



# J R C T E C H N I C A L R E P O R T S

## PCDD/PCDF, PCB, and Hexachlorobenzene in soil, bottom ash and products from brickmaking sites in developing countries - Results from surveys in Kenya, Mexico, and South Africa

A contribution to the Standardized Toolkit  
for Identification and Quantification of  
Dioxin and Furan Releases in support to  
the Stockholm Convention on Persistent  
Organic Pollutants

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*Picture on the cover page, courtesy of Henk Bouwman, shows an industrial scale brick kiln in South Africa.  
Picture on the next page, courtesy of Charles Mirikau, shows an artisanal brick kiln in Kenya.*

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# PCDD/PCDF, PCB, and Hexachlorobenzene in soil, bottom ash and products from brickmaking sites in developing countries – Results from surveys in Kenya, Mexico, and South Africa

A contribution to the Standardized Toolkit for Identification and Quantification of Dioxin and Furan Releases in support to the Stockholm Convention on Persistent Organic Pollutants



Cracow University  
of Technology



University of Nairobi



## Abbreviations

DL-PCB	Dioxin-like PCBs
GC	Gas chromatograph
HCB	Hexachlorobenzene
HRGC	High Resolution Gas Chromatograph
HRMS	High Resolution Mass Spectrometer
LOD	Limit of Detection
OCDD	Octachlorodibenzo-p-dioxin
OCP	Organochlorine Pesticide
PCB	Polychlorinated Biphenyls
PCDD/PCDF	Polychlorinated Dibenzo-p-dioxins and Dibenzofurans
PeCDD/PeCDF	Pentachlorodibenzo-p-dioxin and Pentachlorodibenzofuran
HxCDD/HxCDF	Hexachlorodibenzo-p-dioxin and Hexachlorodibenzofuran
HpCDD/HpCDF	Heptachlorodibenzo-p-dioxin and Heptachlorodibenzofuran
OCDD/OCDF	Octachlorodibenzo-p-dioxin and Octachlorodibenzofuran
TCB	Tetrachlorobiphenyl
PeCB	Pentachlorobiphenyl
HxCB	Hexachlorobiphenyl
HpCB	Heptachlorobiphenyl
TEQ	Toxic Equivalency (2,3,7,8 TCDD, Equivalent – see A. 1)
POPs	Persistent Organic Pollutants
TCDD/TCDF	Tetrachlorodibenzo-p-dioxin and Tetrachlorodibenzofuran
WHO	World Health Organization

## Units

Basic SI units	SI-derived units	Non-SI units	Magnitudes/prefixes
m (=) metre	°C (=) celsius	a (=) year	M (=) mega ( $10^6$ )
g (=) gramme	J (=) joule	d (=) day	k (=) kilo ( $10^3$ )
s (=) second		h (=) hour	c (=) centi ( $10^{-2}$ )
K (=) kelvin		min (=) minute	m (=) milli ( $10^{-3}$ )
t (=) metric ton		L (=) litre	μ (=) micro ( $10^{-6}$ )



## Executive Summary

Hardly any emission data regarding Polychlorinated Dibenzo-p-dioxins and Dibenzofurans (PCDD/PCDF) and other unintentionally produced POPs are available for brick-production plants in developing countries, mainly due to the lack of infrastructure for sampling flue gasses. In addition, the installations are often small and do not warrant measurements, or are constructed in such a way that conventional stack sampling cannot be performed. However, from the few data available from a previous pilot study in the state of Guanajuato, Mexico, emissions of (PCDD/PCDF) from brick production turned out to be low. PCDD/PCDF emission factors to air were between 0.045 $\mu\text{g}$  TEQ (wood-fired kiln) and 0.20  $\mu\text{g}$  TEQ (waste-oil-fired kiln) per tonne of bricks produced. The TEQ contributions of dioxin-like PCB were between 1% and 10%, and HCB concentrations were about three orders of magnitude higher than the total TEQ.

Since the data obtained from the Guanajuato study describe only a fraction of the technologies and fuels employed worldwide in the brickmaking process, it remained unclear as to how far these air emission factors can be applied to other, so far uninvestigated, installations elsewhere.

In this study, we conducted an indirect validation of the representativeness of the emission factors obtained from the Guanajuato study by comparing unintentional persistent organic pollutants (POPs) in the neighboring top soils, production ash and bricks from a series of brick kilns in different world regions, thus covering a broader range of technologies and fuels involved.

Two large-scale industrial and one small subsistence brick kiln in South Africa, six small subsistence brick kilns in Kenya, and 10 commercial backyard kilns in Mexico (including those in Guanajuato where the emission factors had been determined) were investigated.

The aim of this study is to investigate whether the air emission factors obtained from the Guanajuato study can be applied to other kilns that use a broader range of technologies and fuels. This indirect validation is based on the premise that air emissions of unintentionally produced POPs can be assumed to be similar when concentrations in surrounding soils, bottom ash and bricks are similar.

With one exception, PCDD/PCDF in bottom ash and bricks from the Mexican sites were rather uniformly distributed among the investigated kilns. WHO<sub>2005</sub>-TEQs were typically in the lower ng/kg, including those sites where air emission factors were determined in the earlier study. Assuming that PCDD/PCDF concentrations in bottom ash and bricks are indicative of those in air emissions, the range of air emission factors obtained in Guanajuato appears to be applicable to all but one of the investigated sites in Mexico. Dioxin-like PCB, as seen in the earlier emission measurements, showed negligible contributions to the overall dioxin-like toxicity in all sites and matrices.

Brick kilns in South Africa and Kenya displayed similar, although somewhat lower, PCDD/PCDF concentrations in ash and bricks. This, together with the overall lower concentrations in the nearby soils, supports the assumption that the air emission factors obtained from the two kilns in Guanajuato can be applied in South Africa and Kenya as an upper limit estimate for brickmaking emissions in the investigated sites.

Summary Table: Average, Median and Maximum Concentrations in soil, bottom ash and bricks												
	Kenya				South Africa				Mexico			
	Av	Med	Max	<i>n</i>	Av	Med	Max	<i>n</i>	Av	Med	Max	<i>n</i>
<b>Surrounding soil</b>												
<b>PCDD/PCDF</b> <i>pg TEQ/g</i>	0.14	0.14	0.23	8	0.19	0.10	0.69	21	2.7	0.44	18	21
<b>DL-PCB</b> <i>pg TEQ/g</i>	0.11	0.060	0.63		0.033	0.032	0.086		0.094	0.036	0.50	
<b>HCB</b> <i>pg/g</i>	20	20	21		63	19	280		318	69	2400	
<b>Background soil</b>												
<b>PCDD/PCDF</b> <i>pg TEQ/g</i>	0.18	0.17	0.24	3	0.17	0.11	0.33	3	0.42	0.24	0.78	3
<b>DL-PCB</b> <i>pg TEQ/g</i>	0.031	0.04	0.047		0.053	0.015	0.14		0.054	0.066	0.066	
<b>HCB</b> <i>pg/g</i>	17	17	17		231	17	660		388	550	550	
<b>Bottom ash</b>												
<b>PCDD/PCDF</b> <i>pg TEQ/g</i>	0.13	0.14	0.24	8	0.32	0.06	1.2	4	11	0.43	131	13
<b>DL-PCB</b> <i>pg TEQ/g</i>	0.034	0.034	0.0051		0.011	0.010	0.019		0.82	0.048	0.90	
<b>HCB</b> <i>pg/g</i>	43	32	100		73	48	177		242	83	1700	
<b>Bricks</b>												
<b>PCDD/PCDF</b> <i>pg TEQ/g</i>	NA	NA	NA	0	0.050	0.053	0.06	3	4.1	0.20	15	7
<b>DL-PCB</b> <i>pg TEQ/g</i>	NA	NA	NA		0.022	0.0072	0.053		0.10	0.014	0.39	
<b>HCB</b> <i>pg/g</i>	NA	NA	NA		17	17	18		36000	500	120000	
<b>Notes:</b> Concentrations middle bound, all TEQs in WHO 2005 NA (=) not analysed												

The soil transects taken in the vicinity of the investigated kilns in Mexico generally did not display the clear spatial concentration gradients that could be expected for undisturbed soils

under the impact of a point source. This may be due to the high level of urbanisation around the Mexican kilns, resulting in disturbed soils and emissions (including historic ones) from other urban and small-scale industrial activities. In South Africa and Kenya, the concentrations were too low to establish interpretable gradients. Consequently, the concept of assessing the emission source strength of these kilns indirectly through contamination gradients in the surrounding soil partially failed. Nevertheless, the concentrations recorded in soils from urban and remote areas in this study are useful for generating a global view of the environmental impact of brickmaking, and for supplementing the fragmentary database on soil contamination by POPs in developing countries.

The predominately low concentrations of unintentionally produced POPs in soils around the brickmaking sites indicate that brickmaking in developing countries, including when certain secondary fuels are used, is not a significant source of unintentionally produced POPs. The concentrations of PCDD/PCDF, PCB and HCB in brick and bottom ash were also generally low.

The overall low concentrations of the investigated POPs in the soils around the brickmaking sites indicate that brickmaking has minor environmental and health impacts in developing countries, including when secondary fuels are used. Even in the PCDD/PCDF “hotspots” of some Mexican soils, the concentrations are still acceptable for playground or agricultural soil use according to German standards. The concentrations of PCDD/PCDF, PCBs and HCB in brick and bottom ash were also found to be generally low, and do not pose a risk to the environment or human health. This, together with the comparably low emission factors determined for brick kilns so far, suggests that the co-firing of waste in the brick-production process can be an adequate waste management option for high-caloric wastes in developing and transition countries, if more sophisticated waste combustion technologies are not available.

It would be useful to extend this survey to brick kilns from other regions and to other production technologies, in a first step by screening bricks and bottom ash, in order to confirm and refine the few available emission factors for brickmaking in developing countries. Sporadically higher PCDD/PCDF concentrations in bricks and ash, as seen in one of the sites in Mexico, should be supplemented by emission measurements from those installations.

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## 1. Background

The parties to the Stockholm Convention (SC) on Persistent Organic Pollutants (POPs) are obliged to submit, along with their national implementation plan, a national inventory of the sources and estimated releases of their unintentionally<sup>1</sup> produced POPs (PCDD/PCDF, PCB, hexachlorobenzene, and pentachlorobenzene).

Most parties to the SC already have emission inventories of PCDD/PCDF and PCB and partially of hexachlorobenzene and pentachlorobenzene. While, in the northern hemisphere, these inventories are based on measurements of the various emission sources (e.g. the EU Dioxin Inventory 1999/2002 - <http://ec.europa.eu/environment/dioxin/download.htm#stage2>), only few emission data are available for the technologies used in developing or emerging countries.

In order to provide all parties, including developing countries and countries with economies in transition, with a suitable tool for preparing their inventories, thus producing a comparable database of releases of unintentionally produced POPs, the Conference of the Parties (COP) to the SC mandated the United Nations Environment Programme (UNEP) with developing the Toolkit for Identification and Quantification of Releases of Dioxins, Furans and Other Unintentional POPs (Toolkit) <http://chm.pops.int/Overview/tabid/372/Default.aspx>. The Toolkit is a protocol for identifying sources and estimating releases of unintentionally produced POPs to air, land, water, products and residues.

This information shall be used as a basis to develop action plans to address priority sources at the national level (National Implementation Plan, NIP) and to reduce POP releases. The final version of the Toolkit has to be endorsed by the Conference of the Parties (COP) of the SC. The Toolkit was initiated in 1999 by UNEP Chemicals, and was later welcomed by the COP (SC-2/5). The first edition of the Toolkit was released in 2005 (UNEP Chemicals, 2005).

The application of the Toolkit basically involves three elements:

- First, the identification of sources, including each of the source categories listed in Annex C - parts II and III, and a strategy for identifying new source categories.
- Second, emission factors for releases of unintentionally produced POPs to five vectors – air, water, land, products and residues. These emission factors are expressed as the amount of unintentionally produced POPs per tonne of fuel, or products within the classes of each source category<sup>2</sup>.
- Third, the national activity level within the respective class or source category; this must be estimated by the user.

The combination of emission factors and activity levels gives a national and class- or source-category-specific emission rate expressed in amounts of unintentionally produced POPs released to the five vectors.

---

<sup>1</sup> According to Annex C of the SC, these are the POPs released unintentionally from various processes, while the other POPs subject to the Convention are mainly pesticides or industrial chemicals such as intentionally produced PCB. Many pesticides (e.g. DDT and Lindane) and PCB have been banned for years in most countries, and the focus of the SC is more on the correct handling of obsolete stocks of legacy POPs and contaminated production sites.

<sup>2</sup> Emission factors for PCDD/PCDF and dl-PCB are expressed in terms of toxic equivalents (TEQ).

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, as mandated by decision SC-3/6. The group highlighted the need for screening PCDD/PCDF sources that are poorly characterised in the Toolkit to date. Among these, brick kilns in developing countries were the given highest priority because the activity rates in this source category are high and no data on PCDD/PCDF or other unintentionally produced POPs are yet available. It was also noted that the type of fuel used for brickmaking is not addressed in the Toolkit.

Brickmaking in developing countries, using simple technologies which do not provide for any abatement of emissions, is a source category that becomes particularly important when economies start to grow and demand for construction materials increases. Traditionally, bricks are made using virgin biomass as fuel. Apart from the overuse of resources in the vicinity of the kilns, the increasing scarcity of virgin biomass leads to the uncontrolled use of alternative fuels, often high-caloric waste such as plastic materials, waste oils, etc. Consequently, releases of hazardous compounds, particularly unintentionally produced POPs, may become an issue in national emission inventories. In addition to occupational health, public health may be a concern, since production sites are often part of settlement areas, and biota may also be adversely affected.

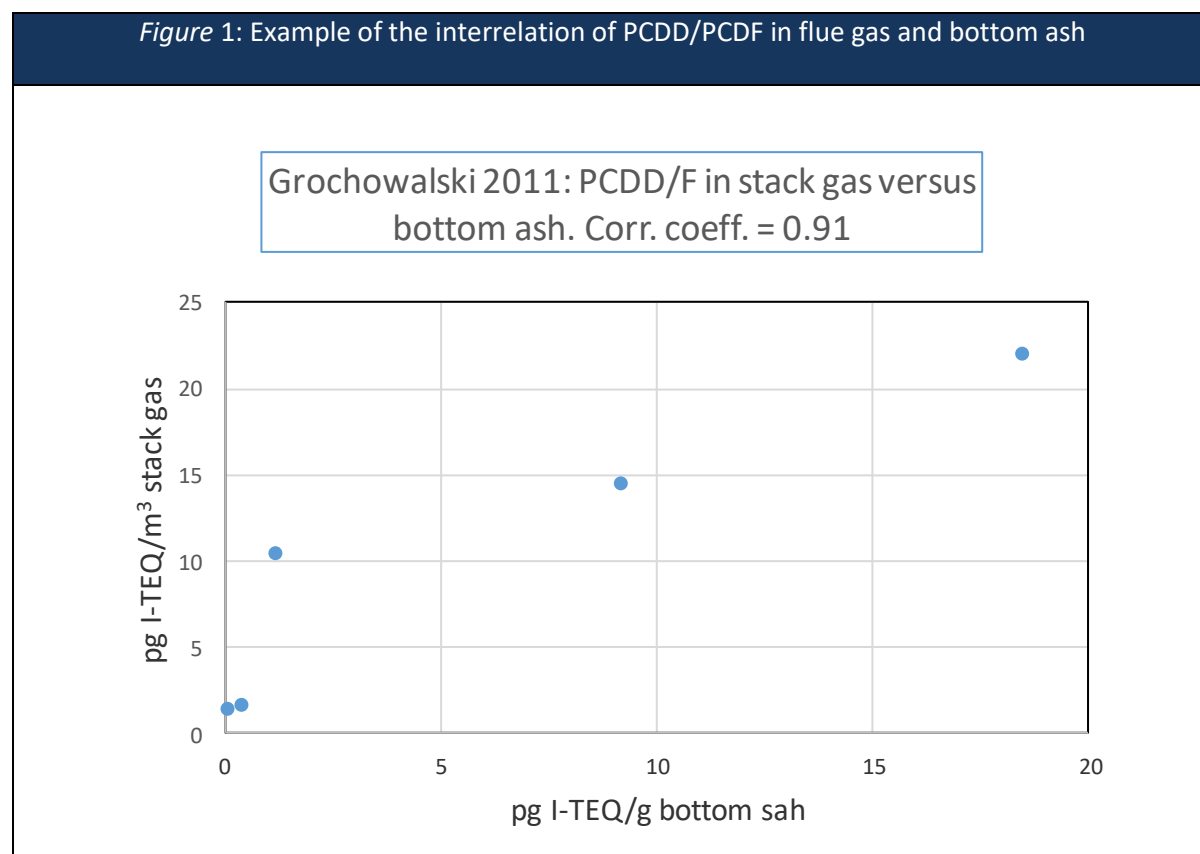
Hardly any emission data are available for brick production technologies employed in developing countries, mainly due to the lack of infrastructure to execute the measurements. In addition, such installations are often small and do not warrant measurements or are constructed in such a way that traditional in-stack measurements cannot be performed. However, judging from the few data available from a pilot study in the state of Guanajuato, Mexico, PCDD/PCDF emissions to air from brick production seem to be low, with PCDD/PCDF emission factors (EFs) to air of between 0.045 $\mu$ g TEQ (wood-fired kiln) and 0.20  $\mu$ g TEQ (waste-oil-fired kiln) per tonne of bricks produced. PCB contributed between 1 and 10% of total TEQ, and HCB levels were about three orders of magnitude higher than the total TEQ. (Maiz et al., 2010). Mexico was selected for this study because it is a transition or “middle income” country that has the scientific and technical infrastructure for executing the emission sampling, whereas in “low income” developing countries it would be difficult and costly to undertake such experiments. In addition, the Mexican partner INE CENICA was able to provide an in-kind contribution to cover the costs of sampling. In 2013, the emission factors obtained from the Guanajuato study of emissions to air, and for products (bricks) and residues (ash) from this study, were included in the current Toolkit revision for source group 4 (UNEP Chemicals 2013).

