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Releases of PCDD/Fs, PCBs, PAHs and HCB through bottom ashes from brick kilns operating with different kind of fuels - Results from a pilot study in Mexico

A contribution to the update and review of the Standardized Toolkit for Identification and Quantification of Dioxin and Furan Releases

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Abbreviations

B(a)P	Benzo(a)Pyrene
DL-PCBs	Dioxin like PCBs
GC	Gas chromatograph
HCB	Hexachlorobenzene
HCH	Hexachlorocyclohexane
HRGC	High Resolution Gas Chromatograph
HRMS	High Resolution Mass Spectrometer
PAHs	Polycyclic Aromatic Hydrocarbons
PCBs	Polychlorinated Biphenyls
PCDD/Fs	Polychlorinated Dibenzo(p) dioxins and Dibenzofurans
POPs	Persistent Organic Pollutants
OCDD	Octachlorodibenzodioxin
OCP	Organo Chlorine Pesticide
TEQ	Toxic Equivalency (2,3,7,8 TCDD Equivalent)
WHO	World Health Organisation

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1. Introduction

The parties of the Stockholm Convention (SC) on Persistent Organic Pollutants (POPs) are obliged, along with their national implementation plan, to submit a national, sector-specific emission inventory of unintentionally♦ released POPs (PCDD/Fs, PCBs and Hexachlorobenzene).
While most countries in the Northern Hemisphere have such inventories already available (e.g. the EU Dioxin Inventory 1999/2002 - http://ec.europa.eu/environment/dioxin/download.htm#stage2), few data are available from developing or emerging countries.
In order to provide these countries with a suitable instrument for conducting the inventory and producing a comparable data base on the unintentional releases of POPs, the conference of the Parties (COP) to the SC mandated UNEP to develop a toolkit. This Toolkit is a calculation scheme for a world-wide estimation of unintentional POPs releases, specified by regions and sectors. This information shall be used at a later stage as a basis for proposals to reduce these emissions and the related implementation monitoring (Follow up to decision SC-2/13 on Effectiveness Evaluation of the Stockholm Convention (SC)). For this reason the final version of the Toolkit has to be endorsed by the Conference of the Parties (COP) of the SC. The toolkit has been developed in 1999 by UNEP Chemicals and was adopted by the COP later on.
The Toolkit consists basically of 2 elements:
First, emission factors for (*unintentional*) releases of PCDD, PCDF, expressed in amount TCDD Toxicity Equivalents (TEQ) per ton of fuel, educts or products within a specific sector. Recently also Hexachlorobenzene, which is released unintentionally from secondary Aluminum refinery (Cl-Ethane precursor), and the 6 marker PCBs were included. Second, the national activity (or consumption) within the respective sector or category. The combination of emission factors and activity data yields in a national and sector-specific emission rate expressed in amounts released to air, water, residuals and products.

The second meeting of the Expert Group for the *Update and Review of the Standardized Toolkit for Identification and Quantification of Dioxin and Furan Releases*, held from 5 to 7 December 2007 in Geneva, identified priority areas for updating and improving the Toolkit. The group highlighted the need for screening dioxin/furan sources that so far are poorly characterized in the Toolkit. Among these, brick kilns in developing countries were given highest priority because so far no data on PCDD/F or other POPs are available. The Expert Group recommended as a first step to measure soil or vegetation samples close to (small) brick kilns in developing countries to obtain preliminary orientation on the impact from this source. Wherever possible, samples should be taken from typical kilns using different fuels, *e.g.,* biomass, fossil fuels (coal), waste oils. It was noted that the type of fuel is not addressed in the Toolkit. As a follow up of this recommendation a *Proposal for Screening for Unintentional POPs close to Brick Kilns in Developing Countries* has been prepared jointly by UNEP and the JRC. The concept of the proposal is to conduct a preliminary assessment of the environmental impact of the brick production. A comparison with existing data about soil contamination around diffuse emission sources with known emission factors will allow a first approximation of the emission factors from brick production. Sampling campaigns for soils in the vicinity of typical brick kilns are under execution since November 2008 in South Africa, Kenya and Mexico.

As an initial first step in order to assess the potential influence of different fuels or waste being co-incinerated, a pre-campaign on ashes was executed in Guanajuato/Mexico during April 2008. In

♦ According to Annex C of the SC, these are the POPs released unintentionally from various processes, while the others are mainly pesticides produced on purpose. These pesticides (e.g. DDT and Lindane) are banned since years in most of the countries and the focus of the SC is more on the correct handling of obsolete stocks and contaminated production sites.

addition - since the releases with residues are part of the Toolkit – first emission factors on bottom ashes from brick production should become available.

2. Experimental

Bottom ash samples from 4 brick kilns were taken in the state of Guanjuato, Mexico in April 2008

Table 1: Overview on the bottom ash samples

Field code	JRC Labcode	Gross weight (g)	Net weight (g)
Brick 1	08-206	27.6	5.0
Brick 2	08-207	30.3	7.7
Brick 3	08-208	28.9	6.3
Brick 5	08-209	25.05	2.4

The sampling was executed by Gunther Umlauf with assistance from Pablo Maiz (Gamatek SA de CV), Teresa Ortuño and Salvator Blanco (DGCENICA-INE) and Julia Serrano (IEE-G) on 2 sites: Abasolo Municipality on 15/04/2008 and El Refugio, in León Municipality on 16/04/2008[1].

2.1 Site description

2.1.1 The site of Abasolo Municipality - stationary kilns

Location: (20º26'46,38" N; 101º32'17,38" E).

In the State of Guanajuato there are 2170 brick kilns, of which 365 are located in Abasolo Municipality, one of the oldest and most important brick producers in the state.

Bricks are made of a mix of clay from different nearby areas, including Cuerambaro, animal farm dung and wood dust, all combined with water. The bricks are dried at ambient temperature for 15 days.

Typically, the full capacity in each kiln is in the range of 15,000 to 18,000 bricks; however there are some that reach up to 30,000 units. Main fuel used in this area is tar "combustóleo" provided by small entrepreneurs that may mix residues of tar, heavy oil or even used car oil. Therefore, the characteristics of this fuel are not constant. According to another local source of information "combustóleo" is the heavy oil that PEMEX, the Petroleum company sells to the brick makers.

The kiln is charged with fuel during 5 to 6 hours, after that for 2 more days it is smouldering and cooling down. Three to four persons are involved in the feeding of fuel.

At least one time per month the brick kiln is operated, but typically each 15 to 20 days.

[1] IEE-G stands for Instituto de Ecología de Guanajuato. DGCENICA-INE stands for Dirección General del Centro Nacional de Investigación y Capacitación Ambiental del Instituto Nacional de Ecología.
Gamatek is a private company collaborating with DGCENICA-INE in this project.

SAMPLING SITES:

Site 1 (Brick 1).
Location: Echegaray Street, Barrio Brinco del Diablo. Brick kilns are besides the street. Schools and hospital are close by.
Capacity Kiln: 11,000 units
Status: Empty kiln
Fuel: dust wood, farm animal dung, garbage with some plastics, agriculture residues.

Site 2 (Brick 2).
Location: Las Margaritas
Capacity Kiln: 21,000 units
Status: After 6.5 hour combustion.
Fuel: Tar, which is heated previously to liquefy.
1.5 tar barrel + 5 dust wood farm carts is the fuel to obtain 500 bricks

Site 3 (Brick 3).
Location: Vicente Guerrero
Capacity Kiln: 18,000 units
Status: Empty Kiln
Fuel: Wood as complete trunks and branches[2]

2.1.2 The site of Leon- El Refugio - mobile kilns (campaign kilns)

Location: 21º07'49.43"N; 101º 36'43.89E".

