PCDD/F, PCB AND HCB IN SOIL AND ASH FROM BRICK PRODUCTION SITES IN KENYA, SOUTH AFRICA AND MEXICO

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Introduction

Persistent organic pollutants (POPs) pose environmental and health risks. Among many regulatory efforts at national levels their reduction or elimination worldwide is subject to multilateral environmental agreements such as the Stockholm Convention (SC) on POPs.

As a part of their National Implementation Plans (NIPs) the parties to the SC are obliged to compile national inventories of releases of unintentionally generated chlorinated dioxins and furans. For the compilation of the inventories sector-specific emission factors (EFs), that reflect the national situation, are needed. EFs describe the amount of a pollutant released per unit of fuel employed or per unit of product resulting from a specific sector and according to various operational criteria. Total releases per sector can be obtained by multiplying the EFs by the activity of each sector. The SC recommends the use of the Standardized Toolkit for Identification and Quantification of Dioxin and Furan Releases.

A potential source of unintentional POPs worldwide is clay brick production, due to the high activity rates in many countries. This could be significant especially in developing countries, where bricks are often the predominant building material and rising brick production rates occur when the economies start growing.

Hardly any EF data are available for brick production plants in developing countries, mainly due to the lack of infrastructure to execute the measurements. In addition such plants are often small and do not warrant measurements or are constructed in such a way that traditional stack measurements cannot be performed. However, from the little data available from a pilot study in the state of Guanajuato, Mexico, PCDD/F emissions from brick production seem to be low. PCDD/F EFs to air reported from wood and waste oil fired kilns were between 0.045µg TEQ/t (wood) and 0.2 µg TEQ/t (waste oil) per ton of bricks produced (1).

In the present study, an attempt was made to indirectly assess if the brick production in other developing countries are sufficiently described by the EFs obtained in Guanajuato. This was done via the comparison of pollutant concentrations in nearby soils and bottom ashes from local production sites where no emission measurements could be conducted. In addition background soils from all sites were analysed. We report the results from a number of brick production sites in Kenya, South Africa, and Mexico, including the sites in Guanajuato where the emissions were measured. In such way we intend to increase the level of confidence into the EFs presently available in the UNEP Toolkit. The target compounds of this study were PCDD/F, dioxin-like PCB, and hexachlorobenzene.

Location and characterization of the sites

All kilns investigated, including the industrial scale clamp kilns in South Africa, were simple constructions without chimneys and without any fugitive emission control measures in place.

Mexico (MX): The production sites investigated were located in Leon, Salamanca, Abasolo and Juventino Rosas (State of Guanajuato), San Nicolas Tequisquiapan (State of Queretaro) and Chiapa de Corzo (State of Chiapas). The brick production sites in MX are typically small to medium sized installations with a volume between 50 m^3 and 120 m^3 embedded in settlement areas. The kilns are simple pyramidal cube constructions without a chimney, charged and discharged manually and operated 1-3 times per month. Production rate of these kilns ranges between 20 to 80 t/month. The sites contain between 30 and 150 adjacent kilns mostly using similar fuels and raw materials. Typical

fuels recently used were Liquified Petroleum Gas-LPG (Juventino Rosas), wood (Leon), bunker oil "Combustoleo" (Salamanca, Abasolo) and waste oils (Chiapa de Corzo, San Nicolas Tequisquipan).

South Africa (SA): The production sites investigated were in Dididi (Limpopo Province.), Factory M (North West Province) and Factory O (Gauteng). Factory O and Factory M were at industrial scale (approx 50,000 t/month - 70,000 t/month) operated with coal as main fuel. The kilns in Dididi were small artisanal wood-fired kilns (3 m x 3 m x2 m, 18 m^3), constructed occasionally by the local population for personal need. All sites were far away from other urban and industrial activities but DDT is sprayed indoors for malaria control (Ref. 2).

Kenya (KY): The production sites investigated were A, B, C (Kisumu county), and D, E, F (Kakamega county). All sites were small wood fired kilns of artisanal character (3m x 3m x 2 m, 18 m^3), fired only occasionally by the local population for personal need or for local sale. All sites were far away from other urban activities. Reference soils 1, 2 and 3 were taken from sites within the two counties and care was taken to ensure that they were well removed from any activity that may lead to the unintentional production of POPs. In addition, there was no evidence of the sites having previously been used for the production of bricks.

Experimental

In 2009 bottom ashes, ca. 100 g per kiln, were collected randomly from the combustion chamber of the kilns and homogenized. In addition surface soil samples were collected from 0 - 30 cm depth after removal of the vegetation, freeze dried and sieved < 2mm prior to extraction. The distance of the samples from the emission source varied from site to site, depending on the local conditions and access to the installation. Reference (background) samples were collected where possible after individual inspections of the surroundings.