## 2. Objective

Since the air emission factors (EFs) obtained from the Guanajuato study describe only a fraction of the technologies and fuels employed worldwide in brickmaking, it remains unclear as to whether or not these emission factors can be applied to installations elsewhere.

To reduce this uncertainty, we collected additional data on unintentionally produced POPs in soil, bottom ash and bricks (the latter two are used in the Toolkit for the calculation of EFs to land and products) from two large-scale industrial and one small subsistence brick kiln site in South Africa, six small subsistence brick kiln sites in Kenya, and ten commercial backyard kilns in Mexico, thus covering a broader range of technologies and fuels. The sites in Mexico include the environment of the brick kilns where the EFs to air had already been determined. In addition, background soils from all sites were analysed.

The comparison of unintentionally produced POPs levels in impacted soils, ash and bricks shall serve as an indirect validation of the representativeness of the EFs to air, obtained from the Guanajuato study. The underlying assumption is that substantial differences in POPs emissions to air should also be associated with concentration differences in the bottom ash, surrounding soils, and bricks. An example of the interrelation of PCDD/PCDF concentrations in bottom ash is illustrated in *Figure 1* below (Grochowalski & Koniecznyński, 2008; Grochowalski, 2011).



Apart from the objective of validating and supplementing the emission factors from brickmaking with data from the surrounding soils, the study adds to the currently scarce data

describing levels of unintentionally produced POPs in soils from background and urban/industrial sites in developing countries.

The study also provides a brief description of the various technologies applied in this important industrial sector that may serve for future risk assessments and other issues in the context of technological transition and related interactions with quality standards in the environment.

### 3. Field experiments

#### 3.1 Soil sampling - site descriptions

Soil samples were taken according to the protocol described in Annex A2.

##### 3.1.1 Sites in Mexico

Sampling in Mexico was carried out in the provinces of Guanajuato, Querétaro and Chiapas (Figure 2, Figure 3, Figure 4).





Figure 3: Locations of Guanajuato and Querétaro de Arteaga



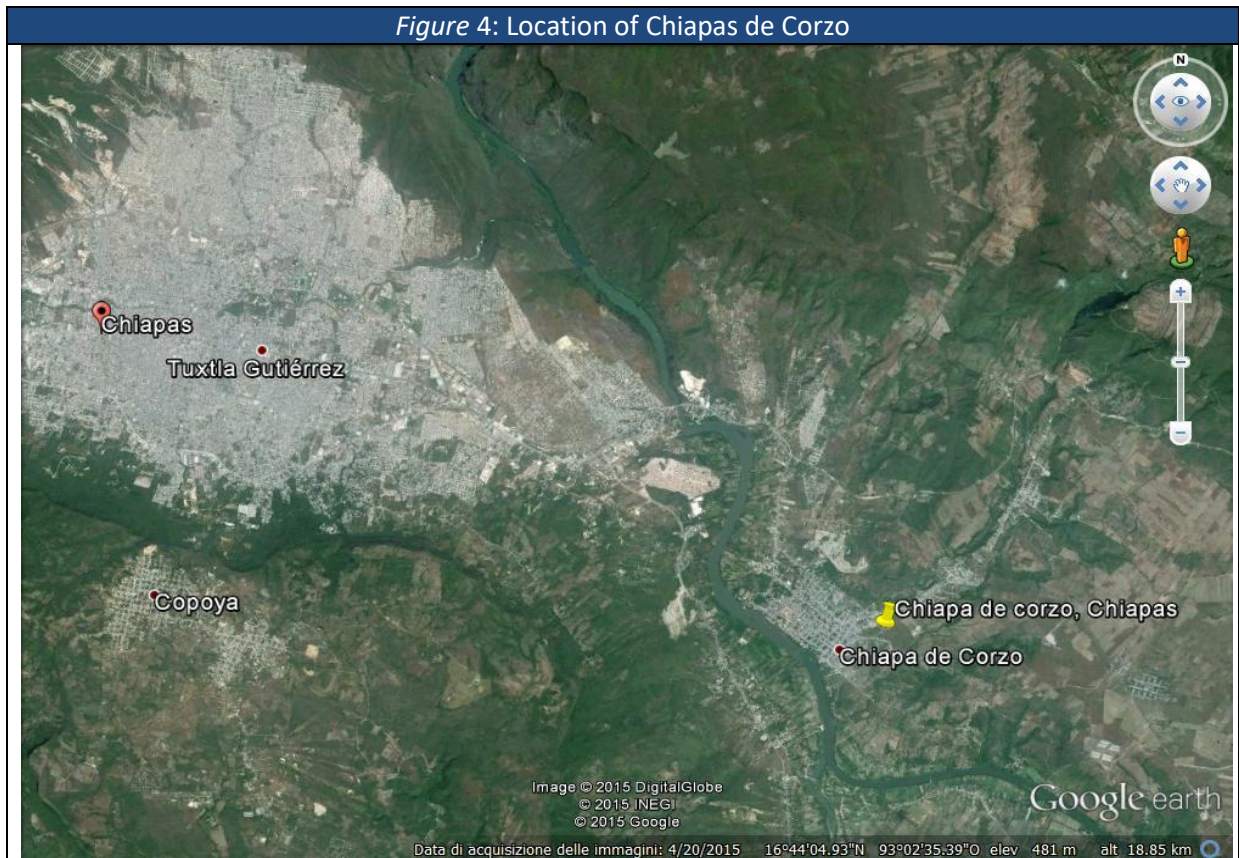
Brickmaking at the sites investigated is undertaken in commercial backyard applications, operated in batches (Umlauf et al., 2009). Up to 100 such kilns, “hornos”, can be found agglomerated in areas with appropriate clay material available nearby, typically surrounded by the settlements of the brick-producing communities.

The bricks are produced either in small stationary kilns, “fijos”, or temporary kilns, “de Campaña”.

The temporary kilns are simple constructions, built at ground level close to the source of appropriate clay. The lower part of the kiln usually consists of three combustion tunnels constructed with burnt bricks that have been loosely stapled together. On top the combustion section, the raw bricks are stapled in the shape of a truncated pyramid (see Figure 6). The raw bricks are stapled together manually in such a way as to leave space for the combustion gases to pass through, providing a sort of integrated chimney system within the kiln. Once the kiln is assembled, a final layer of burnt bricks is added, isolating all external surfaces. As a last step, all external splices are sealed with animal dung, except for the top of the kiln. After the burning process, the kiln is disassembled, except for the combustion section, which is commonly used several times until the local clay reservoir is exhausted.



Stationary kilns are permanent open-top cube-shaped brick constructions, fired from an underground combustion chamber that is separated from the baking zone by a grid. The baking zone is manually charged with raw bricks through a small vertical opening, thereby arranging the bricks in the same way as in the temporary kilns. After filling the chamber with raw bricks, the vertical opening is closed with burnt bricks and the external splices are sealed with animal dung (*Figure 15* and *Figure 22*).



Bricks are handmade using the clay from nearby areas, mixed with farm animal dung, wood dust, and other organic material which acts as a co-fuel during the baking process. The raw bricks are dried at ambient temperature for about 15 days prior to the baking.

Fuels traditionally consist of wood from tree trunks. However, in urbanised areas, various kind of waste-derived fuels such as waste oil are used. In the vicinity of petroleum refineries, small entrepreneurs provide “*Combustóleo*” - a mix of tar and heavy oil. *Combustóleo* and heavy oil is either added as a co-fuel to the wood or preheated and steam-injected after thermal liquidification (see *Figure 12*). Some kilns are also gas-fired.

The brickmaking process consists of two phases: Phase one, “*fuego*”, corresponds to the heating phase, when fuel is continuously supplied to the kiln. The second phase, “*cocción*”, corresponds to the stationary and cooking phase, in which no more fuel is supplied, but the heat from the firing zone is distributed throughout the whole kiln, and the organic material that is incorporated in the brick is combusted.

The *Combustóleo*-fired kilns are fuelled for about 5 to 10 hours, followed by a smouldering process of about two days, while the wood-fired kilns need a longer fuelling period (up to two days).

The kilns on the investigated sites typically produce 15,000 to 18,000 bricks per batch; ranging from 5,000 to 30,000 bricks.

After the baking process, the bricks need up to two weeks' cooling time before they can be manually removed, which results in a production frequency of around two batches per month.

### 3.1.1.1 León - Wood-fired temporary kilns

Figure 5: Location León, site with wood fired temporary kilns

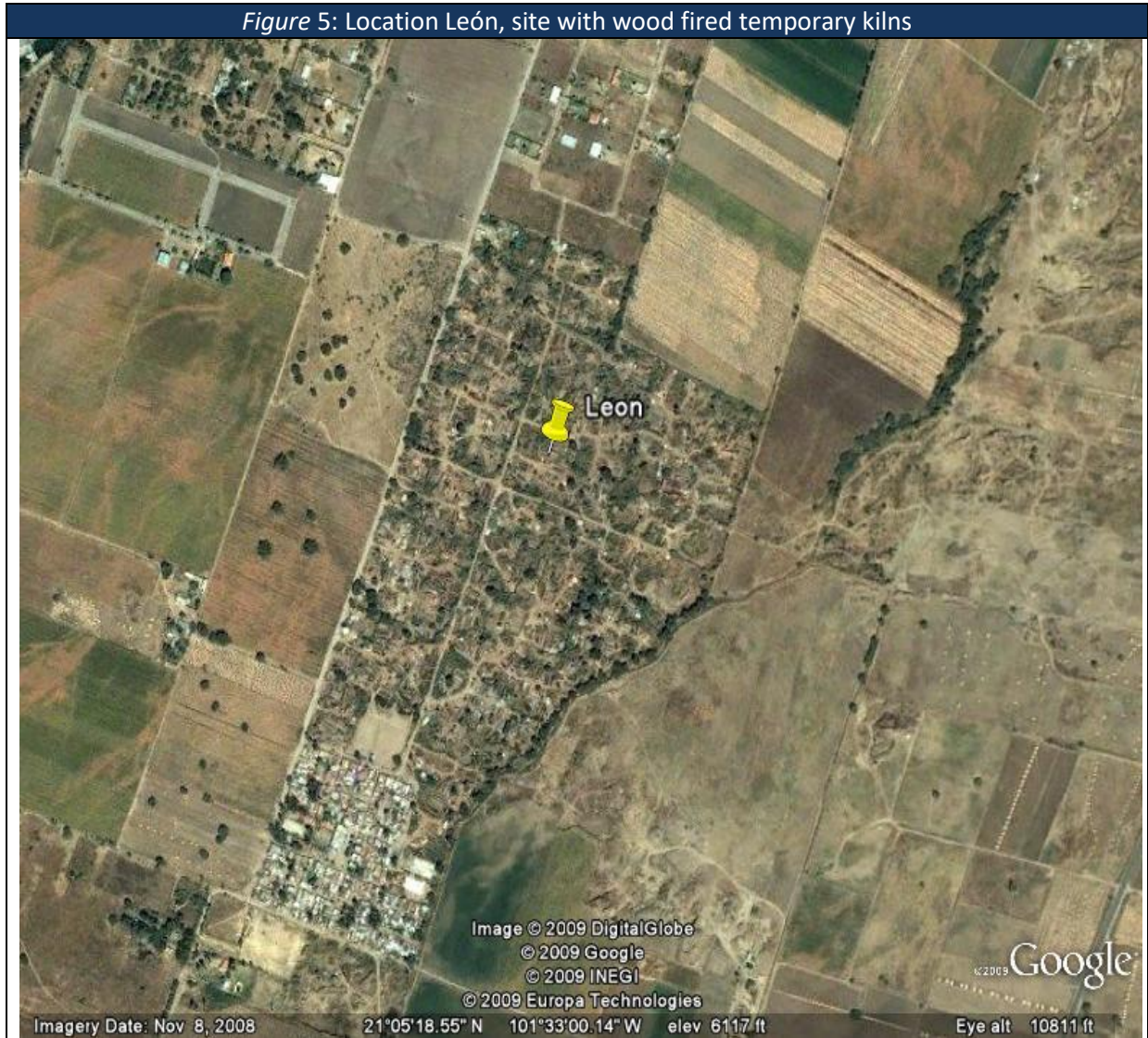


Table 1: León - Characteristics of the site

León 1, El Refugio, Guanajuato	
Location	N 21°05'21.86", W 101° 33' 02.23 León, Guanajuato. Carlos Frías owner León city: 1,278,087 habitants, main activities; agriculture, livestock, industry, trade and tourism
Character	Isolated production site with aprox. 150 temporary kilns, over recent years wood-fired, in the past also combustion of leather waste from shoe manufacturing. This



Table 1: León - Characteristics of the site	
León 1, El Refugio, Guanajuato	
	kiln was sampled (“Brickash 5”) in April 2008 by G. Umlauf. <i>Results available in EUR 23684 EN - 2009</i>
Kiln type	Temporary kiln, 15 years' old, typically 24-30 h of feeding 167 kg of wood/thousand bricks, stage cooling 96 h. Activity: 15,000 bricks/fire; rainy season 15,000 bricks/fire/month, dry season 2 fire/month, in average 20 fire/year and 165,000 bricks/year . Average bricks weight: 3.42 kg
Fuel	Virgin wood (oak, eucalyptus) with 1-2 h firing with LP gas to start the wood fire Wood feeding: 24-30 hours Total cooking time: 30 hours during the experiment Stage cooling time: 96 hours.
Materials for bricks	1 fertile soil + 1 clay soil + 0.1 wood chips + 0.1 horse manure
Samples available	
Emissions	POPs: 27-28/11/08 two samples: one 8.5h sample during the firing (while wood was added) and a second one of 8 h after the wood addition had been stopped. Recording of O <sub>2</sub> , CO, CO <sub>2</sub> , HCl, TOC; relative humidity and temperature continuously monitored (FTIR). <u>Note:</u> A diesel power plant was operating during the measurements to provide energy for the emissions measurements.
Bricks samples	Raw and cooked bricks kept at INE (not sent to Krakow), 13.11.2008
Soil samples	Taken on 13/11/08 by INE at 0-5cm; 10 m, 21 m, 40 m, 75 m and 170 m downwind; sent to the JRC in Dec 08. Background sample in agri-field (suelo blanco INE 2666). Anlsyred by the UBA
Ash	Ash taken on13/11/08 sent to the JRC in Dec 2008. Also taken on 01/12/08 (kept at INE). Brickash 5 taken in April 2008 by G. Umlauf
Other data available	
Temperature profiles	on 28-29/11/2008 (during 45 hours, at 1.2 m, 2.7 m, and 4.3 m heights)
Max temp in bottom	803°C
Max temp on top	144°C
Particulate matter	Perimetral Ambient PM2.5: Perimetral ambient sampling with low-vol portable equipment (minivol), at 1 m (top of the kiln, 30 min sampling) 10 m (top of the van, 6 h sampling), 700 m (top of one of the houses (6 h) in the area of workers houses-

<i>Table 1: León - Characteristics of the site</i>	
<b>León 1, El Refugio, Guanajuato</b>	
	3,000 people). 1 background level sample of 3 h before firing kiln. Low volume portable samplers (minivol); on quartz filter (ions and CO/CE) and Teflon filters for gravimetric and elemental (XRF). Analyses carried out by INE laboratories, finished.
Raw brick materials	Elemental analysis available from INE (C, N, H)
Ash production	6.4 kg/thousand bricks or 1.9 kg/t bricks (21.1.2010)





Figure 7: Location León, soil sampling transect at the temporary kiln ("Horno León")



Figure 8: Location León, background soil at 0.47 km SSW from the kiln

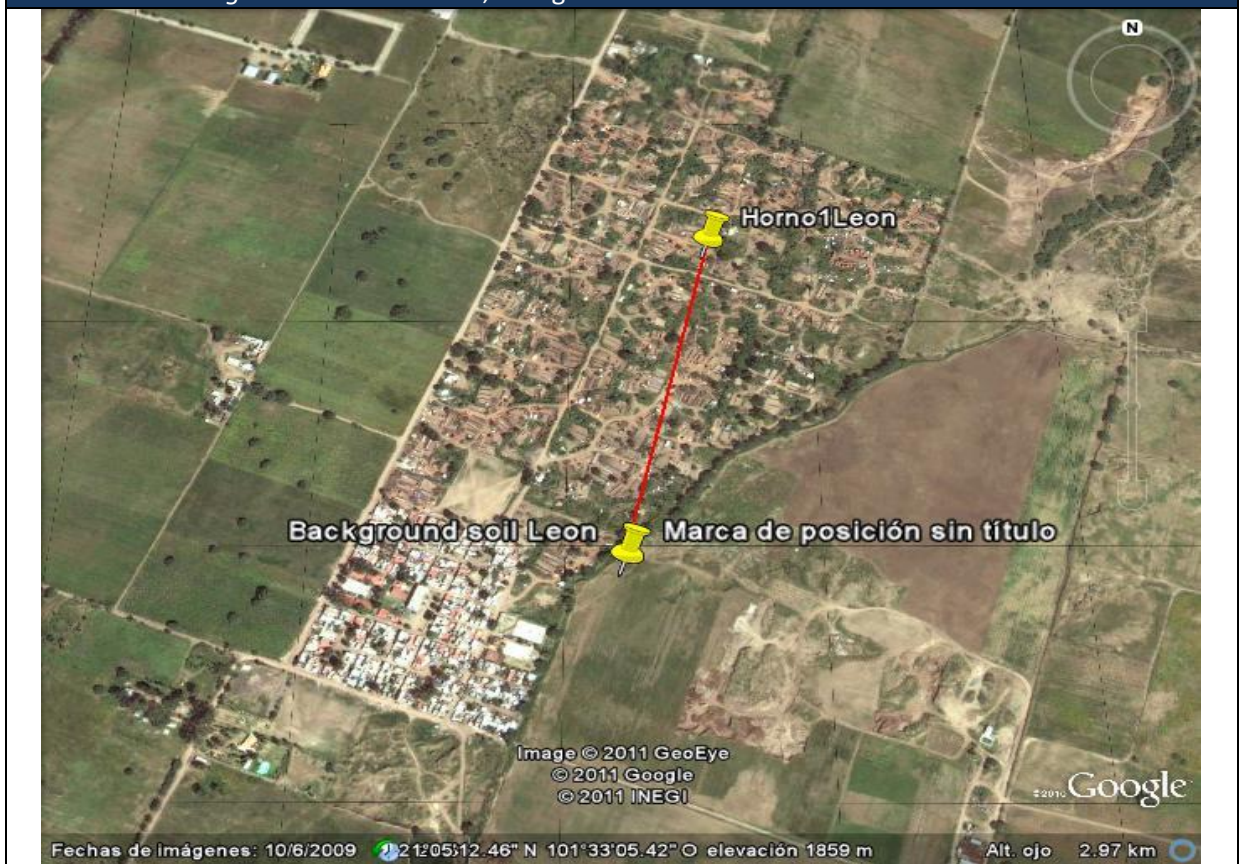


Figure 9: Detail León, soil sampling at 590 m from the kiln



Table 2: Sample identification León

Soil, dist. from Kiln	GIS	Ash	Bricks	Emission
<b>10 m</b> INE 2656-08 (UBA 0911 5038)	21 05'21.58"N 101 33'2.67"W			
<b>21m</b> INE 2658-08 (UBA 0911 5039)	21 05'21.38"N 101 33'3.23"W	Brickash 5 (JRC brick 5)		
<b>40m</b> INE 2660-08 (UBA 0911 5040)	21 05'20.24"N 101 33'4.16"W	INE 2648-08 (JRC DP-09-019)	no	Yes
<b>75m</b> INE 2662-08 (UBA 0911 5041)	21 05'17.58"N 101 33'4.71"W	INE 3345-08 (JRC DP-09-02)		
<b>170m</b> INE 2664-08 (UBA 0911 5042)	21 05'13.18"N 101 33'7.70"W			
<b>Background</b> INE 2666-08 (UBA 0911 5043)	21 05' 6.6" N 101 32' 5.57" W			