El Refugio is a brick kiln area of approximately 100 brick kilns located in the Municipality of León (263 brick kilns). The main fuel is wood either branches, wood chips or used wood (transport boxes). Some years ago residues of shoes and tannery industry were used, which is not allowed anymore. However, it is difficult to exclude the use of that other fuel than wood.

The site of El Refugio is a traditional brick production sites. It consists mainly of mobile kilns as displayed on the cover page, constructed on ground level (the stationary kilns in Abasolo are fired from underground ovens instead). The lower part of the kiln, including the combustion chamber, is set up with burnt bricks. On top the raw bricks are stapled. When all the raw brick are assembled a final layer of burnt bricks is set up, covering all surfaces. As a last step all splices are sealed with animal dung except of the top of the kiln.

Brick kilns in this area were relocated approximately 15 years ago. There are some plans now by the municipality to relocate them since a highway is being planned nearby. The clay is mainly obtained from the banks located nearby this area.

Site 5 (Brick 5).
Location: El Refugio owned by "Carlos", Leon Municipality
Capacity Kiln: 10,000- 15,000 units
Status: Empty Kiln
Fuel: Wood (since 5 years) as complete trunks and branches during 36 hours.
The Clay is mainly from clay banks in Duarte, Loza de los Padres.
Dung is used as bulking agent.

Photos from all sampling locations illustrating the brick making process are provided in the Annex.

[2] although not reported at the time of the sampling, tar may have been used in this kiln even at the very beginning or in previous burning.

2.2 Sampling

Five cold ash samples were collected randomly in the combustion chambers of each kiln using solvent rinsed stainless steel spoons. The individual samples were combined and transferred into a glass container sealed with a Teflon gasket.

Table 2: Description of the samples

Field code	Sample description
Brick 1	GU, 15.04.08, bottom ash, grey powder. Fuel: wood dust, farm animal dung, garbage with some plastics, agriculture residues.
Brick 2	GU, 15.04.08, bottom ash, dark grey powder. Fuel: liquefied tar (preheated).
Brick 3	GU, 15.04.08, bottom ash, light grey powder. Fuel: Wood as complete trunks and branches.
Brick 5	GU, 16.04.08, bottom ash, white powder. Fuel: Wood as complete trunks and branches.

2.3 Analytical determinations

For *PCDD/Fs and PCBs* 2g of samples were Soxhlet extracted with toluene for 24 h after being spiked with internal standards (16 ^{13}C-labelled 2,3,7,8-chlorine-substituited congeners with 400 pg each, except OCDD with 800 pg and 12 ^{13}C-labelled DL-PCBs with 2000 pg each). Extract purification was executed with an automated clean-up system (Power-Prep P6, from Fluid Management Systems, Inc., Watertown, MA, USA).

Two fractions were obtained, one containing mono-ortho substituted PCBs and one containing coplanar PCBs and PCDD/Fs. The purification method was previously described by Abad et al (2000).

All analyses were based on isotope dilution using HRGC-HRMS (high resolution gas chromatography – high resolution mass spectrometry), according to the protocols laid down in U.S. EPA.Method 1613 Method and 1668.

PCDD/Fs, Non-ortho PCBs and HCB were analyzed on double HRGC (Trace GC Ultra, Thermo, Germany) coupled with a DFS mass spectrometer (Thermo Electro Corporation, Bremen, Germany) operating in EI-mode at 45 eV with a resolution of >10000. Quantification was performed on the basis of 1613 and 1668 U.S. EPA methods (U.S. EPA., 1994b, 1999). All compounds were analyzed on BP-DXN 60 m long with 0.25 mm i.d. (inner diameter) and 0.25 µm film (SGE, Victoria, Australia).

The quantified isomers were identified through retention time comparison of the corresponding internal standard and the isotopic ratios between two ions was recorded.

The reported detection limits were calculated individually for each sample on the bases of a signal to noise ratio of 3/1.

For *PAHs and HCB* 1g of ash was extracted with Toluene[3] by Ultrasonification after being spiked with each 100 ng of 16 deuterated PAH internal standards and each 5 ng of 19 ^{13}C-labeled OCP internal standards including 5 ng ^{13}C-labelled HCB.

Ultrasonification was performed for 30 min and the extract was collected in an evaporation tube. Extraction was repeated two times and the combined extract was filtered through 1g of sodium sulphate. The extract was reduced to a volume of 500 µl under a gentle stream of Nitrogen and 100 ng of PAH syringe standard added.

The PAH extracts were analysed in GC/MS Single Ion Monitoring (SIM) on a Thermo DSQ GC with splitless injection of 1 µl of extract. Separation was performed on a DB35-MS capillary column (60 m, 0.25 mm i.d., 0.25 µm film thickness). Quantification was carried out through isotope dilution .

After the instrumental analyses of PAHs, the extract was concentrated to 100µl, and the OCP syringe standard containing 5 ng ^{13}C-labelled β-HCH was added. Subsequently Hexachlorobenzene was analysed with GC-HRMS as described above for PCDD/Fs and PCBs.

Analytical quality was monitored through the recoveries of internal standards and blanks. The Limit of Detection (LOD) was set to signal /noise ratio of 3.

3. Results

3.1 PCDD/Fs and dioxin like PCBs

The concentration (WHO TEQ 2005) of PCDD/Fs and dioxin like PCBs (non ortho fraction) in bottom ash from the wood fired kilns "brick 3" and "brick 5" ranged in between 0.5 and 5 ng WHO_{2005}-TEQ/kg. Interestingly the co-incineration of plastic waste in the "brick 1" kiln did not lead to enhanced PCDD/F concentrations, in spite of the fact that the PCDD/F pattern changed considerably.

For comparison: Launhardt and Thoma (2000) reported PCDD/F concentration ranges of 5-24 ng I-TEQ/kg in bottom ashes from domestic heating with herbaceous biofuel and spruce wood. Wunderli et al. (2000) reported 4.9 ng WHO_{98}-TEQ/kg in bottom ashes from native wood.

In the ash sample of "brick 2", where tar was used as a fuel, WHO_{2005}-TEQs of around 140 ng/kg were measured. This is considerably higher than in the wood fired kilns.

Literature data on PCDD/Fs in bottom ashes from tar fired installations were not found. However, Wang et al. (2009) reported PCDD/F concentrations of 0.74 ng/kg I-TEQ in bottom ash from a heavy oil fired power plant where the emission factors to air were determined as to be 0.19 ng I-TEQ/L of fuel. The combustion conditions in the brick kilns are presumably poor compared to a power plant. This, together with the PCDD/F levels in the ashes that were about 200 fold higher in the tar fired kilns, suggests that tar/waste oil fired brick kilns have the potential of considerable PCDD/F emissions and need further investigation.