Soil and ash samples were spiked with 17 ^{13}C-labelled PCDD/F congeners, twelve ^{13}C-labelled dioxin-like PCB, six ^{13}C-labelled indicator PCB and the ^{13}C-labelled HCB. The ^{13}C-labelled standards (PCB, PCDD/F, HCB) and all solvents (Picograde) used were purchased from LGC Promochem (Wesel, Germany). The cleanup columns were purchased from Fluid Management Systems (Waltham, MA, USA), the Celite and sulphuric acid from Merck (Darmstadt, Germany).

The extraction was done by pressurized extraction (ASE 300, Dionex Corporation, Sunyvale, CA, USA) using toluene as solvent. Further clean-up of the extract comprised treatment with concentrated sulphuric acid adsorbed on Celite followed by a multilayer silica column and an alumina column. The latter was also used to separate PCB and HCB from PCDD/F. Prior to injection, a ^{13}C-labelled syringe standard was added to each fraction.

PCDD/F, PCB and HCB analysis was performed with a high resolution mass spectrometer (Finnigan MAT 95, Thermo Electron GmbH, Bremen, Germany) coupled to a gaschromatograph (Agilent 6890 Agilent Technologies, Waldbronn, Germany) equipped with a cool injection system (Gerstel GmbH, Mühlheim/Ruhr, Germany). PCDD/F were analysed using a polar and a non-polar column (DB5 and DBDIOXIN, respectively; J&W, Agilent Technologies); PCB and HCB were separated on a 60 m non-polar column (DB5, J&W, Agilent Technologies). The mass spectrometer was operated in single ion mode at a mass resolution of 8,000 to 10,000. The identification and quantification was done by isotope dilution according to method EPA 1613.

Results and discussion

Apart of the question of the impact of brick making on the nearby soil levels, the data obtained in this study can be used for a general comparison to concentrations in soil in more developed areas of the northern hemisphere. Only few systematic studies in terms of objectives and methodology that cover large areas are available. In the following we refer to the USEPA 2007 Survey of the USA (3) and the Australian National Dioxin Program from 2004(4).

In all investigated sites, dioxin-like PCB contributed only with negligible amounts to the dioxin like toxicity in soils and ashes and will not be further discussed.

South Africa (SA) and Kenya (KY):

In the African soils around the brick production sites, PCDD/Fs, PCBs and HCB were all below 1 ng/kg TEQ independently of the installation or the fuel used. No interpretable spatial gradients were observed. The same accounts for HCB, except for the industrial sites in SA where slightly higher PCB values were observed near the kilns (*Tables 1a,c*). The bottom ashes displays similar low values below 1 ng WHO_{2005}-TEQ/kg for PCDD/Fs; HCB was at a maximum of 177 ng/kg.

From this data there is no indication that artisanal brick making using virgin wood and even at industrial scale using coal may impact the surrounding soil environments concerning PCDD/Fs, PCBs and HCB.

Table 1a: **Factory M, SA,** Industrial scale field kiln fired with coal

Sample	**PCDD/F**	**dl-PCB**	**HCB**
Soil at dist.	*ng WHO_{2005}-TEQ/kg*		*ng/kg*
136 m S	0.12	0.00	200
263 m S	0.081	0.00	35
354 m S	0.12	0.00	22
447 m S	0.10	0.00	<17
445 m W	0.073	0.00	18
213 m E	0.025	0.00	<17
545 m N	0.086	0.00	<17
668 m E	0.079	0.00	<17
Ref. soil at 12 km SW	*0.30*	*0.00*	*<17*
Bottom ash	0.13	0.024*	177

Table 1b: **Dididi, SA,** artisanal campaign kiln fired with virgin wood

Sample	**PCDD/F**	**dl-PCB**	**HCB**
Soil at a dist. of	*ng WHO_{2005}-TEQ/kg*		*ng/kg*
10 m N	0.053	0.00	19
10 m E	0.096	0.00	<17
10 m S	0.082	0.00	<17
10 m W	0.028	0.00	<17
Ref. soil at 5.5 km	*0.022*	*0.142*	*<17*
Bottom ash	0.0011	0.00	18
Bottom ash	0.062	0.000074	20

**non-ortho PCBs*

Table 1c: **Factory O, SA,** Industrial scale field kiln fired with coal

Sample	**PCDD/F**	**dl-PCB**	**HCB**
Soil at dist.	*ng WHO_{2005}-TEQ/kg*		*ng/kg*
15 m SW	0.34	0.05	160
100 m SW	0.41	0.09	280
200 m SW	0.68	0.05	70
300 m SW	0.48	0.07	91
Ref. soil at 30 km	*0.49*	*0.13*	*140*
Bottom ash	1.16	< 0.039*	75

