	0.0010	0.0001	0.0002	0.0015	0.0002	0.0003
13) 2,3,4,6,7,8-HxCDF	0.1	<0.008	<0.008	<0.0001	<0.0008	<0.00008	<0.0001	<0.0008	<0.00008	<0.0002
14) 1,2,3,7,8,9-HxCDF	0.1	<0.008	<0.0008	<0.0001	<0.0008	<0.00008	<0.0001	<0.0008	<0.0008	<0.0002
15) 1,2,3,4,6,7,8-HpCDF	0.01	0.0038	0.00004	0.0001	0.0046	0.00005	0.0001	0.0044	0.00004	0.0001
16) 1,2,3,4,7,8,9-HpCDF	0.01	<0.0032	<0.00003	<0.00005	<0.0031	<0.00003	<0.0001	<0.0031	<0.0003	<0.0001
17) OCDF	0.001	<0.0165	<0.00002	<0.0003	<0.0161	<0.00002	<0.0003	<0.0163	<0.0002	<0.00003
PCDD/PCDFs-TE	a		0.0034	0.0055		0.0041	0.0075		0.0040	0.0081
temarks : - Rm ³ = Reference	cubic meter fi	or gas condition me	eans at temperature	e of 25 °C, pressure c	of 1 atm and dry be	Isis. (Canada Region	(
- I-TEQ (Internationa	Toxicity Equiv	valence) = the valu	e is calculated by us	ing the toxicity equiv	valence factors (TE	F).				

Polychlorinated Dibenzo-p-Dioxins Polychlorinated Dibenzofurans 77



Table 6:

Dioxin emissions from stacks at a whisky factory at the temperature of 0°C, 11% oxygen pressure of 1 atm or 760 mm.Hg., dry basis. Table 7:

						Sampling date				
			15/08/12			16/08/12			17/08/12	
Parameters	Ħ		at actual O ₂	at 0°C		at actual O ₂	at 0°C		at actual O ₂	at 0°C
		ng/Nm³	(0.C)	and 11% O ₂	ng/Nm³	(0.C)	and 11% O ₂	ng/Nm³	(0°C)	and 11% O ₂
			(ng I-TEQ/Nm ³)	(ng I-TEQ /Nm ³)		(ng I-TEQ/Nm ³)	(ng I-TEQ /Nm ³)		(ng I-TEQ/Nm ³)	(ng I-TEQ /Nm ³)
Determination of PCDD/PCDFs										
1.3 Total I-TEQ										
1) 2,3,7,-8TCDD	1	<0.0004	<0.0004	<0.0007	<0:005	<0.005	<0.0007	<0.0005	<0.0005	<0.0007
2) 1,2,3,7,8-PeCDD	0.5	6000:0≻	<0.0004	<0.0007	<0.0010	<0.005	<0.0007	<0.0010	<0.0005	<0.0007
3) 1,2,3,4,7,8-HxCDD	0.1	<0.0011	<0.0001	<0.0002	<0.0013	<0.001	<0.0002	<0.0012	<0.0001	<0.0002
4) 1,2,3,6,7,8-HxCDD	0.1	<0.0011	<0.0001	<0.0002	<0.0013	<0.0001	<0.0002	<0.0012	<0.0001	<0.0002
5) 1,2,3,7,8,9-HxCDD	01	<0.0011	<0.0001	<0.0002	<0.0013	±00010	<0.0002	<0.0012	<0.0001	<0.0002
6) 1,2,3,4,6,7,8-HpCDD	0.01	<0.0044	40:00004	<0.0001	<0.0013	<0:00005	<0.0001	0.0085	0.0001	0.0001
7) 0000	0.001	<0.0230	<0.00002	<0.00004	<0.026	<0.00003	<0.00004	<0.0257	<0.00003	<0.0004
8) 2,3,7,8-TCDF	0.1	0.0015	0.0001	0.0002	0.0028	0.0003	0.0004	0.0032	0.0003	0.0004
 1,2,3,7,8-PeCDF 	0.05	6000:0⊳	<0.00004	<0.0001	0.0024	1000.0	0.0002	0.0032	0.0002	0.0002
10) 2,3,4,7,8-PeCDF	0.5	0.0010	0.0005	0.0007	0.0028	0.0014	0.0019	0.0038	0.0019	0.0026
11) 1,2,3,4,7,8-HxCDF	0.1	0.0012	0.0001	0.0002	0.0020	0.0002	0.0003	0.0197	0.0020	0.0028
12) 1,2,3,6,7,8-HxCDF	0.1	<0.0011	<0.0001	<0.0002	0.0019	0.0002	0.0003	0.0178	0.0018	0.0025
13) 2,3,4,6,7,8-HxCDF	0.1	<0.0011	40.0001	<0.0002	0.0014	0.0001	0.0002	0.0097	0.0010	0.0014
14) 1,2,3,7,8,9-HxCDF	0.1	<0.0011	<0.0001	<0.0002	<0.0013	40.0001	<0.0002	0.0032	0.0003	0.0004
15) 1,2,3,4,6,7,8-HpCDF	0.01	0.0110	0.0001	0.0002	0.0126	0.0001	0.0002	0.1717	0.0017	0.0024
16) 1,2,3,4,7,8,9-HpCDF	0.01	0.0051	0.0001	0.0001	0.0070	0.0001	0.0001	0.0553	0.0006	0.0008
17) OCDF	0.001	0.0530	0.0001	0.0001	0.0539	0.0001	0.0001	0.3750	0.0004	0.0005
PCDD/PCDFs-TEQ			0.0010	0.0015		0.0026	0.0036		0.0101	0.0142
Remarks: - Nm ³ = Normal cut	bic meter fo	or gas condition me	ans at temperature	of 0 °C, pressure of	1 atm and dry basi	is. (European Union				
 Pricul (micrimated Diffe 	roxicity cur	undiencej – ure var ve	Ine is calculated by	מאוום מוה נטאוכווץ כקו.	מואמובערב ופרוחוס לי					
² Doluthorinated Dihe	nzofinanc	٥								