Since the ashes are discarded frequently in the surroundings of the brick kilns, including settlement areas and gardens, a comparison with limit values for PCDD/Fs in soils seems indicated. In Germany the Government/Laender Working Group on Dioxins (BLAG, 1992) has proposed guideline values for

[3] As the extract of Brick 2 showed matrix interferences in the SIM mode of the GC/MS, another extraction of 200 mg of sample Brick 2 was performed using n-hexane: acetone (2:1) as solvent.
The quantification of the less volatile PAHs (NAP-PYR) was calculated using the extracts of the Ultrasonification with n-hexane /acetone The quantification of the more volatile PAHs (BaA-BPE) was done using the extracts of the Ultrasonification with toluene. The results obtained for BaA, CHR, BbF, BkF, BaP, IPY, DBA and BPE using the toluene or the hexane/acetone extract differed less than 20 %.

PCDD/Fs in agricultural soil: No limitations are indicated in land use for PCDD/F concentrations < 5 ng I-TEQ/kg. Between 5-40 ng I-TEQ/kg all kind of cultivation is allowed except of pasture use. Above 40 ng I-TEQ/kg only cultivations with proven low PCDD/F transfer into the plants is allowed.

Thus all brick kiln ashes except that of the tar fired instillation would fall into the category of unlimited use and does therefore not pose any particular risk what concerns their PCDD/Fs content.

The ashes from the tar fired kiln "brick 2" instead would fall into the category where the cultivation of food shall be avoided. Moreover the Federal regulation for the protection of soils in Germany (BBodSchV, 1999) requires a soil exchange at PCDD/F levels > 100 ng I-TEQ/kg for children playgrounds, whereas PCDD/F levels < 1000 ng I-TEQ/kg are considered as tolerable for residential areas including public parks, etc. The Federal Ordinance on Sewage Sludge in Germany (AbfKläarV, 1992) prohibits the use of SSL with PCDD\F content > 100/ng/kg as a fertilizer.

The contribution of non-ortho PCBs to the total TEQ was less than 0.1 % when only wood was burnt (Brick 3 and brick 5). In the case of tar combustion in "brick2" the share of PCBs was about 8 % and the co-incineration of plastic in "brick 1" resulted in a contribution of 10 % to the combined TEQ of PCDD/Fs and PCBs. The contribution from other DL-PCBs was negligible.

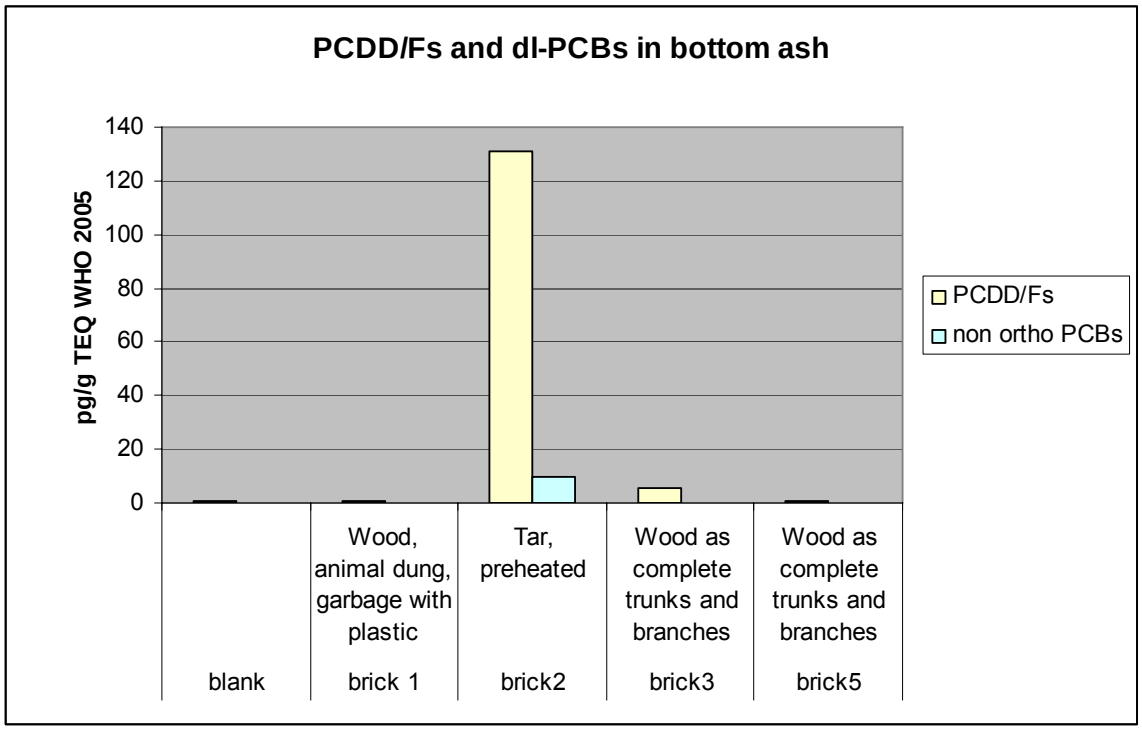

Figure 1: PCDD/Fs and DL-PCBs in bottom ash of kilns operating with different fuels

2,3,7,8- PCDD/F congener patterns in the bottom ashes showed significant differences and were compared to source specific congener patterns available from the literature, applying Principal component analyses (PCA) using *the Unscrambler v. 9.6* (CAMO software AS).

Profiles of the PCDD/F congeners can be used to identify PCDD/F sources in a site and to detect differences among samples. The 2,3,7,8-PCDD/F congener profiles of the combustion samples from Mexico were compared with the congener fingerprint of different industrial and urban emission sources and ambient air profiles of sites with no direct PCDD/F emissions impact. In this way, a PCA was applied to determine the similarity of the combustion samples and how these samples were related to specific sources of PCDD/Fs. PCDD/F emission source fingerprints considered include different types of industry, waste incineration and vehicles fuels as reported in the literature (Buekens et al., 2000; Carroll et al., 2001; Zhu et al., 2008; Lin et al., 2007). Air PCDD/F profiles of sites with no

direct PCDD/F emission impact were taken from different studies in the literature (Tysclind et al., 1993; Hagenmaier et al., 1994; Caserini et al., 2004).

PCA provided a three-dimensional model that accounted for 70 % of the variance. The first PCA (which would explain 45 % of the total variance) is highly and positively correlated with penta, hexa and hepta furans and negatively to OCDD, while the second PCA is positively related to hexa and hepta dioxins and negatively to 2,3,7,8-TCDF.

Samples with similar combustion material (Brick 3 and 5, wood as complete trunks and branches) are located nearby in the PCA graph and they are significantly away from samples Brick 1 and 2, confirming that 2,3,7,8-PCDD/F congener patterns are remarkably different between these two groups of samples.

Brick 3 and 5 (Wood combustion) present 2,3,7,8-PCDD/F congener pattern similar to background air profiles of sites described in the literature as only affected by diffuse pollution mainly coming from disperse domestic combustion emissions into the atmosphere. Moreover, it is interesting to point out that Brick 3 and 5 have also relatively similar fingerprints as emissions from chlorine industry (chloranil, pentachlorophenate, sodium pentachlorophenate, pulp bleaching plants). Therefore, this could be an indication that maybe some pieces of treated wood have been used as combustion material in experiments Brick 3 and 5.

On the other hand, Brick 2 (Preheated tar) is presenting similar contribution on PCA1 as emission samples from coal power plants and lead gas fuel vehicles.

Finally, Brick 1 (Wood, animal dung and garbage with plastic) can not be identified with any of the specific PCDD/F emission sources reported, most probably because this sample consisted of a mix of different combustion materials.