Table 1d: **Sites A, B, C, D, E, F, KY,** artisanal campaign kilns fired with virgin wood. *Blended soil samples taken N,E,S,W at a dist. of 10m*

Sample	**PCDD/F**	**dl-PCB**	**HCB**
	ng WHO_{2005}-TEQ/kg		*ng/kg*
Soil A	0.057	0.63	20
Soil B	0.017	0.00	<17
Soil C	0.21	0.00	20
Soil D	0.062	0.00	20
Soil E	0.0033	0.00	21
Soil F	0.2	0.00	21
Bottom ash A	0.036	0.00	40
Bottom ash B	0.000034	0.00	<17
Bottom ash B	0.11	0.00	78
Bottom ash C	0.12	0.00	27
Bottom ash D	0.045	0.00	100
Bottom ash E	0.23	0.00	34
Bottom ash F	0.068	0.00	30
Ref. soil 1	*0.17*	*0.00*	*<17*
Ref. soil 2	*0.021*	*0.00*	*<17*
Ref. soil 3	*0.15*	*0.00*	*<17*

Mexico (MX):

In Mexico, the situation is more heterogeneous, which may be partially because the kilns there are embedded into other urban activities, and to the fact that other types of fuels that include wastes were used.

For the PCDD/F a clear spatial gradient could be observed only at the Leon site (*Table 2a*), with a maximum concentration of 18 ng *WHO_{2005}*-TEQ/kg found at 10 m distance from the kiln. This was the highest value found in all MX soils. From this point, the concentrations rapidly decreased and at 45 m distance the PCDD/F were fairly below 1 ng *WHO_{2005}*-TEQ/kg and in a range similar to the reference soil. Also, HCB concentrations were higher in the vicinity of the kiln, but with a maximum of 2400 ng/kg only at a distance of 40 m, further on decreasing quickly towards the range of the background soil. As for the PCDD/F the HCB concentration detected at this site was the highest in all MX soils. In contrast, the three bottom ash samples from the kiln were below 1 ng *WHO_{2005}*-TEQ/kg for PCDD/F, and HCB was below the detection limit.

The soils around the 2 kilns in Salamanca (*Tables 2c,d*) displayed lower concentrations of PCDD/F < 1 ng *WHO_{2005}*-TEQ/kg and in the range of the reference soil. HCB was at or even below the level of the reference soil. No interpretable spatial trend was observed. Bottom ashes were at similar levels as seen in Leon.

Table 2a: **Leon, MX,** campaign kiln, virgin wood			
Sample	**PCDD/F**	**dl-PCB**	**HCB**
Soil at dist	*ng WHO_{2005}-TEQ/kg*		*ng/kg*
10 m N	18	0.35	770
21 m N	13	0.52	1500
40 m N	3.5	0.12	2400
75 m N	0.45	0.04	31
160 m N	0.19	0.00	60
Ref. Soil at 0.47 km SW	*0.78*	*0.03*	*63*
Bottom ash	0.58	<0.044*	<150
Bottom ash	0.48	0.027*	< 76
Bottom ash	0.27	0.0067*	< 57
EF to Air	*45 ngTEQ/t brick*	*1.0 ngTEQ/t brick*	*32 µg/t brick*

Table 2b: **Chiapa de Corzo, MX**, campaign kiln fired batch-wise with used car oils and **San Nicolas Tequisquipan, MX,** campaign kiln fired batch-wise with a mix of used car oils and oil refinery residues			
Sample	**PCDD/F**	**dl-PCB**	**HCB**
	ng WHO_{2005}-TEQ/kg		*ng/kg*
Bottom ash	0.36	0.10*	178
Bottom ash	0.18	0.11*	195

Table 2c: **Salamanca 1, MX,** stationary kiln, steam injected bunker oil, started with waste-wood			
Sample	**PCDD/F**	**dl-PCB**	**HCB**
Soil at dist.	*ng WHO_{2005}-TEQ/kg*		*ng/kg*
10 m S	0.023	0.00	67
20 m S	0.60	0.15	100
Ref. Soil at 2 km NW	*0.23*	*0.07*	*550*
Bottom ash	1.7	0.16*	< 67
Bottom ash	0.17	0.028*	< 83
EF to Air	*196 ngTEQ/t brick*	*15ngTEQ/t brick*	*221 µg/t brick*

Table 2d: **Salamanca 2, MX,** stationary kiln, steam injected bunker oil, started with waste wood			
Sample	**PCDD/F**	**dl-PCB**	**HCB**
Soil at dist.	*ng WHO_{2005}-TEQ/kg*		*ng/kg*
15 m NE	0.93	0.07	110
30 m NE	0.49	0.07	220
40 m NE	0.16	0.00	190
65 m NE	0.14	0.04	51
Ref. Soil at 6.4 km NW	*0.23*	*0.07*	*550*
Bottom ash	0.77	0.075*	< 169
Bottom ash	0.25	0.04	< 60