Polychlorinated Dibenzo-p-Dioxins Polychlorinated Dibenzofurans



Dioxin emissions from stacks at a whisky factory at the temperature of 25°C, 11% oxygen pressure of 1 atm or 760 mm.Hg., dry basis.

						Sampling date				
			15/08/12			16/08/12			17/08/12	
Parameters	担		at actual O ₂	at 25°C		at actual O ₂	at 25°C		at actual O ₂	at 25°C
		ng/Nm³	(25°C)	and $11\% O_2$	ng/Nm³	(25°C)	and $11\% O_2$	ng/Nm³	(25°C)	and $11\% O_2$
			(ng I-TEQ/Rm ³)	(ng I-TEQ/Rm ³)		(ng I-TEQ/Rm ³)	(ng I-TEQ/Rm ³)		(ng I-TEQ/Rm ³)	(ng I-TEQ/Rm ³)
Determination of PCDD/PCDFs										
1.3 Total I-TEQ										
1) 2,3,7,-8TCDD	1	<0.0004	<0.0004	<0.0006	<0.0005	<0.0005	40.0006	<0.0005	<0.0005	<0.0006
2) 1,2,3,7,8-PeCDD	0.5	<0.0008	<0.004	<0.0006	€00000>	<0.0005	40.0006	€00000>	<0.0005	<0.0006
3) 1,2,3,4,7,8-HxCDD	0.1	<0.0010	<0.001	<0.0002	<0.0012	<0.0001	<0.0002	<0.0011	<0.0001	<0.0002
4) 1,2,3,6,7,8-HxCDD	0.1	<0.0010	<0.001	<0.0002	<0.0012	<0.0001	<0.0002	<0.0011	<0.0001	<0.0002
5) 1,2,3,7,8,9-HxCDD	0.1	<0.0010	1000.0⊳	<0.0002	<0.0012	<0.0001	<0.0002	<0.0011	<0.0001	<0.0002
6) 1,2,3,4,6,7,8-HpCDD	0.01	<0.0040	<0.0004	<0.0001	<0.0046	<0.00005	40.0001	0.0078	0.0001	0.0001
7) OCDD	0.001	<0.0211	<0.00002	<0.00003	<0.0238	<0.00002	<0.00003	<0.0235	<0.00002	<0.00003
8) 2,3,7,8-TCDF	0.1	0.0014	0.0001	0.0002	0.0026	0.0003	0.0004	0.0029	0.0003	0.0004
9) 1,2,3,7,8-PeCDF	0.05	<0.0008	<0.0004	<0.0001	0.0022	0.0001	0.0002	0.0029	0.0001	0.0002
10) 2,3,4,7,8-PeCDF	0.5	6000.0	0.0004	0.0007	0.0026	0.0013	0.0018	0.0034	0.0017	0.0024
11) 1,2,3,4,7,8-HxCDF	0.1	0.0011	0.0001	0.0002	0.0018	0.0002	0.0003	0.0181	0.0018	0.0025
12) 1,2,3,6,7,8-HxCDF	0.1	<0.0010	<0.001	<0.0002	0.0017	0.0002	0.0002	0.0163	0.0016	0.0023
13) 2,3,4,6,7,8-HxCDF	0.1	<0.0010	<0.0001	<0.0002	0.0013	0.0001	0.0002	0.0089	6000.0	0.0012
14) 1,2,3,7,8,9-HxCDF	0.1	<0.0010	<0.001	<0.0002	<0.0012	<0.0001	<0.0002	0.0029	0.0003	0.0004
15) 1,2,3,4,6,7,8-HpCDF	0.01	0.0100	0.0001	0.0002	0.0115	0.0001	0.0002	0.1573	0.0016	0.0022
16) 1,2,3,4,7,8,9-HpCDF	0.01	0.0047	0:0005	0.0001	0.0064	0.0001	0.0002	0.0506	0.0005	0.0007
17) OCDF	0.001	0.0486	0:0005	0.0001	0.0494	0.00005	0.0001	0.3436	0.0003	0.0005
PCDD/PCDFs-TE(~		6000.0	0.0013		0.0038	0.0053		0.003	0.0130
temarks : - Rm ³ = Reference - I-TEQ (International	cubic meter for Toxicity Equiv	or gas condition me alence) = the value	eans at temperature s is calculated by usi	e of 25 °C, pressure of the toxicity equiving the toxicity equivalence toxicity equiva	of 1 atm and dry ba valence factors (TE	ssis. (Canada Regior F).				