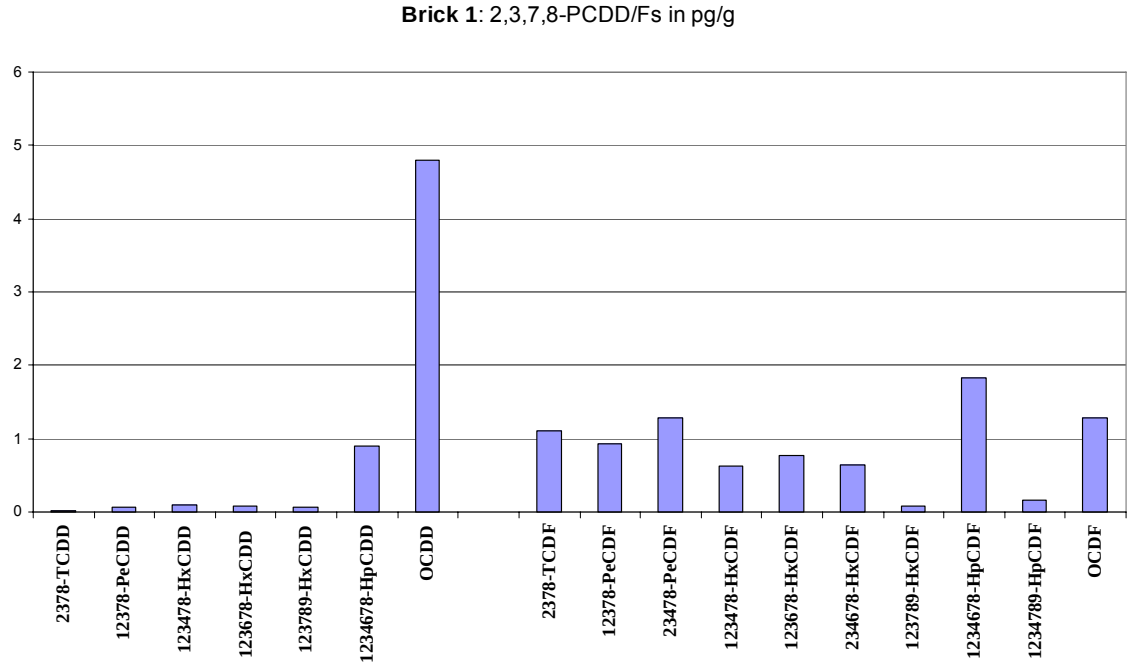

Figure 2: 2,3,7,8 PCDD/F congener pattern in bottom ash of kiln " Brick 1 "

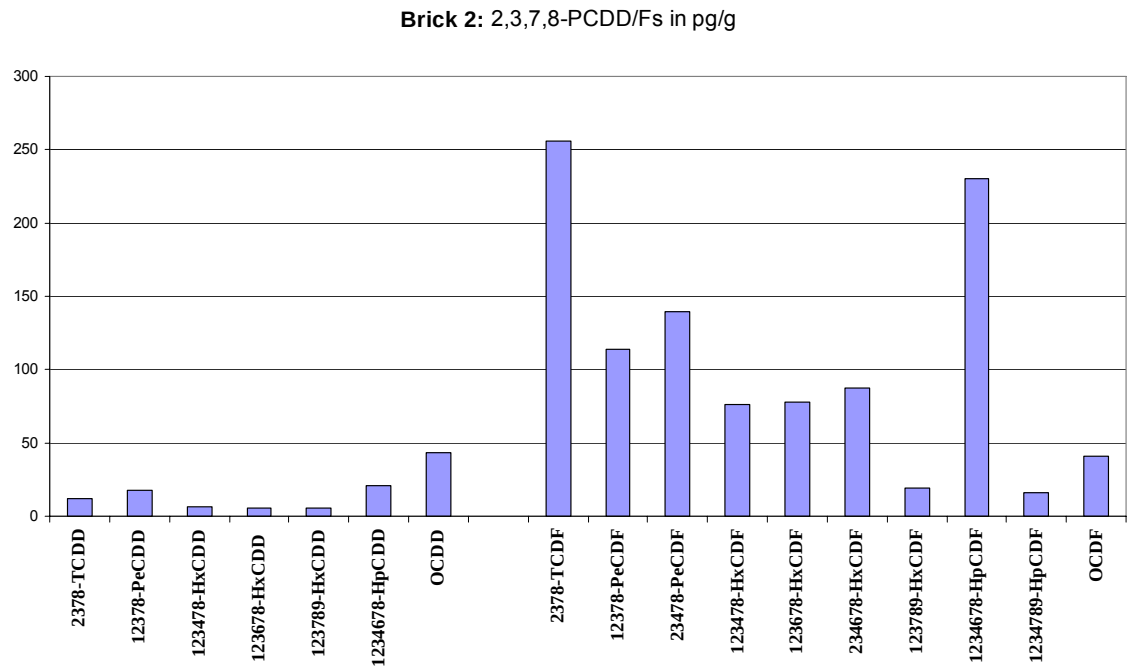

Figure 3: 2,3,7,8 PCDD/F congener pattern in bottom ash of kiln " Brick 2 "

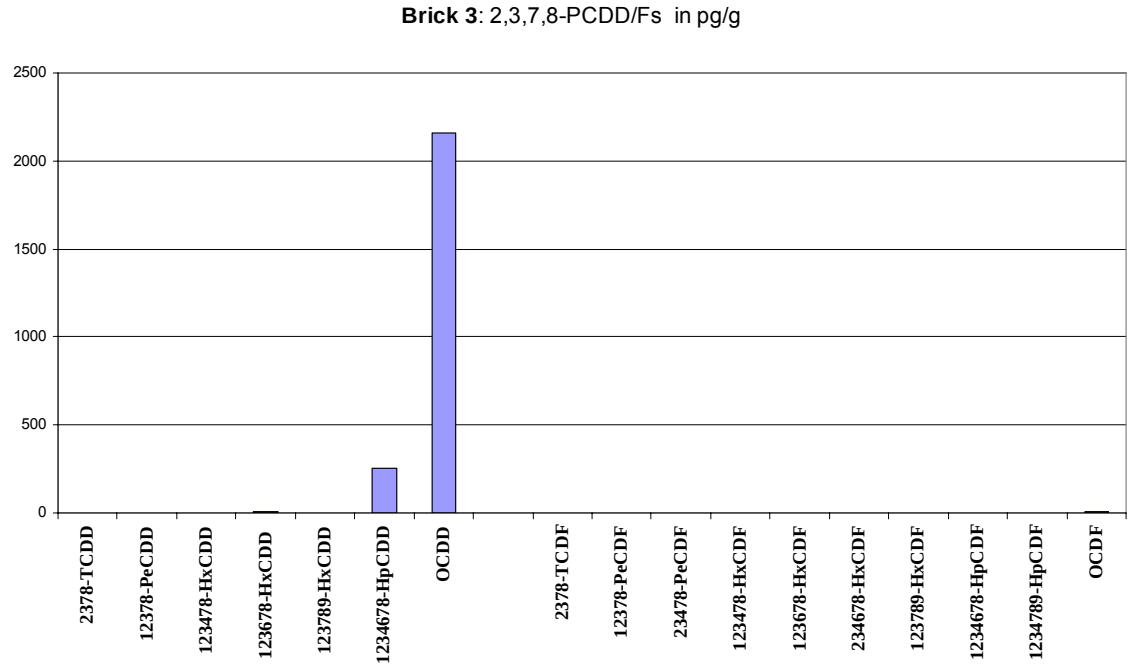

Figure 4: 2,3,7,8 PCDD/F congener pattern in bottom ash of kiln " Brick 3 "