Table 2e: **Abasolo, MX,** stationary kiln fired batch-wise with bunker oil and wood			
Sample	**PCDD/F**	**dl-PCB**	**HCB**
Soil at dist.	*ng WHO_{2005}-TEQ/kg*		*ng/kg*
10 m E	0.31	0.00	91
20 m E	0.43	0.00	50
40 m E	0.077	0.00	52
80 m E	12.3	0.34	500
160 m E	3.75	0.09	290
Bottom ash	>0.81	>0.027*	> 76
Bottom ash	131	9.9	1700
Bottom ash	1.48	0.16*	282

Table 2f: **Juventino Rosas, MX,** campaign kiln, LP Gas			
Sample	**PCDD/F**	**dl-PCB**	**HCB**
Soil at dist	*ng WHO_{2005}-TEQ/kg*		*ng/kg*
10 m NE	0.11	0.04	64
20 m NE	0.66	0.03	69
40 m NE	0.08	0.04	44
80 m NE	0.07	0.00	42
150 m NE	0.14	0.04	32
Bottom ash	<2.3	<0.094*	53

**non-ortho PCBs*

The soil transect in Abasolo (*Table 2e*) displayed low PCDD/F concentrations (< 1 ng WHO_{2005}-TEQ/kg) close to the kiln and a maximum of 12.3 ng WHO_{2005}-TEQ/kg at 80 m distance. Also PCB and HCB maxima were detected at 80 m distance. The 80 m site was located in an agricultural field with no visible urban impact. However, it cannot be excluded that in the past brick production occurred also here.

The concentrations in bottom ashes were more heterogeneous when compared with the other sites. In Abasolo, one isolated maximum PCDD/F value of 131 ng WHO_{2005}-TEQ/kg was found in one ash sample. The high variation of concentrations in the ash there may result from the batch-wise supply of fuel that may favor incomplete combustion in parts of the kiln.

The site in Juventino Rosas (*Table 2f*) displayed the lowest soil concentrations of all compounds investigated in MX (at similar levels as in the African sites) with no gradients along the transect. This site had been set up by the local authorities based exclusively on LPG and has run for only 10 years.

Background levels in comparison to the Northern Hemisphere:

The concentrations of the PCDD/F in the background soils of this study were at a mean of 0.27 ng WHO_{2005}-TEQ/kg (SA), 0.11 ng WHO_{2005}-TEQ/kg (KY) and 0.34 ng WHO_{2005}-TEQ/kg (MX), with a maximum of 0.78 ng WHO_{2005}-TEQ/kg in MX. They are almost one order of magnitude lower when compared to rural soils, taken all over the US in the vicinity of the National Dioxin Air Monitoring Network, which displayed mean values of 1.7 ng WHO_{2005}-TEQ/kg and a maximum of 11 ng WHO_{2005}-TEQ/kg (4). Compared to the situation in Australia, the background soil data from this study fit well into the category of remote soils, where the Australian mean was at 0.24 ng WHO_{2005}-TEQ/kg with maximum levels around 1 ng WHO_{2005}-TEQ/kg (3).

Conclusions

Regarding the initial question whether brick production in other developing countries is sufficiently described by the range of EFs to air determined in Salamanca and Leon (1), we can conclude that in general neither soil nor ash levels found in other sites in MX, SA or KY did exceed those of Salamanca and Leon. In particular the results from SA and KY indicate even lower air emissions. In so far the Mexican EFs can be applied in terms of an upper bound estimate as long as no specific EFs from other countries are available.

The observation that the MX site operated exclusively with LPG, as well as the virgin wood and coal fired sites in Africa, displayed the lowest impact on soils indicates a discrete influence from secondary fuels used for brick making in the MX sites. However, around the MX sites operated with waste derived fuels, the soil transects did not result in clear gradients, although in general higher levels could be seen in the production zones. The lack of spatial coherence may be explained by the high level of urbanization at the brick making sites in Abasolo and Salamanca. The localization of the kilns might have been different in the past; it is also difficult to make sure that undisturbed soil is sampled. Obviously, transect sampling is not suitable to localize sources in these complex environments.

In Leon (MX) instead we sampled a soil transect around a well isolated kiln, where a reasonable gradient with maximum PCDD/F levels close to the kiln was obtained. The high levels found at this site were surprising, since at the time of the sampling only virgin wood was burned, which is also reflected in the low PCDD/F levels in the bottom ashes. However, this site has had brick production for over 30 years and it is known that in the past also wastes from the leather industry were used as a fuel; in so far the situation in the soils may rather reflect the emissions from the past than current ones.

We recommend further screening on bottom ash samples from brick making involving waste derived fuels in other regions of the world to further verify our conclusions.

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