¹⁴ Polychlorinated Dibenzo-p-Dioxins ²⁴ Polychlorinated Dibenzofurans



Table 8:

• Soil residues and ashes from the multicyclone and bottom ashes from the burning chamber. The soil residues of stack were monitored during August 15–17, 2012. TEQ of dioxins and furans in ashes of the multicyclone ranged from 0.0025 (OCDF) to 2.5 (OCDD) ng l-TEQ/kg.

4 Discussion

To assess the health risks associated with the occupational exposure to PM_{10} , organic and elemental carbon of outdoor workers, the incremental lifetime particulate matter exposure (*ILPE*) model was employed and defined as,

$$ILPE = C \times IR \times t \times EF \times ED \tag{1}$$

ILPE = Incremental lifetime particulate matter exposure (pg); C = PCDD/PCDF concentrations (pg m⁻³); *IR* = Inhalation rate (m³ h⁻¹); t = Daily exposure time span (6 h d⁻¹, for two shifts); EF = Exposure frequency (250 d year^{-1 a}, upper-bound value); ED = Exposure duration (25 years ^a, upper-bound value); Note: ^aAdapted from Human Health Evaluation Manual (US EPA, 1991).

According to the methods for derivation of inhalation dosimetry (US EPA, 1994), the inhalation rate of male and female outdoor workers were estimated as 0.89 and 0.49 m³ h⁻¹ respectively. The *ILPE* model was adapted from the probabilistic incremental lifetime cancer risk (*ILCR*) model, which was used to assess traffic policemen exposure to PAHs during their work time in China (Hu *et al.*, [13]). The average values of predicted *ILPE* of total dioxin (i.e. sum of TCDDs, PeCDDs, HxCDDs, OCDD, TCDFs, PeCDFs, HxCDFs, HpCDFs, OCDF) at a whisky factory (Red Bull) were 24.4 ± 17.3 pg and 13.5 ± 9.54 pg for male and female workers over exposure duration of 25 years respectively. Similarly, the average values of estimated *ILPE* of total dioxin observed at vegetable oil factory (Oleen) were 25.0 ± 5.03 pg and 13.8 ± 2.77 pg for male and female workers over exposure duration of 25 years respectively.

5 Conclusion

Emissions of dioxins from stacks of two boilers were investigated at a whisky factory and vegetable oil factory in Samutsakorn Province, Thailand. In the case of the vegetable oil factory, the dioxins and furans (TEQ) were 0.0038-0.0089 ng 1-TEQ/m³. For stack condition measurement, the percent of O₂ was 14.73–16.08%. In the case of the whisky factory, the dioxins and furans (TEQ) were 0.0010-0.0142 ng 1-TEQ/m³. For stack condition measurement, the percent of O₂ was 13.40–15.52%. Despite there being different types of fuels, boilers, burners and operational conditions, the estimated ILPE values of total dioxin of both factories are surprisingly similar to each other.



Acknowledgements

The authors thank Ms. Suparat Duangpichakul from SGS Thailand, Mr. Atip Srisuphaolarn from Thai Beverage Public Company Limited and Mr. Kwanchai Jieam from Oleen Company Limited for their assistances on sampling and chemical analysis. This project was granted by GEF (Project No. GF/RAD /10/003) with UNIDO contract No. 16002508.