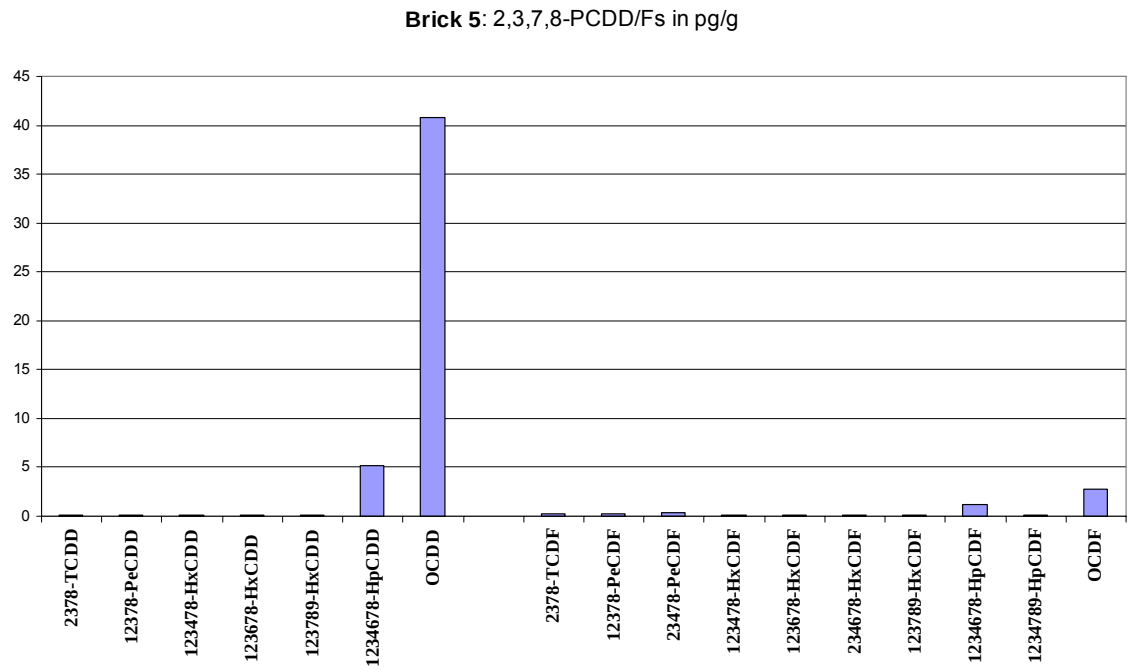

Figure 5: 2,3,7,8 PCDD/F congener pattern in bottom ash of kiln " Brick 5 "

3.2 Hexachlorobenzene (HCB)

The HCB content in bottom ash of "Brick 2" was found to be 1.7 ng/g.

The HCB content in Brick 1, 3 and 5 was under the detection limit (LOD = blank = 0.15 ng/g).

For comparison: In the federal regulation for the protection of soils in Germany (BBodSchV, 1999), soils with an HCB content of < 4 µg/g are considered as suitable for children's playgrounds.

3.3 Polycyclic Aromatic Hydrocarbons (PAHs)

The comparison of PAH in ashes from the different kilns results in a similar picture as seen for PCDD/Fs with kiln "brick2" showing by far the highest values followed by "brick 3". This indicates a contribution of non optimal combustion to the higher PCDD/F concentrations measured in "brick 2" ashes.

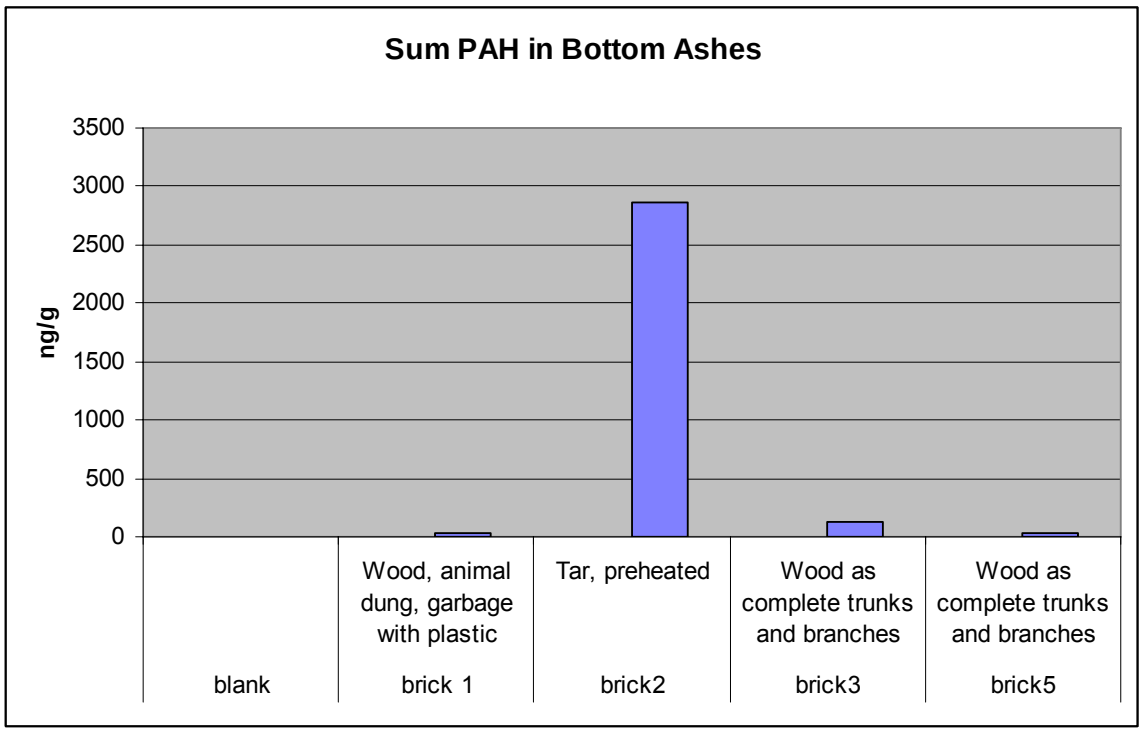

Figure 6: Sum of 16 EPA PAHs in bottom ash of kilns operating with different fuels

B(a)P concentrations in the bottom ash from the tar fired "Brick 2" kiln was 30 µg/kg, which is low compared to the 1 mg/kg alert threshold as laid down in the federal regulation for the protection of soils in Germany (BBodSchV, 1999).

3.4 Emission Factors via residues (bottom ash)

The emission factors resulting for bottom ashes from brick production are given in Table 3 below. Concentrations of PCDD/Fs and PCBs are in WHO 2005 TEQ.

Table 3: Emission factors via residues (bottom ash)

Emission factor via residues (bottom ash)					
	blank	**brick 1** Wood, animal dung, garbage with plastic	**brick2** Tar, preheated	**brick3** Wood as complete trunks and branches	**brick5** Wood as complete trunks and branches
PCDD/Fs ng TEQ/kg	0.47	0.88	131	5.5	0.58
non ortho PCBs ng TEQ/kg	0.017	0.090	9.9	0.047	0.044
HCB ng/kg	<150	<150	1700	<150	<150
16 EPA PAH µg/kg	6	28	2860	125	36

For comparison:

In the Toolkit edition 2.1 from 2005 (UNEP Chemicals 2005) 30-3000 ng I-TEQ/kg in bottom ash from biomass Power plants (6.3.2) are reported and a default of 3000 ng I-TEQ/kg has been selected.