### 3.1.1.2 Salamanca - Combustóleo-fired stationary kilns

Figure 10: Location Salamanca, Combustóleo-fired stationary kiln sites

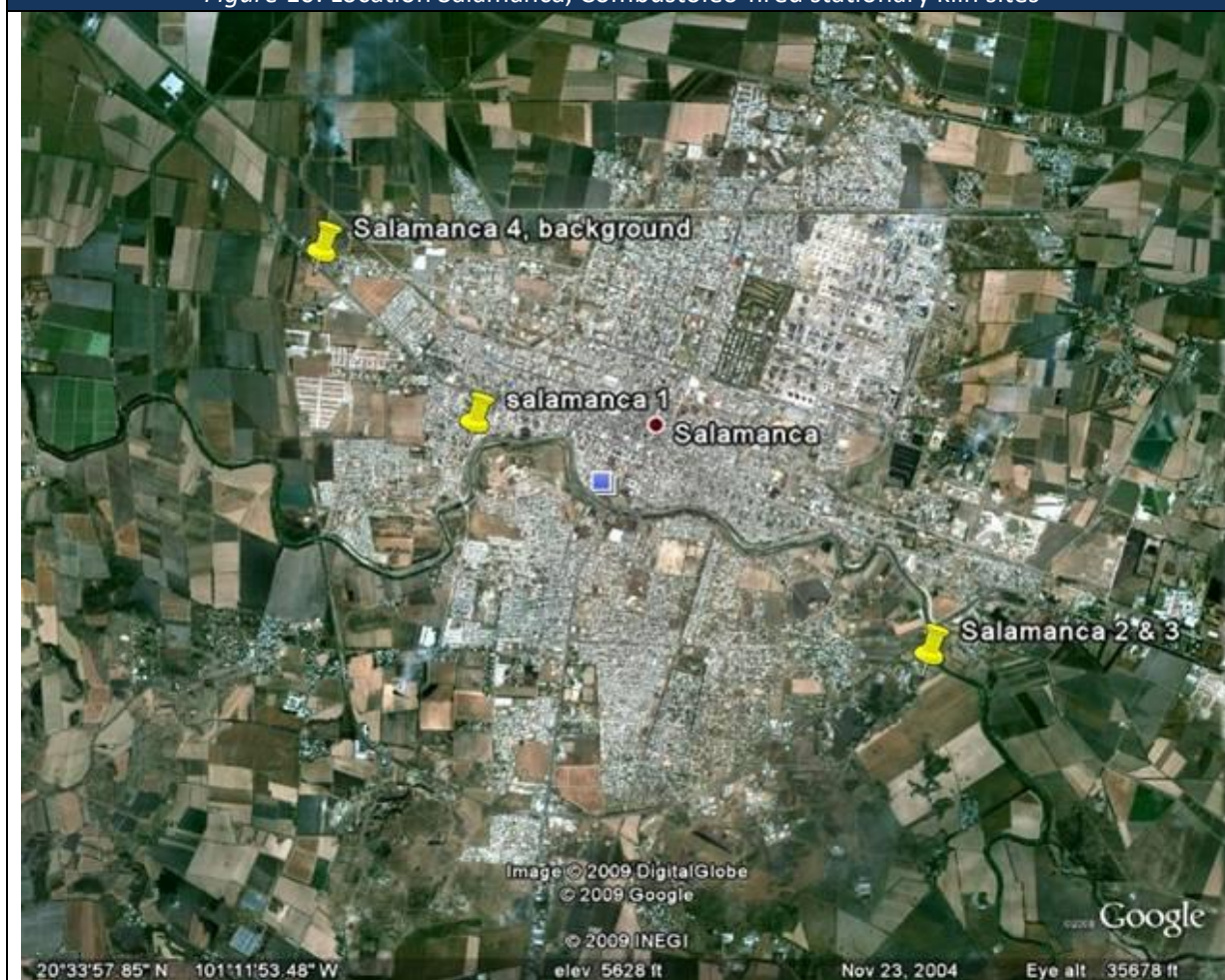


Table 3: Salamanca 1 - Characteristics of the site

Salamanca 1	
Location kiln	N 20°34'11.82", W 101°12'41.56" Southwest of Salamanca downtown. Sr. Morales, owner Salamanca: Number of habitants; 2333623, main activities; Agriculture, livestock, industry, trade, tourism.
Character	Embedded in other production sites/urban activities of Salamanca City.
Kiln type	Stationary kiln (10 years old). About 17 h heavy oil feeding with steam injection in a proportion 50:50. Activity: 6000 bricks/fire; rainy season 1 fire/month, dry season 2 fire/month; at average 20 fire/year and 120000 bricks/year . Average brick weight: 3.84 kg.
Fuel	"Combustóleo". Elemental analyses done (SEDQUIA) and heat value (UAMI). Consumption of 183 liter/thousand bricks. Fuel feeding: 17 hours Stage cooling time: 72 hours.

<b>Table 3: Salamanca 1 - Characteristics of the site</b>	
<b>Salamanca 1</b>	
	Boiler heated during 1 h with wood waste and then steam injection.
Materials for bricks	1 fertile soil + 0.2 wood chips + 0.2 horse manure + 1 clay soil (samples kept at INE)
<b>Samples available</b>	
Emissions	25/11/09 two samples: one 6 h during the firing (while fuel was added) and a second one of 3.2 h after the fuel addition had been stopped
Bricks samples	Raw and cooked bricks are kept at INE. Cooked brick sent to Krakow on January 09.
Soil samples	(0-5cm) taken (10/11/08) within the city of Salamanca in an urban neighborhood, nearby of a street (25m), and surrounded by unpaved roads. The kiln is in a site where other two kilns using the same process are located (owned by three brothers). Sent to JRC on December 08. Analyzed by UBA.
Ash	Ash taken on 10/11/08 from last firing on 29/10/08 (approximately 11 days after last fire). And (3338) taken 3/12/2008. Analyzed at JRC.
<b>Other data available</b>	
Temperature profiles	Available (25/11/08), (17 hours, 3 heights: 1.2m, 2.2m, 3.2m)
Particulate matter	PM2.5 ambient air measurements during burning (25/11/09): 1m, 11 m and 85m
Max temp in bottom	890 °C
Max temp in top	712 °C
Ashes production *	2.2 kg /t bricks was determined in a similar kiln in Salamanca on 23.1.2010 , corresponds to 8.9kg/1000 bricks
<b>*Note:</b> Ash is defined as the total mass of residues in the fire chamber after the burn. Apart from the bottom ash itself It may contain mineral substance deriving from the bricks. Since both ash and other residues were sampled and analyzed together for POPs, they are referred to as ashes.	

Figure 11: Detail Salamanca 1, Combustóleo-fired stationary kiln - emission sampling



Table 4: Salamanca 2 - Characteristics of the site

<b>Salamanca 2</b>	
Location kiln	N 20°33'07.53"; W 101°10'23.14" Col. San Diego, Salamanca. Pedro Morales owner Salamanca city: number of habitants; 2333623, main activities; Agriculture, livestock, industry, trade, tourism.
Character	Border of the city, not urban area, nearby field crops (sorgum and corn) and nearby other kilns with similar process. Approx. 300 m there is a road. This kiln was originally selected to be sampled for emissions but was not possible due to lack of electric power for equipment.
Kiln type	Stationary kiln, 18,000 bricks per batch, 18 h heavy oil feeding steam injected. Activity: 18000 bricks/fire; rainy season 1 fire/month, dry season 2 fire/month in average 20 fire/year and 360000 bricks/year.
Fuel	"Combustóleo"



<i>Table 4: Salamanca 2 - Characteristics of the site</i>	
<b>Salamanca 2</b>	
	Boiler heated during 1 h with wood and then steam injection Fuel feeding: 18 hours Total cooking time: 10 hours Stage cooling time: 72 hours
Materials for bricks	1 fertile soil + 1 clay soil + 1 lava rock 1 + 1 cow manure (samples kept at INE)
<b>Samples available</b>	
Bricks samples	both raw and cooked bricks are kept at INE.
Soil samples	taken on 10/11/08 at 5 cm depth, according to protocol: 15 m, 30 m, 40 m, 65 m (no further samples could be taken because of the river)
Ash	Ash taken on 10/11/08 (not sure when the kiln was fired last) sent to JRC in Dec 2008.
<b>Other data available</b>	
Temperature profiles	(20/04/10) (32 hours, 3 heights: 1.2m, 2.2m, 3.2m.)
Max temp in bottom	834°C
Max temp in top	767°C

*Figure 12: Detail Salamanca 1, fuel (Combustóleo) co-injection using steam*



Figure 13: Location Salamanca 1, soil sampling transect at the stationary kiln



Figure 14: Detail Salamanca 1, soil sampling at 20 m from the kiln





Figure 15: Detail Salamanca 2, stationary kiln using steam-injected Combustóleo



Figure 16: Location Salamanca 2 and 3, soil sampling transect at the stationary kilns





Table 5: Salamanca 3 - Characteristics of the site	
Salamanca 3	
Location Kiln	N 20°33'06.72"; W 101°10'20.13". Col. San Diego, Salamanca.
Character	Border of the city, not urban area, nearby field crops (sorgum and corn) and nearby other kilns with similar process. This kiln is 40 m from the site Salamanca 2.
Kiln type	Stationary kiln 19,000 bricks, 18 h heavy oil feeding. Activity of the kiln: 19000 bricks/fire; rainy season 1/fire/month, dry season 2 fire/month in average 20 fire/year and 380000 bricks/year
Fuel	Kiln fired with "Combustóleo" type of heavy oil mixed with residues from heavy oil. Boiler heated during 1 h with waste wood and then steam injection
Materials for bricks	1 fertile soil + 1 clay soil + 1 lava rock + 1 cow manure (samples kept at INE)
Samples available	
Bricks samples	Raw and cooked bricks are kept at INE.
Ash	Ash taken on 11/11/08 (not sure when the kiln was fired) sent to JRC on Dec 08.

Figure 17: Location Salamanca 4, background soil sampling site



<i>Table 6: Salamanca 4 – background soil. Characteristics of the site</i>	
<b>Salamanca 4</b>	
Location	N 20°35'3.50"; W 101°13'28.28"
Character:	Vacant lot, Irapuato Salamanca highway entrance, the soil samples were taken 0-5 cm, approximately. 2.4 kilometer from monitoring brick kiln (Salamanca 1) This site was chosen as a background site with no impact of nearby kilns. Next to a small fireworks production site.
<b>Other data available</b>	
no	

*Figure 18: Detail Salamanca 4, background soil site*



<i>Table 7 : Salamanca 5 - Characteristics of the site</i>	
<b>Salamanca 5</b>	
Location Kiln	Location: N 20°34'12.45", W 101°12'41.18" approximately 10 m of monitoring brick kiln (Salamanca 1). Salamanca city: number of habitants; 2333623, main activities; Agriculture, livestock, industry, trade, tourism.
Character	Embedded in other production sites/urban activities

Table 7 : Salamanca 5 - Characteristics of the site	
Salamanca 5	
Kiln type	Stationary kiln, Similar to Salamanca 1, Combustóleo fed for 23h
Fuel	Similar to Salamanca 1
Materials for bricks	Similar to Salamanca 1
Samples available	
Bricks samples	3340-08

Figure 19: Location Salamanca 5, brick sampling





Figure 20: Detail Salamanca 5, stationary kiln

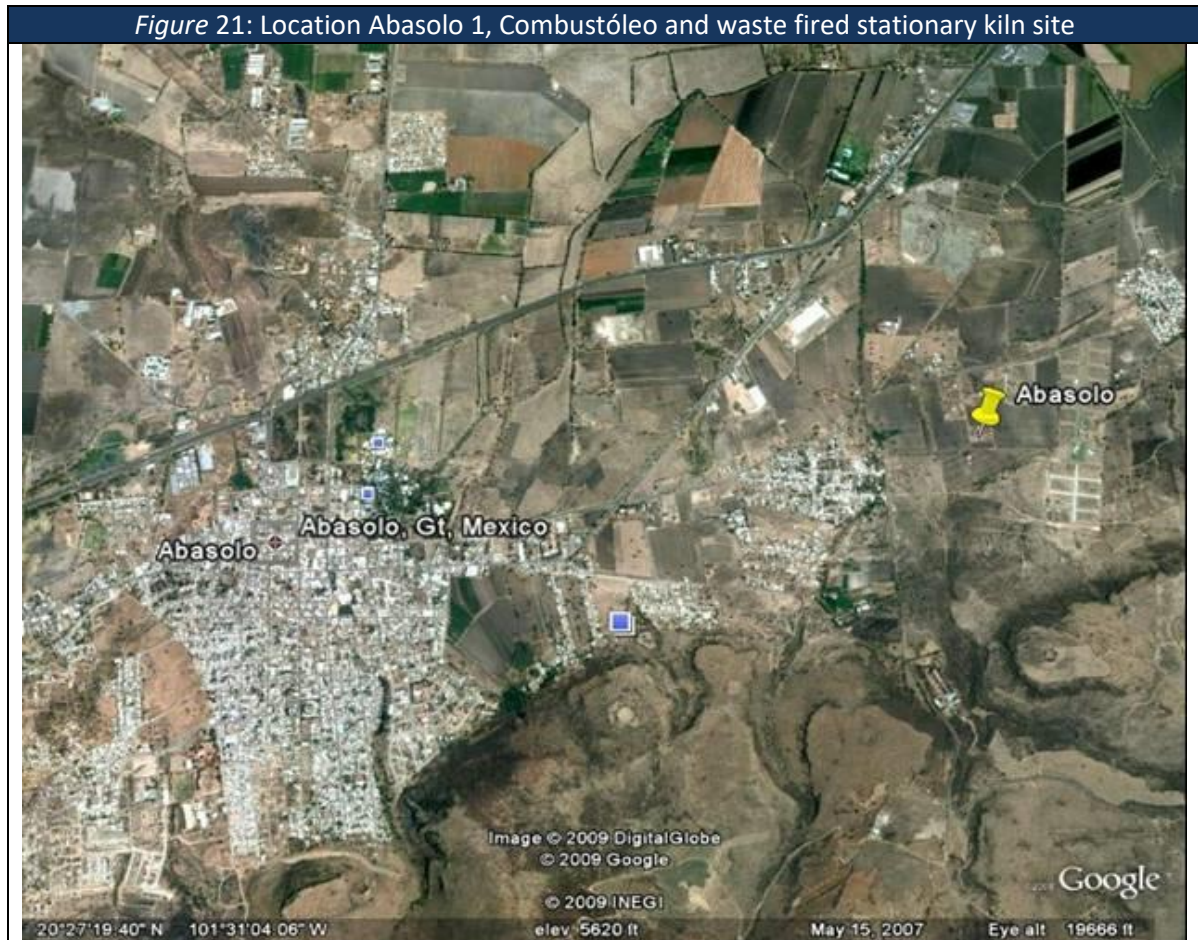


Table 8: Salamanca - Sample identification

Soil	GIS	Ash	Bricks	Emission
<b>Salamanca 1</b>				
<b>10 m</b> INE 2556-08 (UBA 0911 5026)	20°34'11.36" N 101°12'41.53" W	INE 2549-08 (JRC DP-09-013) INE 3338-08 (JRC DP-09-020)	INE 3335-08 (KRK Salamanca 1)	yes
<b>20 m</b> INE 2558-08 (UBA 0911 5027)	20°34'10.49" N 101°12'41.60" W			
<b>Salamanca 2</b>				
<b>15 m</b> INE 2571-08 (UBA 09115028)	20°33'07.84" N 101°10'22.93" W	INE 2564-08 (JRC DP-09-014)		
<b>30 m</b> INE 2574-08 (UBA 0911 5029)	20°33'08.12" N 101°10'22.62" W			