References

- [1] Charnley, G. & Kimbrough, D. R., Overview of exposure, toxicity, and risks to children from current levels of 2,3,7,8-tetrachlorodibenzo-p-dioxin and related compounds in the USA. *Food and Chemical Toxicology*, Vol. 44 (5), pp. 601–615, 2006.
- [2] Schecter, A., Piskac, A. L., Grosheva, E. I., Matorova, N. I., Ryan, J. J., Fürst, P., Päpke, O., Adibi, J., Pavuk, M., Silver, A. & Ghaffar, S., Levels of dioxins and dibenzofurans in breast milk of women residing in two cities in the Irkutsk region of Russian Siberia compared with American levels. *Chemosphere*, 47 (2), pp. 157–164, 2002.
- [3] Long, M. & Bonefeld-Jørgensen, E. C., Dioxin-like activity in environmental and human samples from Greenland and Denmark. *Chemosphere*, 89 (8), pp. 919–928, 2012.
- [4] Manscher, O. H., Heidam, N. Z., Vikelsøe, J., Nielsen, P., Blinksbjerg, P., Madsen, H., Pallesen, L. & Tiernan, T. O., The Danish incinerator dioxin study. Part 1. *Chemosphere*, 20 (10–12), pp. 1779–1784, 1990.
- [5] Rose, C. L. & McKay, W. A., PCDDs (dioxins) and PCDFs (furans) in selected UK lake and reservoir sites — concentrations and TEQs in sediment and fish samples. *Science of The Total Environment*, 177 (1– 3), pp. 43–56, 1996.
- [6] Dyke, P. H., Foan, C., Wenborn, M. & Coleman, P. J., A review of dioxin releases to land and water in the UK. *Science of The Total Environment*, 207 (2–3), pp. 119–131, 1997.
- [7] Wenning, R., Dodge, D., Peck, B., Shearer, K., Luksemburg, W., Della Sala, S. & Scazzola, R., Screening-level ecological risk assessment of polychlorinated dibenzo-p-dioxins and dibenzofurans in sediments and aquatic biota from the Venice Lagoon, Italy. *Chemosphere*, 40 (9–11), pp. 1179–1187, 2000.
- [8] Grassi, P., Fattore, E., Generoso, C., Fanelli, R., Arvati, M. & Zuccato, E., Polychlorobiphenyls (PCBs), polychlorinated dibenzo-p-dioxins (PCDDs) and dibenzofurans (PCDFs) in fruit and vegetables from an industrial area in northern Italy. *Chemosphere*, 79 (3), pp. 292–298, 2010.
- [9] Sasamoto, T., Ushio, F., Kikutani, N., Saitoh, Y., Yamaki, Y., Hashimoto, T., Horii, S., Nakagawa, J. & Ibe, A., Estimation of 1999–2004 dietary daily intake of PCDDs, PCDFs and dioxin-like PCBs by a total diet study in metropolitan Tokyo, Japan. *Chemosphere*, 64 (4), pp. 634–641, 2006.

- [10] Mato, Y., Suzuki, N., Katatani, N., Kadokami, K., Nakano, T., Nakayama, S., Sekii, H., Komoto, S., Miyake, S. & Morita, M., Human intake of PCDDs, PCDFs, and dioxin like PCBs in Japan, 2001 and 2002. *Chemosphere*, 67 (9), pp. S247–S255, 2007.
- [11] Li, Y., Wang, P., Ding, L., Li, X., Wang, T., Zhang, Q., Yang, H., Jiang, G. & Wei, F., Atmospheric distribution of polychlorinated dibenzo-pdioxins, dibenzofurans and dioxin-like polychlorinated biphenyls around a steel plant Area, Northeast China. *Chemosphere*, 79 (3), pp. 253–258, 2010.
- [12] Sun, S., Zhao, J., Leng, J., Wang, P., Wang, Y., Fukatsu, H., Liu, D., Liu, X. & Kayama, F., Levels of dioxins and polybrominated diphenyl ethers in human milk from three regions of northern China and potential dietary risk factors. *Chemosphere*, 80 (10), pp. 1151–1159, 2010.
- [13] Hu, Y., Bai, Z., Zhang, L., Wang, X., Zhang, L., Y, Qingchan, Zhu, T., 2007. Health risk assessment for traffic policemen exposed to polycyclic aromatic hydrocarbons (PAHs) in Tianjin, China. Science of the Total Environment 382, 240–250.