For waste wood and waste biomass Incineration (6.1.6) a range of 4- 23000 ng I-TEQ /kg is reported for fly ash. No data on bottom ash are reported

For household heating and cooking with biomass (6.3.4) a default of 1000 ng I-TEQ /kg has been selected for bottom ash of contaminated biomass fired stoves. For virgin biomass fired stoves the default of 10 ng I-TEQ /kg has been selected.

The preliminary findings in bottom ashes from brick making indicate emission factors - depending on the kind of fuel used - ranging at the lower end of the 2 categories virgin/contaminated wood reported for biomass cooking (6.3.4.) and considerably lower than the emission factors set for biomass-fired power plants.

4. Conclusions

From the few data available it appears that co-incineration of waste in the brick making process can result in higher PCDD/F, PCB, HCB and PAH emissions via bottom ashes, when compared with brick making using virgin wood. This suggests that tar/waste oil fired brick kilns have the potential of considerable PCDD/F emissions and need further investigation.

Consequently the aspect of fuel and in particular co-incineration of wastes has to be taken into consideration for the further experimental planning related to POPs emissions from brick making in developing countries.

However, the preliminary findings in bottom ashes indicate PCDD/F emission factors - depending on the kind of fuel used - ranging at the lower end of the emission factors for small and large scale combustion of biomass.

The environmental impact from the common practice of discharging the bottom ashes in the vicinity of the kilns needs further evaluation. However, what concerns HCB and PAH, levels in the ashes are very low when compared to existing regulations for soils. For PCDD/Fs instead the bottom ashes from the tar/waste oil fired kiln fell into the action levels for agricultural soils and playgrounds in Germany. This suggests the need for an appropriate waste management strategy for brick kiln residues close to residential or agricultural land.