Table 8: Salamanca - Sample identification				
Soil	GIS	Ash	Bricks	Emission
<b>40m</b> INE 2576-08) (UBA 0911 5030)	20°33'08.50" N 101°10'21.48" W			
<b>65m</b> INE 2577-08 (UBA 0911 5031)	20°33'09.11" N 101°10'20.36" W			
<b>Salamanca 3</b>				
	20°33'06.72" N 101°10'22.13" W	INE 2584-08 (JRC DP-09-015)		
<b>Salamanca 4</b>				
Background INE 2592-08 (UBA 0911 5032)	N 20°35'3.50"; W 101°13'28.28"			
<b>Salamanca 5</b>				
	N 20°34'12.45", W 101°12'41.18"		INE 3340-08 (KRK Salamanca 5)	

### 3.1.1.3 Abasolo - Combustóleo- and waste-fired stationary kilns



<b>Table 9: Abasolo 1 - Characteristics of the site</b>	
<b>Abasolo 1</b>	
Location Kiln	N 20°27'28.82", W 101°30'09.07" - Camino a San Isidro, Col. El Saucillo, Abasolo, Guanajuato. México. Manuel Medina (owner)
Character	one of the 300 brick kilns located in this small city. This kiln is located in the border of the urban area, surrounded by some field crops (sorgon and corn). This kiln was chosen since the kiln sampled on April 08 was too close to other kilns and soils samples were more difficult to take.  Abasolo city: number of habitants; 77094, main activities; Agriculture, livestock, industry, trade, tourism and forestry.
Kiln type	Stationary kiln, 15 years old, 5 h fuel feeding. 24 h cooking, stage cooling 36 h. 25000 bricks/fire. Activity: Dry season 1fire/month in average 12 fire/year and 300000 bricks/year.
Fuel	Combustóleo mixed with virgin wood chips (tree bark), 132 kg/thousand bricks.
Materials for bricks	1 fertile soil + 1 wood chip +1 clay soil + 1 soil (kept at INE)
<b>Samples available</b>	
Bricks samples	Raw and cooked bricks kept at INE, cooked brick sent to Krakow on Jan 09
Soil samples	Taken on 12/11/08 along with the main wind direction. 10m (0-15 cm) and 20 m (0-20 cm) soil samples in agri-fields close to the production area, 40m (0-15cm), 80m (0-10 cm) and 160m (0-10 cm) samples on agricultural fields. Samples sent to JRC on Dec 08.
Ash	Taken on 12/11/08, pending how many days after last firing, samples sent to JRC on Dec 08. Ash from a similar kiln taken in 4/2008 "Brickash 2"
<b>Other data available</b>	
Temperature profiles	Taken on 17/03/2009 at 0.9m, 2.65m and 3.86m over the ground.
Max temp. bottom	900°C
Max temp. top	860°C
Ash production	7 kg/thousand bricks, determined 22.01.2010.
Particulate matter	PM2.5 Perimetral sampling at the kiln taken on 17/03/09. Perimetral sampling during burning (17/03/09) at 10 m SE, above ground, 5 m NE 5m above a house, 10 m SE 1m on the ground. Integrated samples of 30 min. Low volume portable samplers (minivol); quartz filter (ions and CO/CE) and Teflon filters for gravimetric and elemental (XRF). Analyses done by INE laboratories, finished.  PM2.5 and PM10 ambient measurements in Abasolo: Potentially impacted living areas.



Figure 22: Detail Abasolo 1, stationary kiln where the soil transect was taken



Figure 23: Detail Abasolo, Combustóleo and waste fired stationary kiln ( Brickash 2)



Figure 24: Location Abasolo 1, soil sampling transect at the stationary kiln



Figure 25 : Detail Abasolo 1, soil sampling at 80 m from the kiln





**Table 10: Abasolo 5 - Sample identification of additional bricks collected to confirm the high levels measured in Abasolo 1 (INE 404/09)**

Description	GIS	Bricks
Abasolo 5, kiln operated with Combustóleo/wood in batches as Abasolo Located in los Pirules Colonia Margaritas Abasolo, owner A. Rios.	N 20°26'34.96" W 101°32'20.90"	INE 317/10, taken 5 beds below the top on 21.01.2010, sent to Krakow.
		INE 732/10, taken 5 beds below the top on 21.01.2010, sent to Krakow.

**Table 11: Abasolo - Sample identification**

Soil, dist from Kiln Abasolo 1	GIS	Ash	Bricks	Emission
<b>10 m</b> INE 2628-08 (UBA 0911 5033)	N 20°27'29.38" W 101°30'08.81"	INE 2620/08 (JRC DP-09-017)  INE 2626/08 Carbon (JRC DP-09-018)	INE 404-09 (KRK Abasolo 1)  INE 317/10 (KRK Abasolo 5)  INE 732/10 (KRK Abasolo 5)	No
<b>20 m</b> INE 2630-08 (UBA 0911 5034)	N 20°27'29.43" W 101°30'08.21"			
<b>40 m</b> INE 2632-08 (UBA 0911 5035)	N 20°27'29.49" W 101°30'06.08			
<b>80 m</b> INE 2634-08 (UBA 0911 5035)	N 20°27'29.48" W 101°30'04.30			
<b>160 m</b> INE 2636-08 (UBA 0911 5037)	N 20°27'29.47" W 101°29'59.07			

### 3.1.1.4 Juventino Rosas - LP gas-fired temporary kilns

**Table 12: Juventino Rosas - Characteristics of the site**

Table 12: Juventino Rosas - Characteristics of the site	
Location Kiln	N 20°35'17.80"; W 101°00'11.00" Juventino Rosas, Guanajuato. Mr. Filiberto Medina (owner)
Character	Isolated brick kilns park (30 kilns) that were built on virgin soil in 2003.
Kiln type	Temporary kiln, 5 years old, 60 liter of gas/thousand bricks, heating stage 14 h, stage cooling 96 h. Activity of the kiln: 25,000 bricks/fire every 90days during rainy season. Dry season one fire every 45days. At average 5 fire/year and 125,000 bricks/year
Fuel	Kiln fired with wood/clothes for 1-2 h and then LP gas (12 h feeding).
Brick materials	1 fertile soil + 0.5 wood chips + 0.5 horse manure (kept at INE)
Samples available	
Bricks samples	Thermogravimetric and thermodifferential analysis: The thermal

Table 12: Juventino Rosas - Characteristics of the site

Other data available	
Temp. profiles	19/03/09 (during 36 hours, at 3 levels)
Max temp. bottom	300°C.
Max temp. top	60°C
Ash production	5.56 kg/thousand bricks.
Particulate matter	PM2.5: on 19-20/03/09. Perimetral ambient sampling with low vol (minivol), at 10 m NW 6m on another brick kiln, 12m NE 3m over one house, 10 m SW on the ground. Integrated samples of 30 min at different temperatures in the brick kiln with low vol. (minivol); quartz filter (ions and CO/CE) and Teflon filters for gravimetric and elemental (XRF). INE labs.
Ash	Taken on 12/11/08, taken between 3-4 days after last firing
Soil samples	Taken on 12/11/2008. 10 and 20 m (0-5cm) in close to the urban/production zone, 40m in (0-15 cm) an agri field that seems to be an ancient production zone, 80m and 150m (down to 10 and 15 cm depth) are well isolated agricultural soils. Sent to the JRC on Dec. 08.
	transformation of samples of raw bricks was investigated between room temperature and 1000 °C analysis done at UAMI on raw bricks

Figure 26: Location Juventino Rosa, LP gas fired temporary kiln site

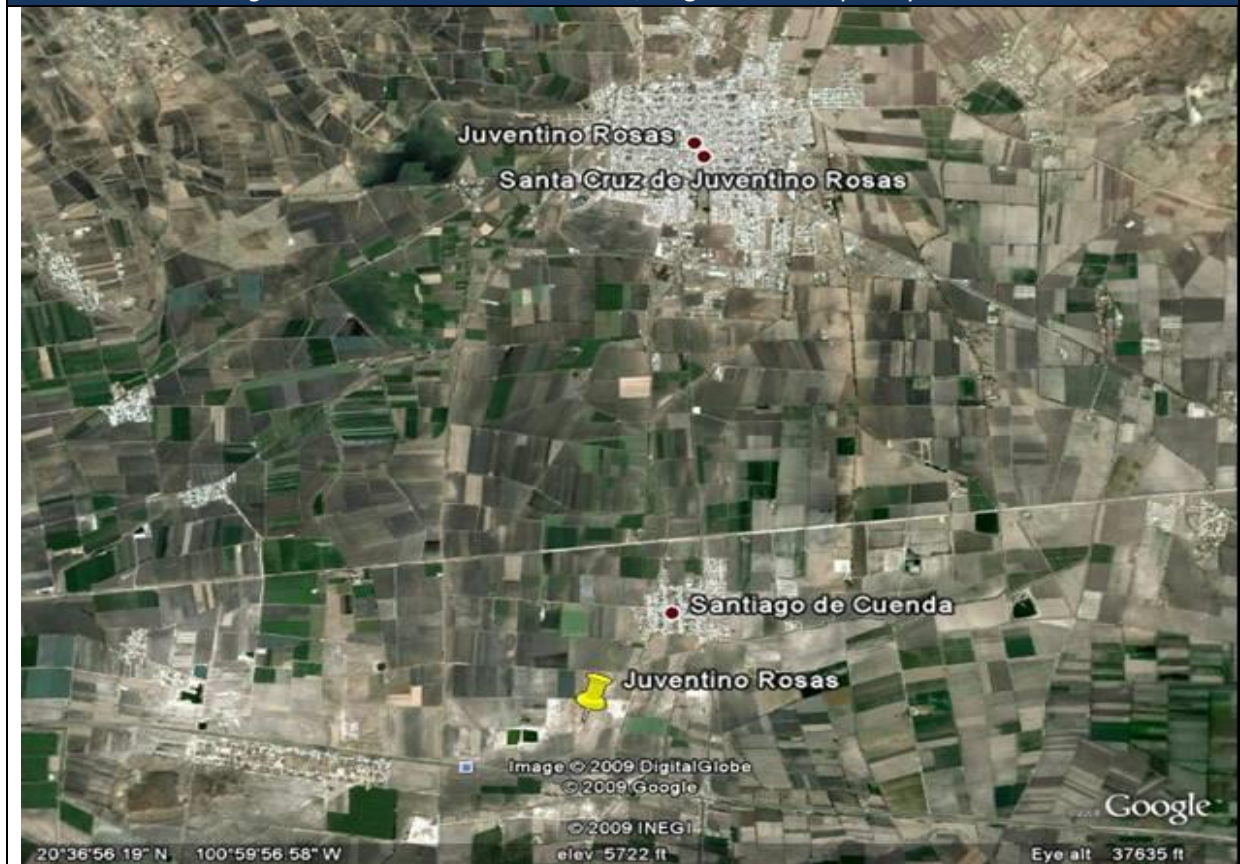


Figure 27: Detail Juventino Rosas, LP gas fired temporary kiln



Figure 28: Location Juventino Rosas, soil transect at the temporary kiln





Figure 29: Detail Juventino Rosas, soil sampling at 20 m from the kiln



Table 13: Juventino Rosas - Sample identification

Soil, dist. from Kiln	GIS	Ash	Bricks	Emission
<b>10 m</b> INE 2605-08 (UBA 0911-5044)	N 20°35'17.71" W 101°00'10.48"	INE 2598-08 (JRC DP-09-016)		
<b>20 m</b> INE 2607-08 (UBA 0911-5045)	N 20°35'17.60" W 101°00'10.00"			
<b>40 m</b> INE 2609-08 (UBA 0911-5046)	N 20°35'18.00" W 101°00'08.50"			
<b>80 m</b> INE 2611-08 (UBA 0911-5047)	N 20°35'19.90" W 101°00'06.27"			
<b>150 m</b> INE 2614-08 (UBA 0911-5048)	N 20°35'24.27" W 101°00'05.31"			

### 3.1.1.5 Chiapa de Corzo, Chiapas – Waste-oil fired temporary kilns

Figure 30: Location Chiapa de Corzo, Chiapas, waste oil fired temporary kiln site

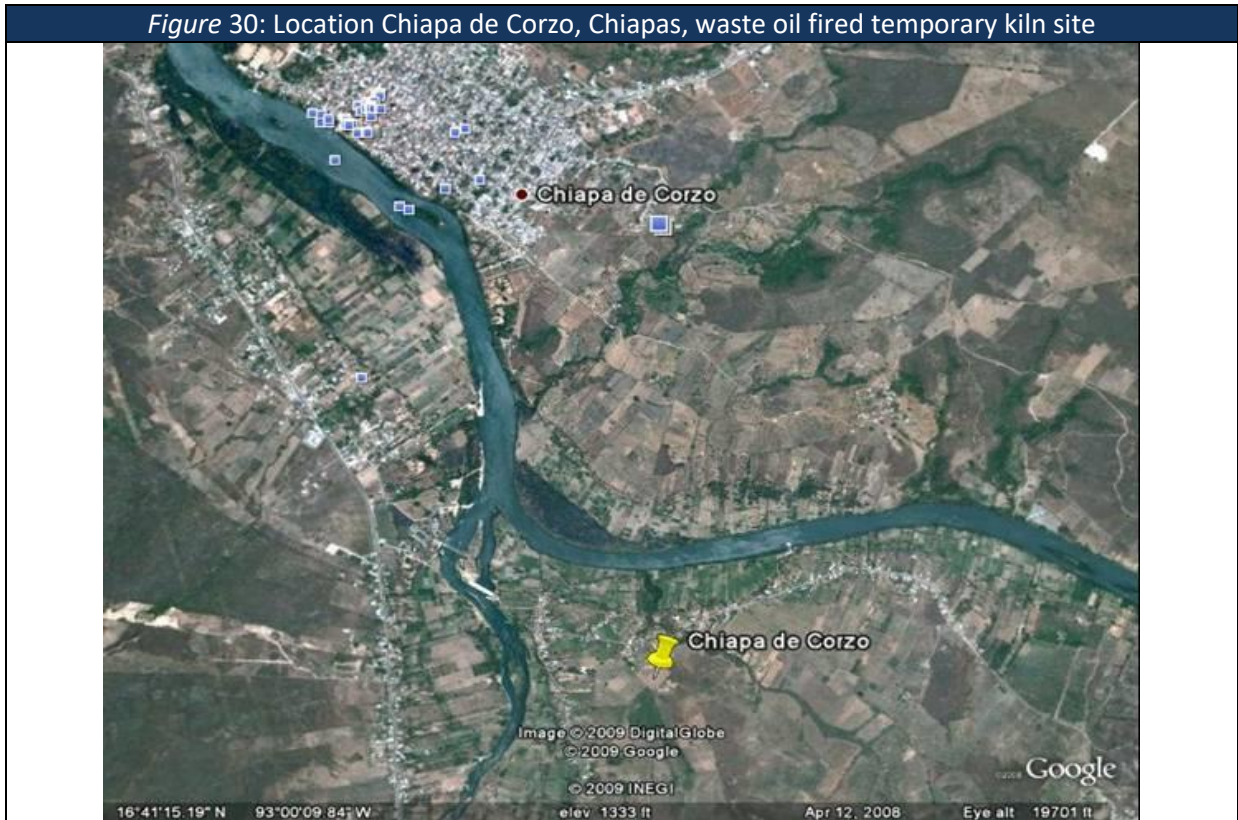


Table 14: Chiapa de Corzo - Characteristics of the site

Location Kiln	N 16°40'24"; W 93°00'5.7" at 410 m asl, comunidad Rivera Monterico. Chiapa de Corzo city: number of habitants 73,552. Main activities: Agriculture, livestock, tourism
Character	Embedded in other production sites/urban activities
Kiln type	Temporary kiln; 30,000 bricks/batch, 24 h fuel feeding.
Fuel	Mixture of used car oils and other types of used oils, feed during 24 hrs.
Materials for bricks	clay + cacao residues
<b>Samples available</b>	
Bricks samples	Raw and cooked kept at INE. Cooked sample sent to Krakow on Feb 09.
Soil samples	(0-10cm) 10m, 20m, 40m, 80m, 160 m. Samples taken along the main wind direction. All agri soils. Taken on 23/02/09. Have not been sent to JRC since ash and brick results were low.
Ash	Taken on 12/11/08, sample sent to JRC
<b>Other data available</b>	
Caloric value of the fuel determined at INE-UAM Thermogravimetry and differential thermal analysis done at UAM on raw bricks.	

Figure 31: Location Chiapa de Corzo, Chiapas, waste oil fired temporary kiln



Table 15: Chiapa de Corzo - Sample identification

Soil, dist. from Kiln	GIS	Ash	Bricks	Emission
Soils not analysed since ash was very low in concentration	N 16°40'24" W 93°00'5.7" (Kiln position)	INE 361/09 JRC DP-09-104	INE 353-09 KRK Chiapa de Corzo	



Figure 32: Location Chiapa de Corzo, soil sampling transect at the temporary kiln



### 3.1.1.6 Queretaro –Waste oil fired temporary kilns

Table 16: Queretaro San Nicolas Tequisquiapan - Characteristics of the site

Location Kiln	N 20°28.932' , W 99°56.140' a 1760 m, San Nicolás Tequisquiapan, Querétaro
Character	One of the 200 brick kilns located in a semirural community nearby a tourist village (Tequisquiapan). Two years ago nearby community asked intervention of Government since they were concerned of toxics emissions.
Kiln type	Temporary kiln, 10,000 bricks/ batch, 40 h process
Fuel	Used car oils and other type of used oils, they also used the cake residual from a car lubricant process production.
Materials for bricks	Soil clay + fertile soil + manure and water from the river (contaminated with effluents from different nearby small industries)



**Table 16: Queretaro San Nicolas Tequisquiapan - Characteristics of the site**

Samples available	
Bricks samples	Raw and cooked samples kept at INE. Cooked sample sent to Krakow.
Ash	Taken on 27/02/09 sent to JRC
Other data available	
Caloric value of the fuel determined at INE-UAM	

**Figure 33: Location Tequisquiapan (Querétaro), waste oil fired temporary kiln site**



**Table 17: Queretaro San Nicolas Tequisquiapan - Sample identification**

Soil, dist. from Kiln	GIS	Ash	Bricks	Emission
Soils not analysed.	N 20°28.932', W 99°56.140' (Position kiln)	INE 403-09 (JRC DP-09-103)	INE 399-09 (KRK Tequisquiapan)	no

### 3.1.2 Sites in South Africa

An overview on the sampling sites in South Africa is displayed in **Error! Reference source not found.**Figure 34.