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6. Annex

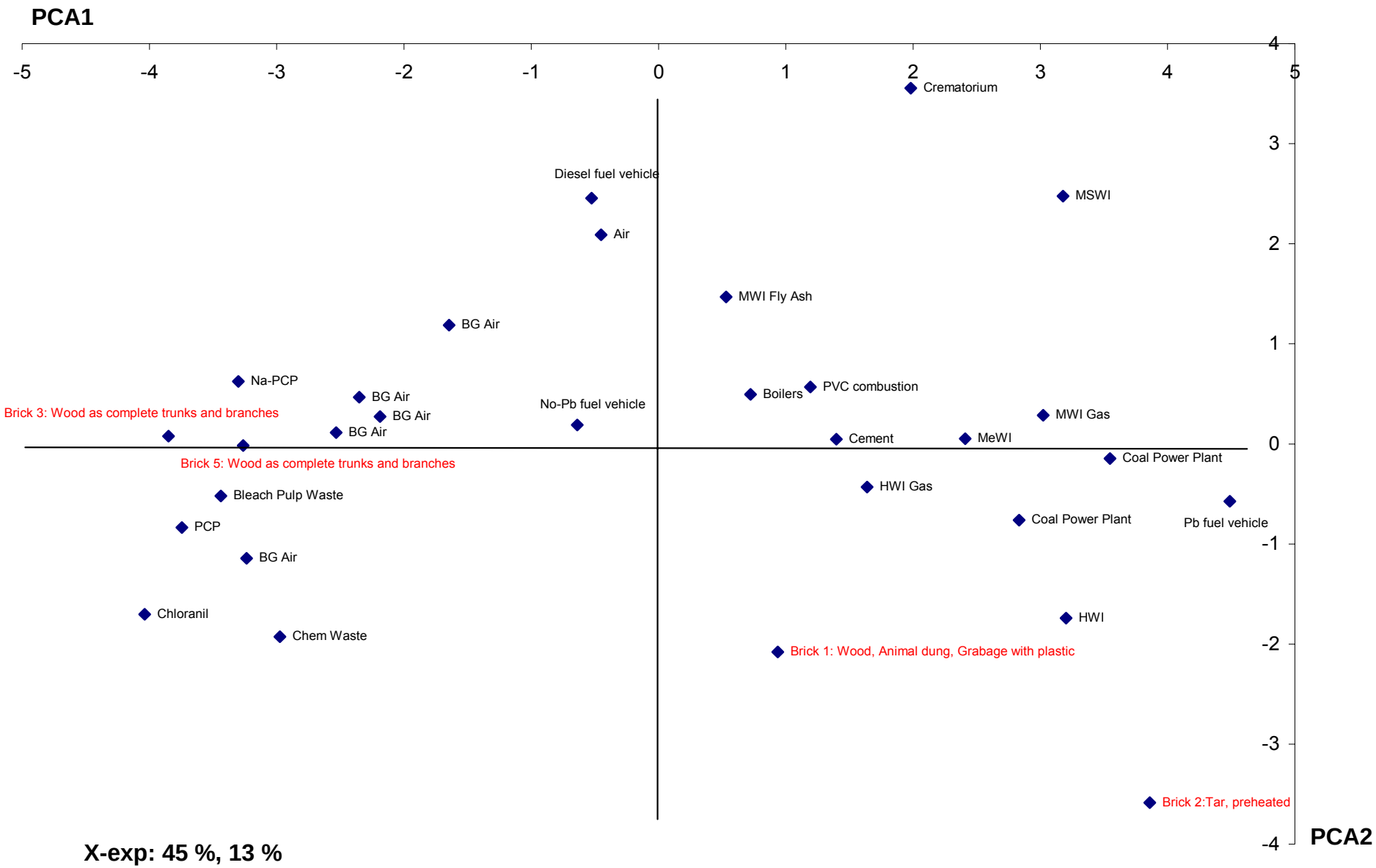
6.1 Data

6.1.1 PCDD/Fs

Sample name:	**B lank**	Brick 1	Brick 2	Brick 3	Brick 5
Type of sample:	**Analytical Blank**	ıimal dung, garbage wi	Tar, preheated	; complete trunks and l	complete trunks and t
Volume sampled:	**2**	1.99	2.02	2	2.08
Data analysed:	**18/09/08**	19/09/08	19/09/08	19/09/08	19/09/08
Concentration:	**pg/g**	pg/g	pg/g	pg/g	pg/g
2,3,7,8 - substituited PCDD/Fs					
2378-TCDD	**0.14**	**0.02**	12.29	**0.62**	**0.16**
12378-PeCDD	**0.17**	**0.07**	17.58	**0.52**	**0.13**
123478-HxCDD	**0.06**	**0.10**	6.59	0.60	**0.11**
123678-HxCDD	**0.18**	**0.08**	5.82	5.07	**0.18**
123789-HxCDD	**0.09**	**0.07**	5.96	2.33	**0.17**
1234678-HpCDD	1.02	0.90	20.92	251.00	5.15
OCDD	7.27	4.79	43.30	2161.85	40.74
2378-TCDF	**0.16**	1.10	255.52	**0.33**	**0.22**
12378-PeCDF	**0.12**	0.93	114.16	**0.37**	**0.26**
23478-PeCDF	**0.14**	1.29	139.40	**0.58**	**0.33**
123478-HxCDF	**0.14**	0.63	76.07	**0.26**	**0.08**
123678-HxCDF	**0.10**	0.77	78.11	**0.32**	**0.10**
234678-HxCDF	**0.18**	0.64	87.43	**0.37**	**0.16**
123789-HxCDF	**0.02**	**0.08**	19.27	**0.34**	**0.09**
1234678-HpCDF	**0.44**	1.83	230.52	1.93	1.17
1234789-HpCDF	**0.05**	**0.16**	15.71	**0.26**	**0.11**
OCDF	1.03	1.28	41.13	4.25	2.82
Upper-bound					
I-TEQ	0.42	1.13	152.72	6.85	0.62
1998 WHO-TEQ	0.50	1.15	161.43	5.16	0.64
2005 WHO-TEQ	0.47	0.88	131.29	5.47	0.58
Total PCDD/Fs					
TCDD	**0.00**	**0.00**	121.72	**0.00**	**0.00**
PeCDD	**0.00**	**0.00**	101.26	**0.00**	**0.00**
HxCDD	**0.00**	**0.00**	64.21	36.12	0.00
HpCDD	1.54	1.75	40.71	416.93	8.06
OCDD	7.27	4.79	43.30	2161.85	40.74
TCDF	**0.00**	17.97	3992.00	**0.00**	**0.00**
PeCDF	**0.00**	12.69	1722.12	**0.00**	**0.00**
HxCDF	**0.00**	5.63	759.72	**0.00**	**0.00**
HpCDF	**0.00**	2.85	312.75	7.47	2.64
OCDF	1.03	1.28	41.13	4.25	2.82
Total PCDDs	8.80	6.54	371.20	2614.91	48.80
Total PCDFs	1.03	40.42	6827.73	11.72	5.46
Total PCDD/Fs	9.83	46.96	7198.93	2626.62	54.26
Recovery %					
2378-TCDD 13C12 STD	33.04	49.08	55.23	13.30	19.11
12378-PeCDD 13C12 STD	36.25	54.30	50.21	12.92	33.21
123478-HxCDD 13C12 STD	50.08	78.85	79.97	17.85	60.37
123678-HxCDD 13C12 STD	48.43	74.90	73.18	16.74	54.27
1234678-HpCDD 13C12 STD	38.46	67.60	49.99	13.45	46.51
OCDD 13C12 STD	32.74	63.36	35.66	10.67	43.53
2378-TCDF 13C12 STD	30.36	42.76	39.04	12.15	14.58
12378-PeCDF 13C12 STD	37.47	52.38	47.07	13.89	25.75
23478-PeCDF 13C12 STD	36.71	58.54	47.65	13.82	29.45
123478-HxCDF 13C12 STD	44.97	74.32	65.53	15.67	49.96
123678-HxCDF 13C12 STD	48.91	75.70	65.63	16.16	52.64
234678-HxCDF 13C12 STD	50.18	87.59	64.20	16.85	59.04
123789-HxCDF 13C12 STD	44.22	75.26	62.05	14.94	48.42
1234678-HpCDF 13C12 STD	41.25	69.05	45.64	13.30	31.68
1234789-HpCDF 13C12 STD	40.24	66.71	46.79	13.57	47.44

Bold numbers are LOD

PCA on 2,3,7,8 PCDD/Fs



X-exp: 45 %, 13 %

6.1.2 Non ortho dioxin-like PCBs

Sample name:	B lank	Brick 1	Brick 2	Brick 3	Brick 5
Type of sample:	Analytical Blank	ıimal dung, garbage w	Tar, preheated	; complete trunks and b	complete trunks and b
Volume sampled:	2	1.99	2.02	2	2.08
Data analysed:	18/09/08	19/09/08	19/09/08	19/09/08	19/09/08
Concentration:	pg/g	pg/g	pg/g	pg/g	pg/g
Non-ortho-substituited PCBs					
PCB-81	**0.1305**	**0.2350**	19.0374	**0.4162**	**0.4699**
PCB-77	4.009	4.097	219.407	3.697	2.990
PCB-126	**0.114**	0.812	94.234	**0.402**	**0.402**
PCB-169	**0.1667**	**0.2711**	14.4047	**0.2254**	**0.0965**
Upper-bound					
1998 WHO-TEQ	0.0135	0.0843	9.5913	0.0429	0.0415
2005 WHO-TEQ	0.0168	0.0898	9.8832	0.0474	0.0435
Recovery %					
PCB-81 13C12 STD	17.53	38.57	24.86	10.03	3.51
PCB-77 13C12 STD	24.48	51.39	32.40	13.13	6.01
PCB-126 13C13 STD	49.19	86.66	57.69	18.64	30.61
PCB-169 13C12 STD	57.29	92.12	79.06	19.95	54.82

6.1.3 PAHs

Sample name	**Brick 1**	**Brick 2**	**Brick 3**	**Brick 5**
labcode	average080921-206	080921-08-207-sim1	080921-08-208-sim1	080921-08-209-sim1
weight in g	1.00	1.00/0.2	1.00	2.43
Concentration	ng/g	ng/g	ng/g	ng/g
naphthalene	12.54	940.45	15.93	2.73
acenaphtylene	LOD	366.04	5.19	1.32
acenaphthene	LOD	308.58	LOD	LOD
fluorene	LOD	30.20	1.83	LOD
phenanthrene	6.11	591.89	42.19	13.88
anthracene	0.27	88.56	1.42	0.16
fluoranthene	1.87	103.40	10.38	6.59
pyrene	1.19	166.50	22.79	2.11
benz(a)anthracene	0.25	45.35	1.43	0.55
chrysene	0.85	116.80	6.40	0.94
benzo(b)fluoranthene	0.34	18.55	1.96	0.85
benzo(j+k)fluoranthe	0.20	12.81	2.41	1.18
benzo(a)pyrene	0.14	29.05	2.39	0.86
Indeno pyrene	0.31	7.24	1.44	0.93
Dibenzo (a,h) anthracer	0.26	2.98	0.45	0.20
Benzo (ghi)perylene	0.39	31.66	4.15	1.09
Upper bound				
Sum PAH	28.05	2860.06	124.67	35.67
LOD				
naphthalene	0.14	1.61	0.60	0.13
acenaphtylene	1.44	6.46	1.42	0.47
acenaphthene	2.44	8.45	4.30	1.56
fluorene	0.75	4.20	1.42	0.73
phenanthrene	0.27	0.77	0.32	0.03
anthracene	0.27	1.03	0.32	0.03
fluoranthene	0.05	1.40	0.58	0.03
pyrene	0.05	1.40	0.58	0.03
benz(a)anthracene	0.05	1.80	0.01	0.02
chrysene	0.15	1.80	0.06	0.03
benzo(b)fluoranthene	0.06	2.10	0.18	0.14
Benzo(j+k)fluoranthene	0.13	3.20	0.36	0.27
benzo(a)pyrene	0.11	3.00	0.35	0.13
Indeno pyrene	0.03	2.63	0.30	0.14
Dibenzo (a,h) anthracer	0.04	0.98	0.07	0.09
Benzo (ghi)perylene	0.03	3.93	0.22	0.04
Recoveries in %				
naphthalene	103.74	24.05	59.25	79.74
acenaphtylene				
acenaphthene	80.67	59.90	53.92	72.18
fluorene	93.76	not done	62.97	94.25
phenanthrene	61.78	83.47	37.33	65.80
anthracene	86.96	97.56	48.73	95.00
fluoranthene	78.33	93.11	56.18	73.18
pyrene	86.90	88.58	58.42	76.41
benz(a)anthracene	145.83	85.31	99.84	101.53
chrysene	130.55	77.50	86.72	96.71
benzo(b)fluoranthene	110.45	85.46	68.83	97.77
Benzo(j+k)fluoranthene	126.29	106.26	55.84	78.71
benzo(a)pyrene	129.02	89.90	59.75	88.54
Indeno pyrene	113.42	89.24	70.18	122.46
Dibenzo (a,h) anthracer	120.30	100.78	73.76	129.86
Benzo (ghi)perylene	105.75	74.60	56.90	112.35

6.2 Photo documentation of the sampling

6.2.1 Ash samples

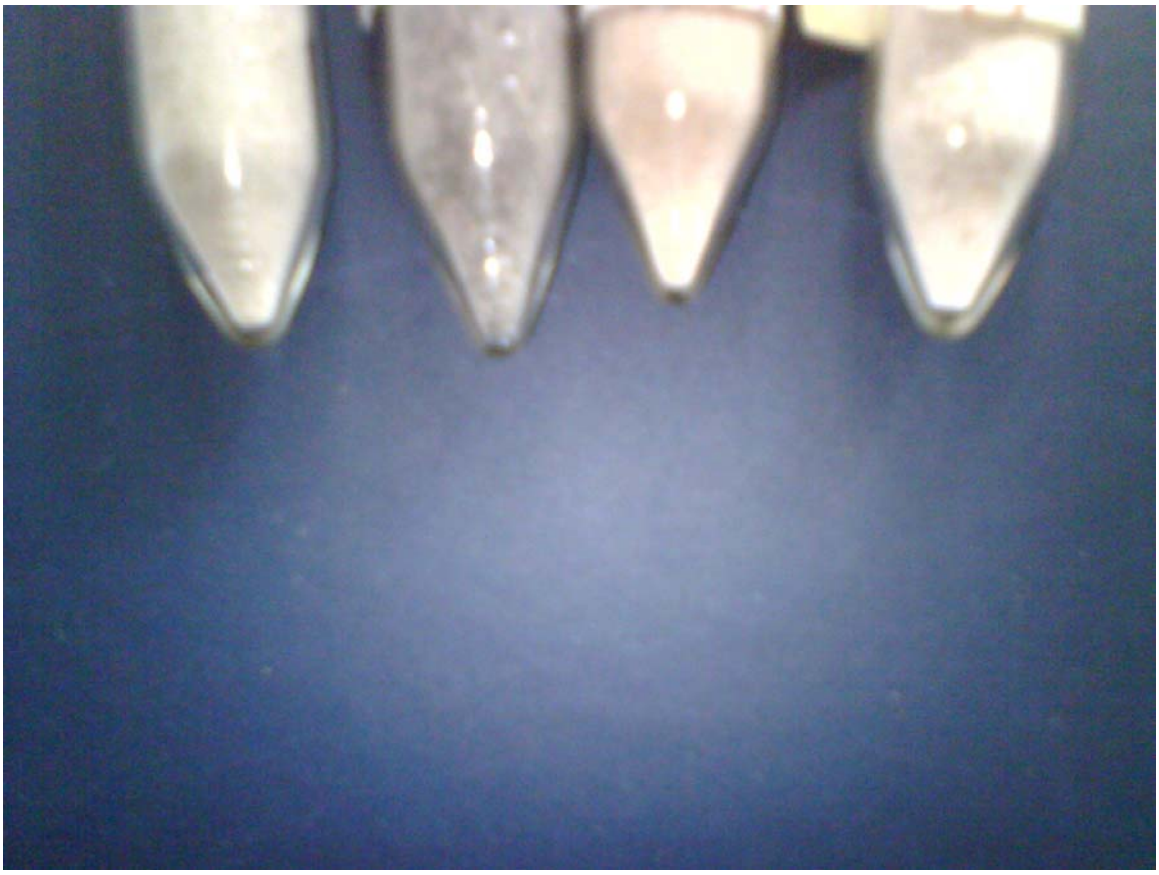


Photo 1: Ash samples in the lab, brick 1, 2, 3, 5 from left to right

6.2.2 Brick making in Abasolo Municipality

Photo 2: Brick 1. Stationary kiln with underground firing

Photo 3: Inside view into an empty stationary kiln

Photo 4: Charging of a stationary kiln with raw bricks

Photo 5: View on the top of a stationary kiln in the initial burning phase

Photo 6: Brick 1. Location of the ash sampling

Photo 7: Brick 1, fuel, ashes in the background

Photo 8: Brick 1, more fuel

Photo 9: Brick 1, Drying of the raw bricks. Ingredients (clay, dung and saw dust) visible

Photo 10: Brick 2, Stationary kiln, fuel (tar) and ashes visible

Photo 11: Brick 3, Stationary kiln, wood fired

6.2.3 Brick making in El Refugio

Photo 12: Brick 5. Manual brick making

Photo 13: Brick 5. Drying of the raw bricks and ingredients

Photo 14: Brick 5. Clay and dung used for brick production

Photo 15: Brick 5. Mobile brick kiln with burnt bricks under de assembling

Photo 16: Brick 5. Mobile kiln under fire

Photo 17: Brick 5. First kiln under demontage (red bricks), second kiln sealed with dung and ready to burn

Photo 18: Brick 5. Raw bricks made of dung and clay

European Commission

EUR 23684 EN – Joint Research Centre – Institute for Environment and Sustainability

Title: Releases of PCDD/Fs, PCBs, PAHs and HCB through bottom ashes from brick kilns operating with different kind of fuels - Results from a pilot study in Mexico. A contribution to the update and review of the Standardized Toolkit for Identification and Quantification of Dioxin and Furan Releases

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Abstract
The Standardized Toolkit for Identification and Quantification of Dioxin and Furan Releases is aimed at supporting the parties to the Stockholm Convention (SC) on Persistent Organic Pollutants (POPs) in setting up their national implementation plan, which includes the characterization of unintentional releases of POPs (in this case PCDD/Fs, PCBs and HCB) from all relevant sectors. To this end the toolkit combines sector specific activity data with related emission factors for releases to air, land, water, residues and products.
In 2007 the Expert Group for updating and improving the Toolkit, chaired by the Secretariat of the SC (SSC) and UNEP, identified priority areas of research. The group highlighted the need for screening POPs sources that so far are poorly characterized in the Toolkit. Among these, brick kilns in developing countries were given highest priority since so far, no data were available.
The Expert Group recommended as a first step to measure soil or vegetation samples close to (small) brick kilns in developing countries to obtain preliminary orientation as to the impact from this source.
In the fore field of the experimental planning the question in how far different kinds of fuels, in particular waste derived fuels, may impact the formation of POPs was approached through the analyses of bottom ashes from kilns co-incinerating waste in comparison with brick kilns operated with virgin wood.
The results from bottom ash reveal a distinct impact on the presence of POPs in the brick making process when waste, and in particular residual oil, is co-incinerated, thus suggesting to include the brick kilns operated with waste fuels as a different category into the toolkit and to include the issue of co-incineration of waste into the experimental set up.
The PCDD/F emission factors via the bottom ashes itself range at the lower end of similar categories in the toolkit referring to the ashes from the combustion of biomass.

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