Brickmaking in South Africa is characterized by large commercial operations and small artisanal manufacture in lesser developed areas. About 3.5 billion bricks are commercially produced in SA per year. Standard South African stock bricks (222 x 106 x 73 mm) weigh 3 – 3.5 kg. Therefore, 1 000 finished bricks weigh about 3.5 tons. For every 1 000 bricks, at least 4 tons of material must be dried, fired to a temperature of 1 000° - 1 200°C depending on the clay used.

Four types of commercial kilns were used in South Africa: The Down Draught kiln, the Hoffman-type Transverse Arch kiln (TVA.), the Tunnel kiln and Clamp kiln. The Down Draught kilns have been discontinued because of costs. Currently, for every clamp kiln operation, about 4 tunnels and 14 Hoffman kilns are in use.



Firing in the TVA kiln is continuous. Green bricks are placed in front of the fire while fired bricks are removed from behind it. The bricks are fired by the combustion gasses. In the tunnel kiln, the fire is stationary while the bricks move past it on cars.

In clamp kilns, some fuel is mixed into each brick. The bricks are packed in a longitudinal layered formation, containing millions of bricks at a time. The clamp has a layer of scintle coal, equivalent to two layers of bricks, at the bottom. The scintle is set alight, igniting the bricks itself. Clamp kiln firing can take up to three weeks and temperatures can be as high as 1 400°C in the center of the clamp.

Traditional clamp-like kilns, similar to those used in Kenya, and equivalent to temporary kilns in Mexico (this report) are common in the more rural areas. Fuel is locally gathered wood and sometimes some coal. There is no information on how many bricks are being made in this way.

### 3.1.2.1 SABK1 – Coal-fired industrial-scale kiln

<i>Table 18: SABK1 - Characteristics of the site</i>	
Location Kiln	North-West Province, South Africa. 25 57S 25 24E
Character	Isolated, medium sized, commercial, clay brick manufacturing site. Located 10 km from closest town, and 1 km from closest major road. No other industrial sources are in the vicinity. Area type is savannah, with isolated homesteads located in tribal lands. Agriculture largely communal grazing of cattle and goats. Low rainfall prevents large-scale crop farming. Regular grassland fires reduce much of the grasslands.
Kiln type	Commercial, medium-scale, clamp kiln operation. 3 kilns in operation at any one time, depending on demand. There are about 3.5 million bricks per kiln. Activity: Active since 1980. Yearly production of approximately 28.5 million clay bricks for a total of about 88 920 ton bricks per year.
Fuel	Duff (fine coal) mixed into the clay at 7.5% of mass. Coal lumps used for external firing. No other fuel used
Materials for bricks	Clay mined locally. Coal mined and trucked in from other sources.
Product	Stock brick = 22.5 X 10.5 X 7 cm. 3.166 kg
<b>Samples available</b>	
Bricks samples	1, sent to UBA
Soil samples	Square sampling design and one background soil.
Ash	Bottom ash from kiln just cooled down (SABK1 bottom Ash), sent to JRC. Raw brick ingredients (fluff & duff, fine coal mixed into clay), sent to JRC.

Figure 35: Location SABK1, coal fired industrial scale kiln



Figure 36: Detail SABK1 , clamp kilns





Figure 37: Detail SABK1, open-cast clay mine



Figure 38: Detail SABK1, fired clamp kiln with bottom ash





Figure 39: Detail SABK1, brick ingredient "duff" (fine coal)



Figure 40: Location SABK1, soil sampling sites

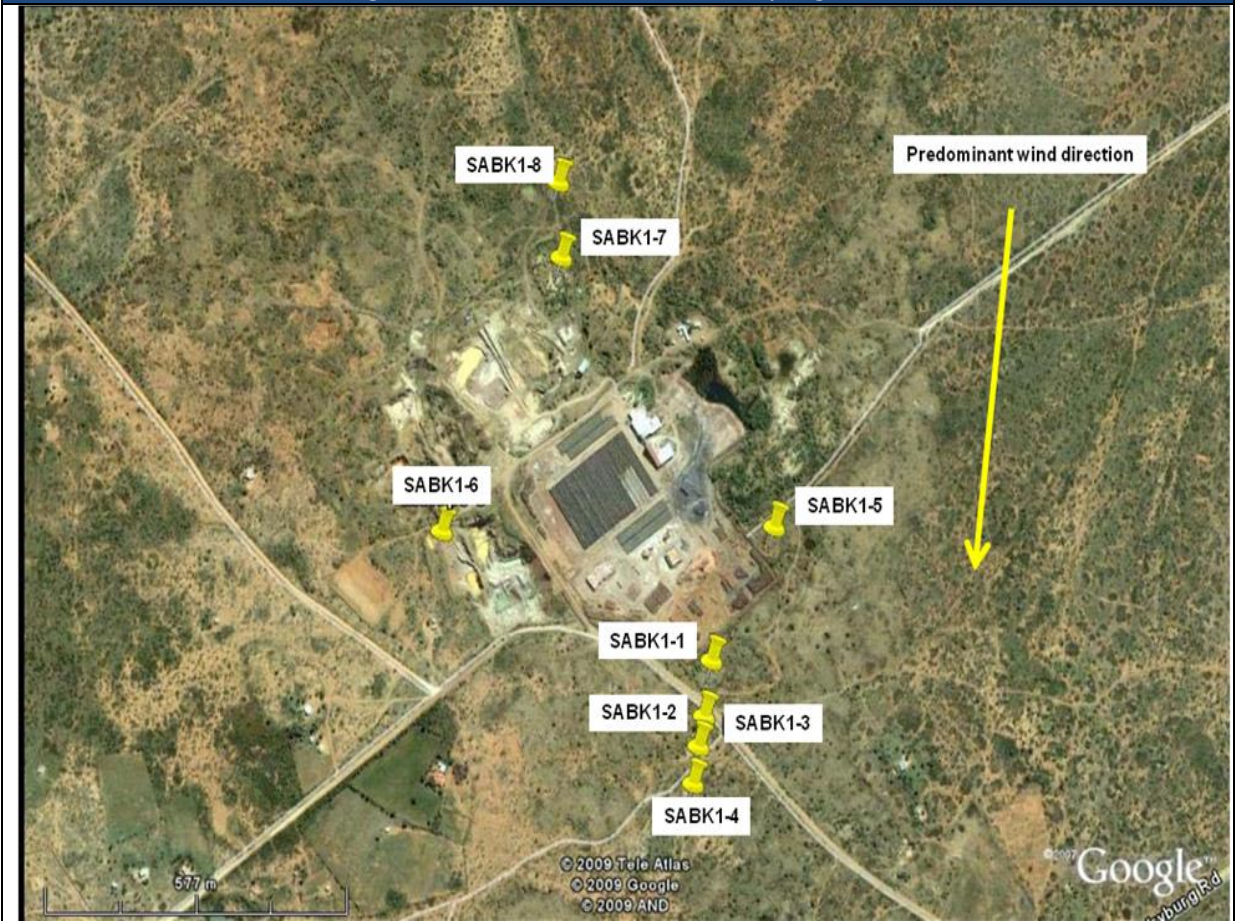




Figure 41: detail SABK1, soil sampling site downwind from clamp kiln



Figure 42: Detail SABK1-9, (background sampling site), 12 km east of SABK1



Table 19: SABK1 - Sample identification				
Soil, dist. from kiln	Coordinates	Ash	Ingredients	Brick
136 m SABK1-1A UBA 0911 5007	25 54S 25 31E	SABK1 Ash JRC DP-09-073	SABK1 duff JRC DP-09-074	SABK1 brick UBA 1011 5965
263 m SABK1-2A UBA 0911 5008	25 54S 25 31E			
357 m SABK1-3A UBA 0911 5009	25 54S 25 31E			
447 m SABK1-4A UBA 0911 5010	25 54S 25 31E			
445 m SABK1-5A UBA 0911 5011	25 54S 25 31E			
213 m SABK1-6A UBA 0911 5012	25 54S 25 31E			
545 m SABK1-7A UBA 0911 5013	26 01S 25 34E			
688 m SABK1-8A UBA 0911 5014	25 54S 25 31E			
12,1 km SABK1-9A background UBA 0911 5015	25 57S 25 24E			

### 3.1.2.2 SABK2 – Coal-fired industrial-scale kiln

Table 20: SABK2 - Characteristics of the site	
Location Kiln	Vereeniging, South Africa, 26 35E 27 57S
Character	Commercial clay brick manufacturing. Operating near other large metallurgical, petrochemical, coal mining, and manufacturing plants, in the centre of the Vaal Triangle (Gauteng Province), the largest industrial complex in South Africa. There is some agriculture interspersed. Vereeniging has approximately 794 600 inhabitants, but many more are located in other towns and cities close by the brick factory.
Kiln type	Commercial, large-scale clamp kiln operation. 10-20 kilns in operation at any one time, depending on demand. Active since 1984. Yearly production of approx. 345 million (993 600 tons) bricks.
Fuel	Per annum: Duff (fine coal) 22.4 ton, mixed into the clay (2 000 000 G Joules). Per annum: Coal lumps used for external firing 26.5 ton (662 000 G Joules). Paper pulp waste sometimes also mixed in.

Table 20: SABK2 - Characteristics of the site

Table 20: SABK2 - Characteristics of the site	
	The above is for 345 million bricks (993 600 tons)
Materials for bricks	Mineral clay mined opencast on-site, not from any rivers or wetlands. Approximately 980 000 tons of clay mined per annum. Other ingredients are sourced locally.
Product	Stock brick = 21.5 X 10 X 7 cm. Kg 2.882 kg
Samples available	
Brick samples	Brick sent to UBA, 2 Bricks kept at North-West University. SABK2 paper pulp A, fuel mixed into clay. Mix of subsamples from different spots in pile, sent to JRC. SABK2 duff, fine coal mixed into clay. Mix of subsamples from different spots in pile, sent to JRC
Soil samples	Sent to JRC, analyzed by UBA, Duplicates of all samples kept at North-West University.
Ash samples	Ash from kiln just cooled down. Mix of subsamples from different spots in kiln (SABK2 Bottom ash). Sent to JRC , Duplicate kept at North-West University

Figure 43: Location SABK2, coal fired industrial scale kiln





Figure 44: Detail SABK2, bottom ash sampling



Figure 45: Detail SABK2, brick ingredient "fluff" (waste paper pulp)





Figure 46: Detail SABK2, brick ingredient “duff” (fine coal)



Figure 47: Detail SABK2, clay quarry on site



Figure 48: Location SABK2, overview and sampling sites



Figure 49: Detail SABK2, soil sampling downwind from the clamps (in the background)





Figure 50: Detail SABK2-3, soil sampling (kiln in the background)



Figure 51: Location SABK2, production and background site



Figure 52: Detail SABK2, background site



Table 21: SABK2 - Sample identification

Soil, dist. from kiln	Coordinates	Ash	Ingredients	Bricks
<b>15 m</b> SABK2-1A UBA 0911 5020	26 35S 27 57E	SABK2 bottom Ash JRC DP-09-076	SABK2 duff JRC DP-09-075  SABK2 paper pulp JRC DP-09-077	SABK2 brick UBA 1011 5964
<b>100 m</b> SABK2-2A UBA 0911 5021	26 35S 27 57E			
<b>200 m</b> SABK2-3A UBA 0911 5022	26 35S 27 57E			
<b>300 m</b> SABK2-4A UBA 0911 5023	26 35S 27 57E			
<b>430 m</b> SABK2-5A UBA 0911 5024	26 35S 27 57E			
<b>23 km</b> SABK2 <b>background</b> UBA 0911 5025	26 47S 27 53E			



### 3.1.2.3 Dididi - Wood fired informal kiln

Figure 53: Location Dididi, wood fired informal kiln site

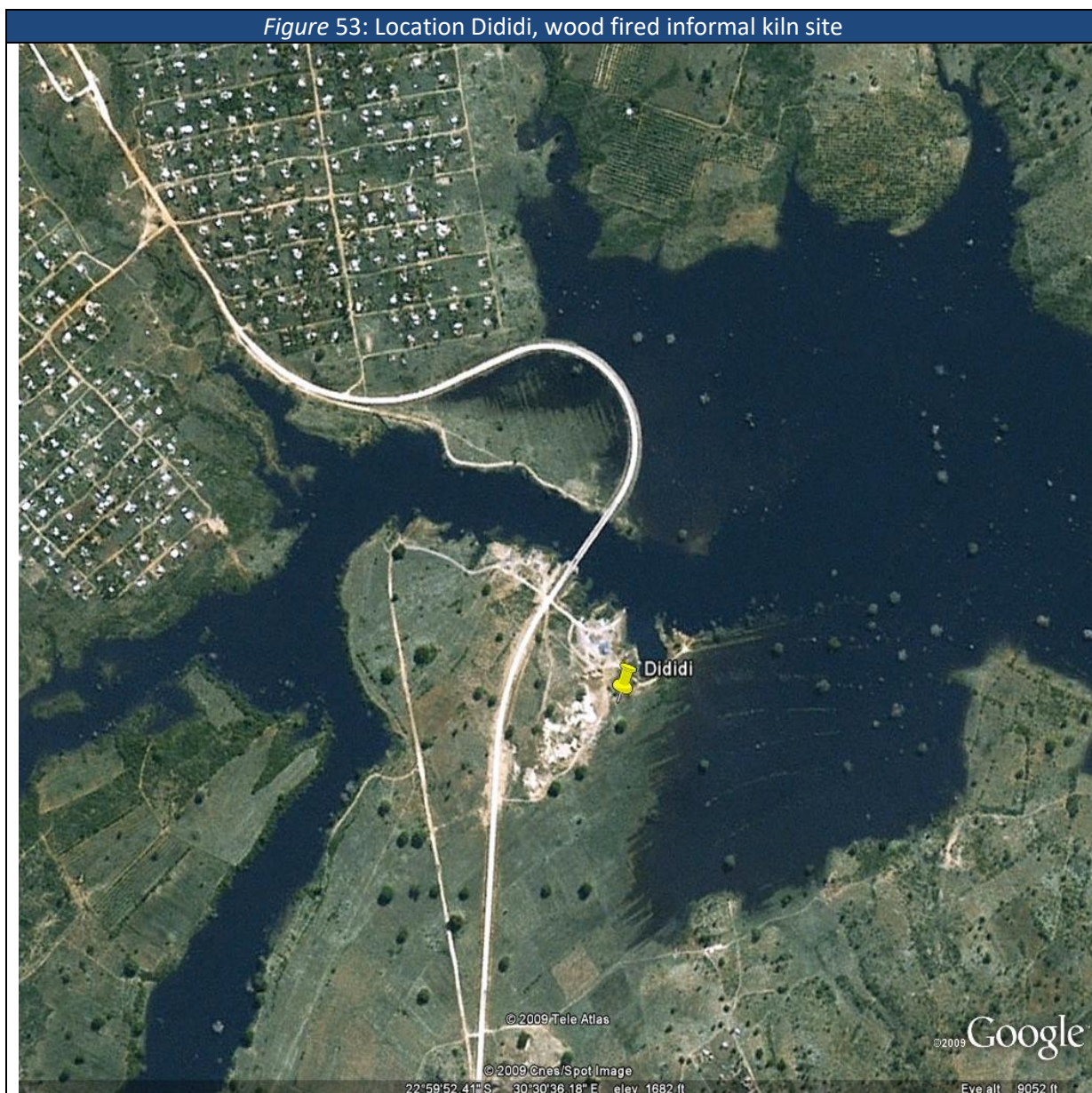


Table 22: Dididi - Characteristics of the site

Table 22: Dididi - Characteristics of the site	
Kiln location	Artisanal brickmaking activity. These are small-scale, unregulated operations found often in tribal areas far away from commercial factories. The activity is intermittent and not an ongoing concern. Very little information is available on this activity.
Character	The northern region of the Limpopo Province is one of the poorest areas in South Africa, but is slowly developing. The sites sampled here were also in a malaria area where DDT is used in indoor residual spraying, but DDT residues are known from sediments and fish. Artisanal brickmaking seems to be diminishing, as bricks from commercial companies are now becoming more available.



*Table 22: Dididi - Characteristics of the site*

<b>Samples available</b>	
Kiln type	Clamp kiln equivalent to temporary kiln in Mexico. Per kiln only a couple of 100 bricks are produced per kiln, but there seem to be no continuous production.
Fuel	Only wood, with sometimes little coal, is used.
Materials for bricks	Clay is sourced from very close by the kiln as transport is by hand. Clay is mixed with water only. No additional materials are mixed in. Wood for fuel is sourced locally. Coal is used sparingly as it has to be bought. There are no coal mines close by. Coal is used to start firing as some of the wood is still raw.
Product	Hand-formed stock brick = 28 X 14.5 X 10.5 cm. 6.528 kg.
<b>Other data available</b>	
No information available, but probably similar to same type kilns in Mexico	

*Figure 54: Detail Dididi, informal kiln*



Wet bricks laid out to dry, with PVC tarpaulin to cover against rain. Clay is mined from a quarry to the left.

Figure 55: Detail Dididi, informal kiln. (Left) Ready-packed kiln



Wood fuel can be seen in the trough on the side, and some little coal that is added by to aid combustion. The kiln operator is ready for firing with matches in his hand. (Right) Kiln that has just been fired.

Figure 56: Detail Dididi, informal kiln during the process



Wood is used as fuel. Firing takes about a week. Reservoir can be seen in the background



Figure 57: Detail Didi, informal kiln, construction details (fire chamber and sealing)



Baked brick covers the outside of the clamp, with mud used to seal the holes between

Figure 58: Detail Didi, informal kiln being dismantled



Partially dismantled kiln after the process Ash can be seen in the fire chambers



Table 23: Dididi - Sample identification				
Soil, dist. from Kiln	Coordinates	Ash	Ingredients	Bricks
10 m North Dididi soil 1A UBA 0911 5016	23 00S 30 30E	Bottom ash 438 (2300S 3030E) UBA 1011 5968  Bottom ash 435 (2300S 3032E) UBA 1011 596	No samples available	Basic brick (2300S 3031E) UBA 1011 5966
10 m East Dididi soil 2A UBA 0911 5017	24 00S 30 30E			
10 m West Dididi soil 3A UBA 0911 5018	23 00S 30 30E			
10 m South Dididi soil 4A UBA 0911 5019	23 00S 30 30E			
Dididi reference soil 439 UBA 0911 5967	23 01S 30 34E			

### 3.1.3 Sites in Kenya

An overview on the sampling sites in Kenya is given in *Figure 61*

A large majority of bricks in Kenya are manufactured in small informal kilns located in various parts of the country. There are very few commercial scale brick manufacturing enterprises in the country

These informal kilns sampled were located within agricultural areas where the main activity is peasant farming consisting mainly maize, sugarcane and beans. It is thus notable that the sampled soil, which lay at a depth of about 0-30 cm, would have been mixed up in the process of tilling the soil for agricultural processes.

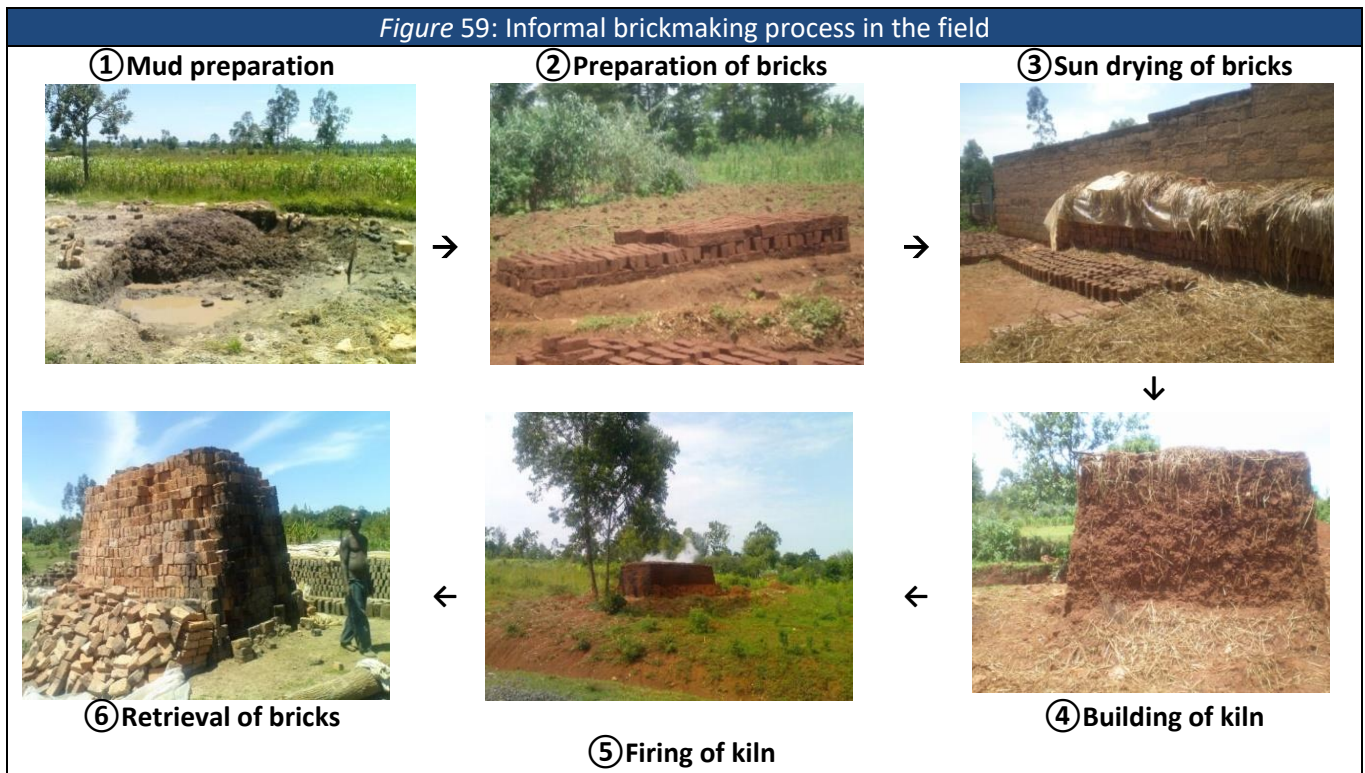
No major activities associated with the production of dioxins and furans were visible in the sampling sites. Care was taken to ensure that there was no visible evidence of such activity in the sites selected. All the sites were located within proximity of a road. The manufacturers do this in order to attract the buyers of the bricks who normally drive along the roads looking for bricks and also to make transportation easy.

The brickmaking process, very similar to that of the temporary kilns in Mexico and South Africa, is carried out in six steps namely:

- Mud preparation:
- Preparation of raw bricks using molds

- Sun drying of bricks: The time taken to dry the bricks depends on the weather conditions
- Building of temporary kiln
- Firing of kiln
- Retrieval of bricks

Figure 59 shows how the process is carried out in the field.



Mud preparation involves excavation of soil within the vicinity, mixing it with water and kneading it until consistent. No additional materials are added into the mixture. It is then put into moulds and sun dried. The process of sun drying is totally dependent on the weather conditions. The bricks are normally covered with grass during this period, however in case of rain, PVC is used.

The kiln is constructed by stacking up the bricks and leaving fire chambers at the bottom. The outside is then plastered with mud. The number of bricks ranges between 2000 – 10,000 bricks per batch.

Figure 60 shows an example of such a kiln.

Figure 60: Typical production site in Kenya



The firing phase normally lasts between 2 – 3 days. During the initial phase, small pieces of wood are first fed into the chambers and lit. After catching fire, the larger logs are added until the predetermined amount is all in. The chambers are then sealed and the kiln is left burning until no more smoke is visible indicating that all the wood has been burnt. The kiln is left to cool down and dismantled. About 3 tonnes of wood are used to produce about 10 tonnes of brick. It was not possible to accurately determine the quantity of ash produced.



Figure 61: Overview on the sampling sites in Kenya



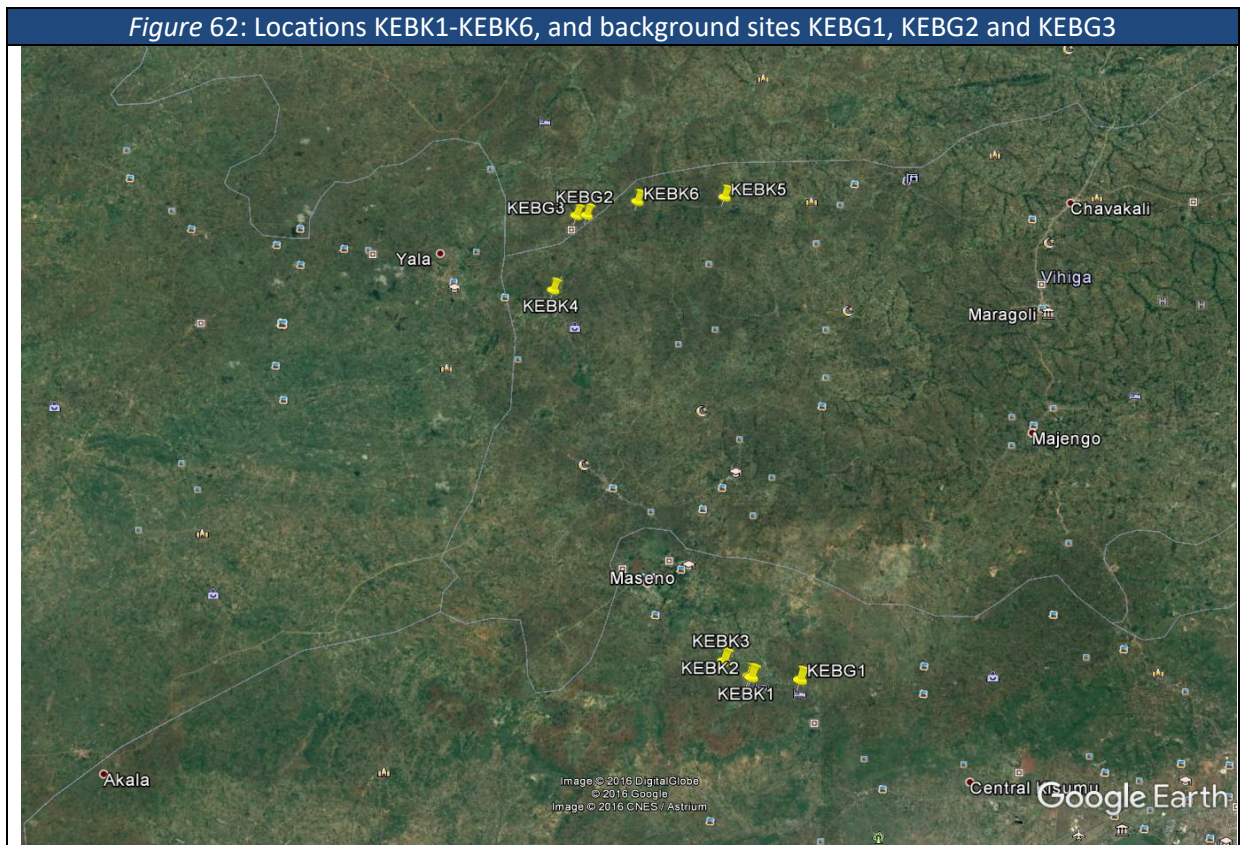
Table 24: Sites A, B, C, D, E & F - Characteristics of the sites

Location Site A KEBK1	Temporary kiln located appx. 20 Meters from the road
Location Site B KEBK2	Temporary kiln located appx. 20 Meters from the road
Location Site C KEBK3	Temporary kiln located appx. 20 Meters from the road
Location Site D KEBK4	Temporary kiln located appx. 30 Meters from the road
Location Site E KEBK5	Temporary kiln located appx. 10 Meters from the road
Location Site F KEBK6	Temporary kiln located appx. 20 Meters from the road
Kiln type	Informal kilns using the local soil nearby to produce bricks
Fuel	Virgin Wood
Materials for bricks	Local soils. No other materials are added.
Size of brick	Average weight of brick 2.5kg

Table 24: Sites A, B, C, D, E & F - Characteristics of the sites

Samples available	
Soil samples	<p><b>A:</b> Composite agricultural soil samples around the kiln (0-30cm depth ). undisturbed soils at 10 m distance surrounding the kiln (note top soil at this depth would have been mixed for cultivation purposes)</p> <p><b>B:</b> Two composite agricultural soils as A</p> <p><b>C, D, F:</b> One composite agricultural soil as A</p> <p><b>E:</b> One composite agricultural soil at 1 m distance around the kiln</p>
Ashes	<p><b>A:</b> One sample sent to UBA Vienna</p> <p><b>B:</b> Three samples sent to UBA Vienna</p> <p><b>C, D, E, F:</b> One sample each sent to UBA Vienna</p>
Other data available	
Activity of the kilns	2000-10,000 bricks per batch. Occasional production
Ash production	Approximately 3kg of ash per 10 tons of brick

Figure 62: Locations KEBK1-KEBK6, and background sites KEBG1, KEBG2 and KEBG3





### 3.1.3.1 KEBK1, KEBK2 & KEBK3 and their background site KEBG1

Figure 63: Location sites KEBK1, KEBK2, KEBK3



Figure 64: Detail KEBK1, drying of raw bricks





Figure 65: Detail KEBK2, drying of raw bricks (covered with grass)



Figure 66: Detail KEBK3, informal kiln





Figure 67: Detail site KEBK3, burnt bricks and partially dismantled kiln



Figure 68: Detail site KEBK3, clay excavation for brickmaking





Figure 69: Location of background site KEBG1

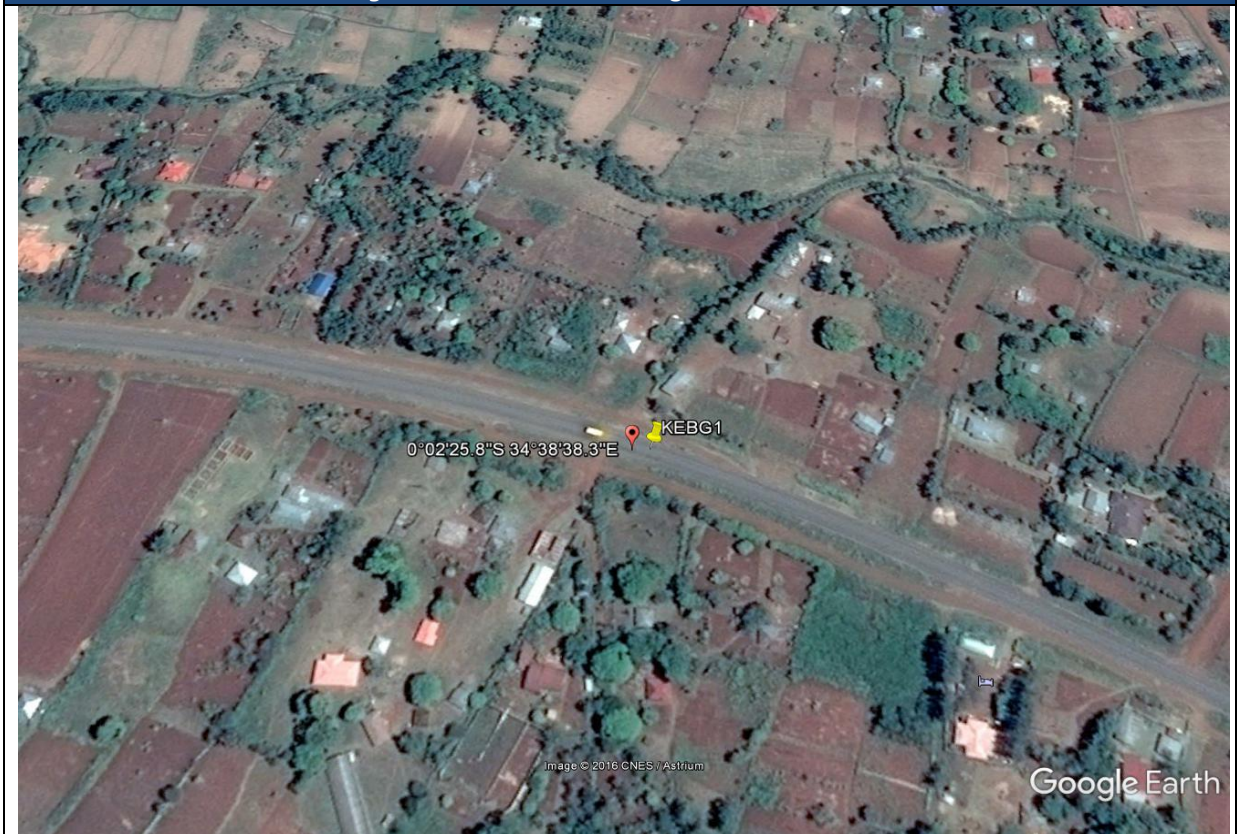


Figure 70: Detail site KEBG1, background site 1





### 3.1.3.2 KEBK4, KEBK5 & KEBK6 and related background sites KEBG1 and KEBG2

Figure 71: Location sites KEBK4, KEBK5, KEBK6

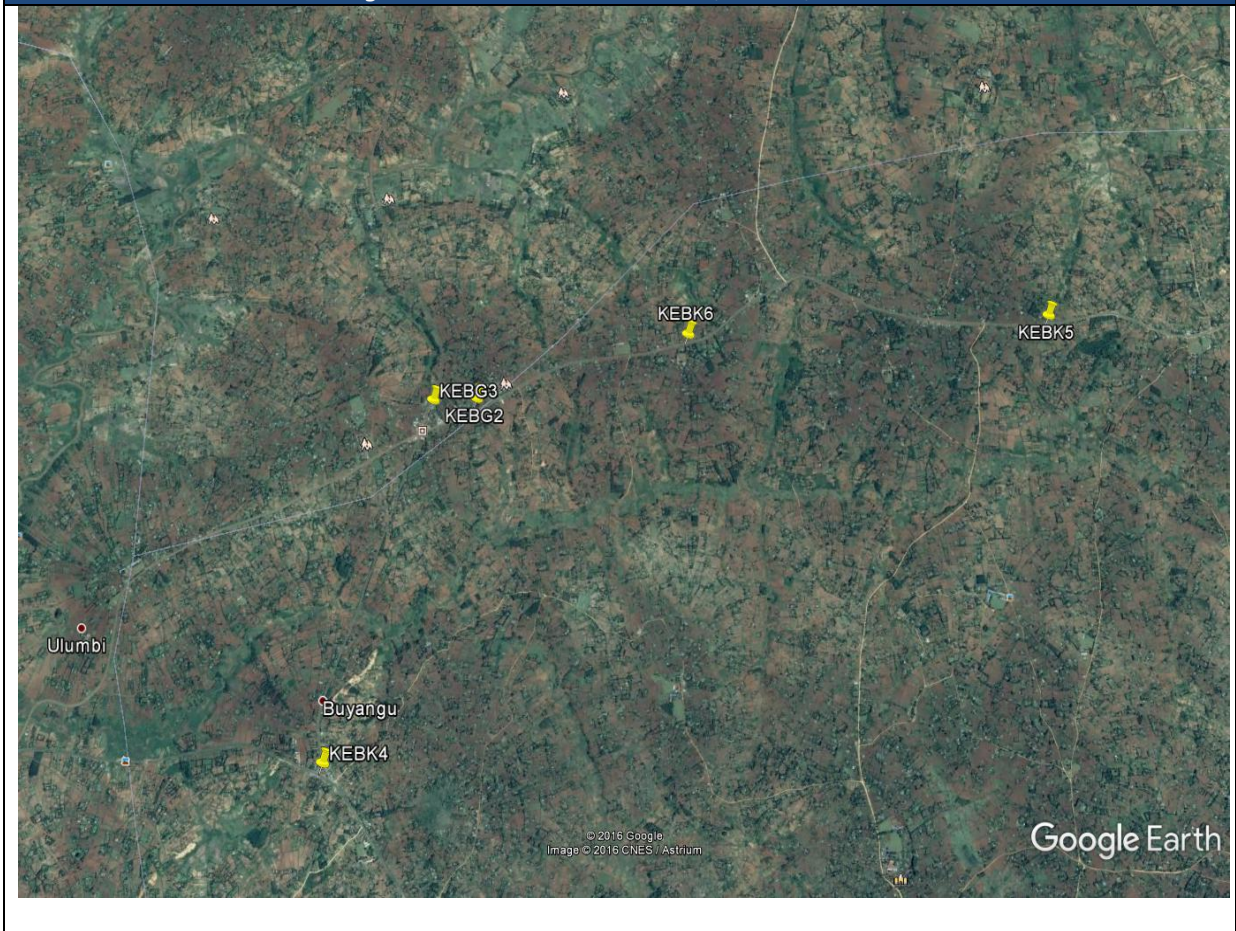


Figure 72: Detail site KEBK4, dried raw bricks ready for baking





Figure 73: Detail site KEBK5, clay excavation and raw bricks (front)



Figure 74: Detail site KEBK5, dried raw bricks prior to baking





Figure 75: Detail site KEBK6, informal kiln ready for firing



Figure 76: Detail site KEBK6, clay excavation for brickmaking





Figure 77: Location of the background sites KEBG2, KEBG3



Figure 78: Detail site KEBG2, background site 2

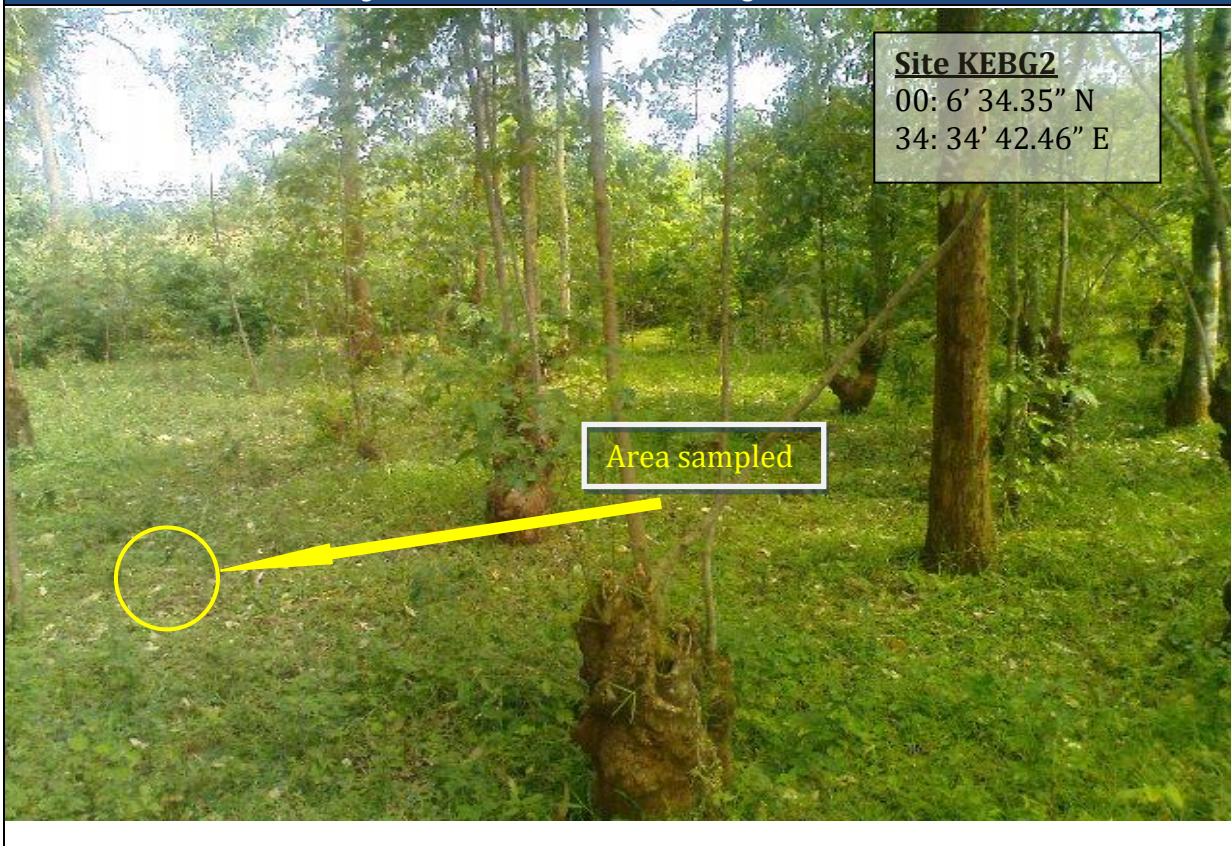




Table 25: Identification of the codes used for instrumental analysis	
Site name on Map	Site name for instrumental analysis
KEBK1	Site A
KEBK2	Site B
KEBK3	Site C
KEBK4	Site D
KEBK5	Site E
KEBK6	Site F
KEBG1	Background 1
KEBG2	Background 2
KEBG3	Background 3

Table 26: Sites A, B, C, D, E and background sites - Sample identification		
Soil, dist from Kiln	GIS	Ash
<b>10m</b> <b>SITE A</b> Soil, Kiln 20m from road (UBA 0912 5668)	00° 22' 22" S 34° 37' 43" E	Ash sample Kiln A, UBA 0912 5670
<b>10 m</b> <b>SITE A</b> Soil, Kiln near the road (UBA 0912 5669)		2 <sup>nd</sup> Ash sample Kiln B, UBA0912 5671 Ash sample Kiln B2, BA 0912 5672
<b>10 m</b> <b>SITE B</b> Soil Kiln 20m from road (UBA 0912 5673)	00° 02' 23" S 34° 37' 46" E	1 <sup>st</sup> Ash sample Site B Kiln B UBA 0912 5675
<b>10m</b> <b>SITE B</b> Soil Kiln near the road (UBA 0912 5674)		
<b>10m</b> <b>SITE C</b> soil (UBA 0912 5676)	00° 02' 05" S 34° 37' 15" E	Ash sample SITE C UBA 0912 5677
<b>10 m</b> <b>SITE D</b> soil (UBA 0912 5678)	00° 05' 05" N 34° 34' 05" E	Ash sample SITE D UBA 0912 5679
<b>1m</b> <b>SITE E</b> soil (UBA 0912 5680)	00° 06' 56" N 34° 37' 19" E	Ash sample SITE E UBA 0912 5681
<b>10 m</b> <b>SITE F</b> soil (UBA 0912 5682)	00° 06' 51" N 34° 35' 40" E	Ash Sample SITE F UBA 0912 5683
<b>Background Site 1</b> soil (UBA 0912 5684) <b>1.6 km from kilns</b>	00 2'25.84" S 34 38' 38.31" E	

<b>Background Site 2</b> soil (UBA 0912 5685) <b>2 km from kilns</b>	00 6' 34.35" N 34 34' 42.46" E	
<b>Background Site 3</b> soil (UBA 0912 5686) <b>2 km from kilns</b>	00 6' 34.42" N 34 34' 30.61" E	



## 3.2 Analytical determinations – overview

For more details, see A.3 Analytical Methods.

### 3.2.1 Soils and ash at the UBA Vienna

Parameter / group	Description
PCDD/PCDF , DL-PCB, I-PCB and HCB in solid samples according the USEPA Methods 1613 and 1668	Spiking of the sample with 17 <sup>13</sup> C <sub>12</sub> labeled PCDD/PCDF, 18 <sup>13</sup> C <sub>12</sub> labeled PCB and <sup>13</sup> C <sub>6</sub> labeled HCB (surrogates). Extraction by ASE with toluene. Sample clean-up by three step column chromatography. Addition of an internal recovery standard. Qualitative and quantitative determination by means of isotope dilution method on a gas-chromatographic / mass-spectrometric system at a resolution of 8000 – 9000.

### 3.2.2 Bricks at the Krakow University

Parameter / group	Description
PCDD/PCDF , DL-PCB, and HCB in solid samples according the USEPA Methods 1613 and 1668	Crushing of the brick with planetary mill Spiking of the sample with 15 <sup>13</sup> C <sub>12</sub> labeled PCDD/PCDF, 12 <sup>13</sup> C <sub>12</sub> labeled PCB and <sup>13</sup> C <sub>6</sub> labeled HCB (surrogates). Extraction by Soxhlet with toluene. Extract clean-up by sulfuric acid wash and three step column chromatography. Addition of an internal recovery standard. 2 <sup>13</sup> C <sub>12</sub> labeled PCDD/PCDF Qualitative and quantitative determination by means of isotope dilution method on a gas-chromatographic / tandem mass-spectrometric system (MS/MS). Standard reference materials analyzed in parallel

### 3.2.3 Ash at the JRC

Parameter / group	Description
PCDD/PCDF , DL-PCB, and HCB in solid samples according the USEPA Methods 1613 and 1668	Spiking of the sample with 17 <sup>13</sup> C <sub>12</sub> labeled PCDD/PCDF, 18 <sup>13</sup> C <sub>12</sub> labeled PCB and <sup>13</sup> C <sub>6</sub> labeled HCB (surrogates). Extraction by Soxhlet with toluene. Sample clean-up by three step column chromatography. Addition of an internal recovery standard. Qualitative and quantitative determination by means of isotope dilution method on a gas-chromatographic / mass-spectrometric system at a resolution of 10000. Standard reference materials analyzed in parallel.

## 4. Results and discussion

### Toolkit relevant Note 1:

For the temporary kiln in León and the stationary kiln in Salamanca, among other sites subject to soil and bottom ash sampling in this study, emission factors (EFs) to air were determined in an earlier study (Maiz et al. 2010).

Because of budget and logistic limitations, it was not possible to execute additional emission measurements for other type of kilns, fuels etc. used for the brickmaking in other developing regions.

In contrast to emission measurements, soil and bottom ash sampling can be conducted without specialized equipment and at lower costs, thus allowing a broader coverage of processes and regions.

The starting point for the evaluation of the results presented in the present study is based on the assumption that high emissions of POPs into the air should materialize in a significant POPs gradient in the source-near top soils, in higher POPs contents in the bottom ashes, and in the products (bricks in our case).

Via the comparison of the soil, ash and brick data from a number of additional brickmaking sites in Mexico, South Africa and Kenya sites with the ones from the brick kilns in León and Salamanca, where EFs are available, we intend to evaluate the general applicability of those EFs for the use in the Toolkit in developing countries.

### 4.1 Mexico

#### 4.1.1 León

In *Table 27*, the results in soils and ashes of this site are displayed, together with the EFs obtained during the measurements at the virgin wood fired temporary kiln in León. The orientation of the sampling sites with respect to the kiln can be obtained from *Figure 7*.

It can be seen that soils sampled at distances of 10 m, 21m and 40 m from the kiln display higher concentrations in the topsoil (0-5 cm) for PCDD/PCDF, DL-PCB and HCB. The samples taken at the distances of 75m and 160 m were in the concentration range measured at the background site.

The highest PCDD/PCDF concentration in soil was 18 ng WHO<sub>2005</sub>-TEQ/kg measured at a distance of 10m from the kiln. The contribution of the PCB is negligible on a TEQ basis, similar to what was observed for the emission factors. Although the levels detected in León were among the highest found for PCDD/PCDF and HCB in this study, the extent of soil contamination there does not pose a risk when considering the land use in this region.<sup>3</sup>

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<sup>3</sup> The PCDD/F levels in soil they are fairly below existing action levels in Germany. The land use specific German guideline values (target concentrations in I-TEQ) do not require any (remediation) action at concentrations that are <40 ng/kg for crop cultivation, < 100 ng/kg for playgrounds, <1000 ng/kg for residential areas and 10000 ng/kg for industrial areas (BLAG, 1992 and BbodSchV 1999).



In contrast to the soils, bottom ashes, taken in April and November 2008, show consistently low contamination for all compounds. They do not pose any risk regarding the compounds investigated, even if used as fertilizers for crop cultivation<sup>4</sup>.

The inconstancy between (in relative terms) high contamination of the soils in comparison with the bottom ashes may be explained by historical factors. In the past tannery wastes were used as a fuel at the León site. These wastes contain Pentachlorophenol (PCP) and other PCDD/PCDF precursors<sup>5</sup>.

In so far it can be presumed, that the higher emissions from the past are still conserved in the soils, while the current practice of brickmaking using virgin wood leads to low emissions, as indicated by the low EFs and the low concentrations in the bottom ashes.

Table 27: Results for León, virgin wood site				
Distance	PCDD/PCDF	dI-PCB	HCB	Field code
<i>m</i>	<i>ng WHO<sub>05</sub>-TEQ/kg</i>		<i>ng/kg</i>	
10	18	0.35	770	INE 2656/08
21	13	0.50	1500	INE 2658-08
40	3.5	0.12	2400	INE 2660-08
75	0.46	0.020	23	INE 2662-08
160	0.20	0.0125	60	INE 2664-08
Background	0.78	0.031	63	INE 2666/08
Ash	0.58 <sup>#</sup>	<0.044 <sup>**</sup>	<150	JRC Brickash 5
Ash	0.34	0.014 <sup>*</sup>	<76	INE 2648-08
Ash	0.14	0.0030 <sup>*</sup>	<57	INE 3345/08
EF to Air <sup>§</sup>	45ng I-TEQ/t	1.0 ng WHO <sub>2005</sub> -TEQ/t	32µg/t	
<b>Notes:</b> <i>0 - 5 cm sampling depth</i> <i>* Co planar PCB</i> <i># upper bound</i> <i>§ per ton of bricks produced; Maiz et al. 2010</i>				
Results validated in Oct .2011, middle bound.				

<sup>4</sup> German soil legislation considers PCDD/F levels < 100 ng I-TEQ/kg in sewage sludge applied as a fertilizer in agriculture as acceptable to ensure long term soil and crop quality (AbfKlärV (1992).

<sup>5</sup> In Europe PCP application was banned for its potential of PCDD/PCDF release (European Commission, 1996)

## 4.1.2 Salamanca

### 4.1.2.1 Salamanca 1, 5

In *Table 28* the results in soils, ashes and bricks from the Combustóleo fired stationary kilns Salamanca 1 and 5 are displayed. At the site Salamanca 1, where the EFs to air were available, 2 top soils (0-15cm), 2 bottom ashes and one brick were sampled (*Table 3*). In addition another brick sample from an identical installation close by (Salamanca 5, *Table 7*) was sampled and included here.

The orientation of the sampling sites with respect to the Salamanca 1 kiln can be obtained from *Figure 13*.

Although the Combustóleo fired kiln Salamanca 1 had resulted in higher emissions to air than in León, the concentrations in the nearby soil were with PCDD/PCDF concentrations below 1 ng WHO<sub>2005</sub>-TEQ/kg more than one order of magnitude below the concentrations seen at the León site. Also the HCB concentrations in the soil were much lower.

Distance	PCDD/PCDF	dI-PCB	HCB	Field code
<i>m</i>	<i>ng WHO<sub>05</sub>-TEQ/kg</i>		<i>ng/kg</i>	
10	0.13	0.0023	24	INE 2556/08
20	0.60	0.15	100	INE 2558/08
Ash	1.6	0.15*	< 67	INE 2549-08
Ash	0.090	0.014*	< 83	INE 3338/08
Brick	<0.030 <sup>#</sup>	<0.01	<100	INE 3335/08 resp. (561/08)
Brick	0.033	<0.01	<100	INE 3340-08
<b>EF to Air<sup>§</sup></b>				
	196 ng I-TEQ/t	15 ng WHO <sub>2005</sub> -TEQ/t	221µg/t	
<b>Notes:</b> <i>0 - 5cm sampled</i> <i>* Co planar PCBs</i> <i># upper bound</i> <i>§ per ton of bricks produced; Maiz et al. 2010</i>				
Results validated in Oct .2011, middle bound				

The concentrations in the bottom ashes were below and around 1 ng WHO<sub>2005</sub>-TEQ/kg. In the two brick samples all compounds were close or at the detection limit in the lower ng/kg range.

### 4.1.2.2 Salamanca 2, 3, 4

The kilns Salamanca 2 and 3 are stationary kilns operated in a similar way as the kilns Salamanca 1 and 2 described above. Salamanca 4 is the corresponding background soil (see *Figure 17*).



In *Table 29* the results from the soil transect around the kiln Salamanca 2 (see *Figure 16*) and each one bottom ash sample from Salamanca 2 and 3 are displayed.

<i>Table 29: Results for Salamanca 2, 3, steam injected Combustóleo sites</i>				
Distance	PCDD/PCDF	dI-PCB	HCB	Field code
<i>m</i>	<i>ng WHO<sub>05</sub>-TEQ/kg</i>		<i>ng/kg</i>	
15	2.1	0.10	130	INE 2571-08
30	0.50	0.065	220	INE 2574-08
40	0.17	0.0027	190	INE 2576-08
65	0.15	0.037	51	INE 2577-08
Background	0.24	0.066	550	INE 2592-08
Ash	0.69	0.073*	< 169	INE 2564-08
Ash	0.17	0.020*	< 60	INE 2584/08

**Notes:**  
*0-5 cm sampled*  
*\*Co planar PCB*

Results validated in Oct .2011, middle bound

The soil samples near the Salamanca 2 kiln show with 2.1 ng WHO<sub>2005</sub>-TEQ/g slightly higher PCDD/PCDF values at a distance of 15 m, which, however, do not exceed the concentrations from the background sample by more than a factor of 5. HCB was even at a lower concentration than seen in the background sample.

Again the ashes display low concentrations below 1 ng WHO<sub>2005</sub>-TEQ/kg

#### 4.1.3 Abasolo

The stationary kilns in Abasolo are similar constructions as the ones in Salamanca, and also the main fuel (Combustóleo) is similar (*Table 9*). The main difference in processing the bricks in Abasolo is the batch wise firing of the fuel, while in Salamanca the fuel had been continuously supplied by steam injection

The site had been selected because it had displayed the highest PCDD/PCDF concentration in bottom ashes among all samples of <131 ng WHO<sub>2005</sub>-TEQ/kg (sample ‘Brickash 2’ in the table below) during a bottom ash screening exercise in April 2008 (Umlauf et al., 2009). Since it had not been possible to identify an appropriate soil transect around the kiln where this first ash sample had been taken, another, identically operated kiln in the vicinity was used in this study.

*Table 30* displays the concentrations in the soils in the vicinity of this kiln (Abasolo 1), together with one brick sample and one ash sample taken there. Since this kiln displayed comparably high PCDD/PCDF and HCB concentrations in one brick sampled in 2008, 2 more brick samples were taken in from a similar kiln close by (Abasolo 5) in 2010 for confirmation purpose.

Table 30: Results for Abasolo 1 and 5, batch fired Combustóleo/waste site

distance	PCDD/PCDF	dl-PCB	HCB	Field code
<i>m</i>	<i>ng WHO<sub>05</sub>-TEQ/kg</i>		<i>ng/kg</i>	
10	0.32	0.0042	91	INE 2628-08
20	0.44	0.0036	50	INE 2630-08
40	0.098	0.0047	52	INE 2632-08
80	12	0.34	500	INE 2634-08
160	3.8	0.090	290	INE 2636-08
Background	none			
Ash	0.43	0.014*	> 76	INE 2620/08
Ash <sup>Δ</sup>	131	9.9*	1700	Brickash 2
Ash/Carbon	1.2	0.16*	282	INE 2626-08
Brick	4.0	0.39	52,500	INE 404-09
Brick <sup>#</sup>	9.5	0.19	120,000	INE 317/10
Brick <sup>#</sup>	15	0.084	77,000	INE 732/10

**Notes:**

10 m sampled 0-15 cm, 20 m sampled 0-20cm, 40m sampled 0-15cm, 80 m sampled 0-10 cm and 160m sampled 0-10 cm

\*Coplanar PCB

# Bricks from Abasolo 5 kiln

<sup>Δ</sup> Sample taken from a similar kiln during the bottom ash screening pre campaign

Results validated in Oct .2011, middle bound

The soil transect in Abasolo displayed low PCDD/PCDF concentrations of < 1 ng WHO<sub>2005</sub>-TEQ/kg up to 40 m from the kiln and a maximum of 12.3 ng WHO<sub>2005</sub>-TEQ/kg at 80 m distance and 3.8 ng WHO<sub>2005</sub>-TEQ/kg at 160 m. Also PCB and HCB maxima were detected at the 80 m distance. The 80 m and the 160 m site were 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 obvious absence of a clear concentration gradient in the soil transect of this site suggests that the topsoil in the vicinity of the kiln had been disturbed either through removal of the surface or by covering the soil with low contaminated residues (the bottom ash concentration at Abasolo 1 was below 1 ng WHO<sub>2005</sub>-TEQ/kg) or raw materials for the brickmaking).

The concentrations in bottom ashes (incl. a carbon residuals collected in the fire chamber) were more heterogeneous when compared to the other sites. An isolated maximum PCDD/PCDF value of 131 ng WHO<sub>2005</sub>-TEQ/kg was found in one of the ash samples, while the other samples were around the 1 ng WHO<sub>2005</sub>-TEQ/kg range. The high variation of concentrations in the ash may result from the batch-wise supply of fuel that may favor incomplete combustion in certain sections of the combustion chamber.



All the brick samples from Abasolo, both from the 2008 and the 2010 sampling exercise displayed high concentrations when compared to all other brick samples investigated in Mexico, South Africa and Kenya. Although these concentrations are insignificant from a viewpoint of human risk, they are worth being further investigated because of their potential implications for the emission inventories when the Toolkit is applied<sup>6</sup>.

#### 4.1.4 Juventino Rosas

This site had been set up by the local authorities based exclusively on LPG and has run for only 10 years. In *Table 31* the results for the soil transect close to a temporary kiln and a corresponding bottom ash sample are summarized.

The top soils of this site displayed the lowest soil concentrations of all compounds investigated in Mexico (at similar concentrations as in the African sites) with no interpretable gradients along the soil transect.

Table 31: Results for Juventino Rosas, LPG site				
Distance from kiln	PCDD/PCDF	dl-PCB	HCB	Field code
<i>m</i>	<i>ng WHO<sub>05</sub>-TEQ/kg</i>		<i>ng/kg</i>	
10	0.14	0.035	64	INE 2605-08
20	0.67	0.033	69	INE 2607-08
40	0.13	0.036	44	INE 2609-08
80	0.082	0.0025	42	INE 2611-08
150	0.15	0.037	32	INE 2614-08
Ash	1.2	0.048*	< 53	INE 2598-08

**Notes:**  
*10 and 20 m sampled 0-5cm, 40m sampled 0-15 cm, 80m sampled 0-10 cm and 150m sampled 0-15cm*  
*\*Co Planar PCB*

Results validated in Oct .2011, middle bound

PCDD/PCDF concentrations in the ash samples were 1.2 ng WHO<sub>2005</sub>-TEQ/kg.

#### 4.1.5 Chiapa de Corzo and Queretaro Tequisquiapan

After the first series of analyses from the 2008 samples from Mexico, which included the Abasolo site, there were indications of enhanced PCDD/PCDF and HCB concentrations particularly in ashes and bricks from kilns using secondary oils under discontinuous supply.

<sup>6</sup> The mass of bricks produced in these types of kilns is around a 100 of tons per batch, while bottom ash production remains in the range of some kg. Consequently, the quantitative estimate of the emission inventory is in particular sensitive to the (correct estimate of the) concentration in the brick, especially, when the emission factors to air are low.

In order to confirm this observation, 2 more sites burning waste oils in batch mode were identified in the provinces of Chiapas and Queretaro and brick and bottom ash samples were taken in 2009.

In the temporary kilns of Chiapa de Corzo used engine oils and other types of waste oil were used as fuel (*Table 14*).

In *Table 32* the results for bricks and bottom ashes are displayed.

<i>Table 32: Results Chiapa de Corzo, waste oil site</i>				
	PCDD/PCDF	dl-PCB	HCB	Field code
	<i>ng WHO<sub>05</sub>-TEQ/kg</i>		<i>ng/kg</i>	
Ash	0.19	0.08*	178	INE 361/09
Brick	0.15	0.014	< 500	INE 353/09
<b>Notes:</b> *Co planar PCBs				
Results validated in Oct .2011, middle bound				

In the temporary kilns of Queretaro used engine oils residual cakes from the lubricant refining process were used as fuel (*Table 16*). In *Table 33* the results for bricks and bottom ashes are displayed

<i>Table 33: Results Queretaro, waste oil fired kiln</i>				
	PCDD/PCDF	dl-PCB	HCB	Field code
	<i>ng WHO<sub>05</sub>-TEQ/kg</i>		<i>ng/kg</i>	
Ash	0.09	0.09*	195	INE 403/09
Brick	0.20	0.011	<500	INE 399/09
<b>Notes:</b> *Co planar PCBs				
Results validated in Oct .2011, middle bound				

The contamination in the bricks and bottom ashes from both kilns in Chiapas and Queretaro - although fueled batch-wise with waste derived oils - is as low as seen before in León, Salamanca, Juventino Rosas, fired with a variety of fuels including waste oils.

In so far the comparably high concentrations in bricks and ash observed in Abasolo could not be confirmed by the data from similar kilns using batch wise supply of waste oils.

#### 4.1.6 Summary Mexico

Due to their low contribution to the total dioxin-like toxicity, PCB will not be discussed further here. *Table 34* provides data on agglomerated concentrations in the soil in the vicinity of the kilns compared to the background soils.

The comparison reveals only a slight impact on the soil environments at most of the brickmaking sites; the average concentration of PCDD/PCDFs near the kilns was about six



times higher than in the non-impacted background soils. However, this is mainly due to two outliers, namely in León (probably historical contamination from fuels that are currently banned) and in Abasolo. 18 ng WHO<sub>2005</sub>-TEQ/kg was the highest PCDD/PCDF concentration detected in a soil in León<sup>7</sup>. For HCB no interpretable differences between background and production sites were found.

If the soil samples from León and Abasolo are excluded from the statistics, no significant differences can be seen between the production sites and the background sites in Mexico.

<i>Table 34: Mexico - Summary soils</i>			
	<b>PCDD/PCDF</b>	<b>dl-PCB</b>	<b>HCB</b>
	<i>ng WHO<sub>05</sub>-TEQ/kg</i>		<i>ng/kg</i>
All soils around the kilns (n= 21)			
Average	2.7	0.094	318
Median	0.44	0.036	69
STD Dev.	5.1	0.14	590
Min.	0.082	0.003	23
Max.	18	0.50	2400
Soils around the kilns, excluding León and Abasolo (n=11)			
Average	0.44	0.047	86
Median	0.15	0.036	64
STD Dev.	0.59	0.04	65
Min.	0.082	0.0025	24
Max.	2.1	0.15	220
Background soils (n=3)			
Average	0.42	0.054	388
Median	0.24	0.066	550
STD Dev.	0.31	0.020	281
Min.	0.24	0.031	63
Max.	0.78	0.066	550
<b>Notes:</b>			
Results validated in Oct .2011, middle bound			

<sup>7</sup> For comparison: The land-use-specific German guidelines do not require any (remediation) action at concentrations that are <40 ng I-TEQ/kg for crop cultivation, < 100 ng I-TEQ/kg for playgrounds, <1,000 ng I-TEQ/kg for residential areas and 10,000 ng I-TEQ/kg for industrial areas (BLAG, 1992; BbodSchV, 1999). The investigated brickmaking sites in Mexico clearly do not fall into the category of contaminated industrial sites with regard to the investigated compounds.

The grouping of the agglomerated soil concentration data according to the fuel used for brickmaking is displayed in *Table 35*. This comparison should be interpreted with care due to the limited availability of data, and the fact that the soils in León might have been impacted by tannery wastes in the past.

The highest average concentrations of all compounds were found in León (virgin wood), followed by Abasolo (Combustóleo, batch supply, highest PCDD/PCDF maximum), Salamanca (Combustóleo, steam-injected) and Juventino Rosas (LPG).

Due to the limited amount of data and the uncertainties discussed in Note 2 below, the environmental impact of different fuels cannot be coherently interpreted from the soil data alone. However, LPG (Juventino) seems to be the cleanest technology, followed by steam-injected Combustóleo (Salamanca). Batch firing of Combustóleo resulted in higher concentrations in the soils. For the virgin-wood-fired kiln environment in León, which seems to be the most contaminated on a relative scale, the situation remains unclear.

<i>Table 35: Concentrations in the soils as a function of the fuel used</i>			
	<b>PCDD/PCDF</b>	<b>dl-PCB</b>	<b>HCB</b>
	<i>ng WHO<sub>05</sub>-TEQ/kg</i>		<i>ng/kg</i>
Wood-fired kiln in León (n= 5 soils)			
Average	7.0	0.20	951
Median	3.5	0.12	770
Min.	0.020	0.013	23
Max.	18	0.50	2400
Combustóleo-fired kilns in Salamanca, steam injection (n=6 soils)			
Average	0.61	0.063	116
Median	0.34	0.051	105
Min.	0.13	0.0027	24
Max.	2.1	0.15	220
Combustóleo-fired kilns in Abasolo, batch supply (n=5 soils)			
Average	3.3	0.089	197
Median	0.44	0.0047	91
Min.	0.098	0.0036	50
Max.	12	0.34	500
LPG-fired kilns in Juventino Rosas (n=5 soils)			
Average	0.23	0.029	50
Median	0.14	0.035	44



Min.	0.082	0.0025	32
Max.	0.67	0.037	69
<b>Notes:</b>			
Results validated in Oct .2011, middle bound			

**Toolkit-relevant Note 2**

The soil transects taken in the vicinity of the investigated kilns did not result in clear spatial concentration gradients (as would be expected for undisturbed soils under the impact of a point source), except in León. This may be due to disturbed top soils, since most of the Mexican sites were located in urban areas. Moreover, in these urbanised environments, which are typical of the Mexican sites, other POP sources may be present or, as the observation in León suggests, historical contamination may have been conserved in the soils. So far, the concept of comparing the current emission source strength of these kilns indirectly through the contamination gradients in the nearby soils, partially failed.

However, the moderate contamination levels in the urban and remote soils recorded in this study indicate a low environmental and health impact of POPs released in the brickmaking process, and supplement the few existing data on soil contamination in developing countries.

Table 36 provides the agglomerated concentration data in bottom ash and bricks from Mexico.

<i>Table 36: Mexico – Summary for bottom ash and bricks</i>			
	<b>PCDD/PCDF</b>	<b>dl-PCB</b>	<b>HCB</b>
	<i>ng WHO<sub>05</sub> -TEQ/kg</i>		<i>ng/kg</i>
All bottom ash (n= 13)			
Average	11	0.82	242
Median	0.43	0.048	83
STD Dev.	36	2.7	444
Min.	0.090	0.0030	53
Max.	131	9.9	1700
Bottom ash, except Abasolo (n=10)			
Average	0.52	0.054	109
Median	0.27	0.046	80
STD Dev.	0.51	0.046	57
Min.	0.090	0.0030	53
Max.	1.6	0.150	195
All bricks (n=7)			

Average	4.1	0.10	35,814
Median	0.20	0.014	500
STD Dev.	5.9	0.14	48,489
Min.	0.030	0.010	100
Max.	15	0.39	120,000
Bricks, except Abasolo (n=4)			
Average	0.10	0.011	300
Median	0.092	0.011	300
STD Dev.	0.085	0.0019	231
Min.	0.030	0.010	100
Max.	0.20	0.014	500
<b>Notes:</b>			
Results validated in Oct .2011, middle bound			

The comparably high concentrations in bricks and ash observed in Abasolo, which were fueled in batches with waste oils, could not be confirmed by the low concentrations at the kilns in Chiapas and Queretaro that were operated in the same manner. Seemingly, batch supply of waste oils does not per se result in higher contamination of bricks and ash.

Abasolo appears to be an isolated outlier for which, on the basis of this investigation, the high concentrations observed cannot be explained. As a hypothesis, potential contamination of the brick ingredients with halogenated precursors may be considered, or the presence of chloride in the clay; in this context further analyses of the raw materials would be desirable.

### **Toolkit-relevant Note 3**

PCDD/PCDF in bottom ash and bricks of all kilns (except in Abasolo) were rather uniformly distributed among the investigated kilns. They were in the range of a few ng WHO<sub>2005</sub>-TEQ/kg and below, including those from the sites in León and Salamanca, where the emission factors had been determined.

So far – presuming that PCDD/PCDF contents in bottom ash and bricks are correlated with the emissions to air – the range of emission factors obtained in León and Salamanca appears to be generally representative of all investigated sites in Mexico, except for a single location in Abasolo.

## 4.2 South Africa

### 4.2.1 SABK1

Table 37 provides the individual concentrations data from the soils in the vicinity of the industrial scale kiln SABK1 in comparison to the background soils together with the concentrations in bottom ash and bricks.

Table 37: Results SABK1, coal-fired industrial scale site				
Distance from kiln	PCDD/PCDF	dl-PCB	HCB	Field code
<i>m</i>	<i>ng WHO<sub>05</sub>-TEQ/kg</i>		<i>ng/kg</i>	
136	0.14	0.022	200	SABK1-1
263	0.10	0.041	35	SABK1-2
357	0.15	0.032	22	SABK1-3
447	0.13	0.040	<17	SABK1-4
445	0.10	0.027	18	SABK1-5
213	0.051	0.035	<17	SABK1-6
545	0.098	0.0032	<17	SABK1-7
688	0.096	0.0060	<17	SABK1-8
Background 12 km	0.33	0.0045	<17	SABK1-9
Ash	0.060	0.012*	177	SABK1-Bottom ash
Ingredient	0.060	0.0076*	< 59	SABK1- duff
Brick	0.055	0.0070	<17	SABK1- brick

**Notes:**  
*top 0-5 cm sampled*  
 \* Co planar PCBs

Results validated in Oct .2011, middle bound

The concentrations of PCDD/PCDF in soil taken around the kiln were low but detectable at levels less than 1 ng WHO<sub>2005</sub>-TEQ/kg. They did not exceed the background level in the soil taken at a distance of 12 km, while PCB and HCB were slightly higher in the samples taken in the vicinity. However, dl-PCBs and HCB were close to the LOD in most samples except of HCB at a distance of 136 m from the kiln, where the maximum of 200 ng/kg was detected.

In ashes and raw brick ingredients no PCDD/PCDF were detected, the resulting middle bound concentrations were below 0.1 WHO<sub>2005</sub>-TEQ/g. DI-PCBs were not detected, and HCB was found only in the bottom ash at 177 ng/kg.



In the brick sample only OCDD was detected, the resulting middle bound concentrations were below 0.1 ng WHO<sub>2005</sub>-TEQ/kg.

Due to the very low concentrations in soil, concentration differences along the transect SABK1-1 → SABK1-4 (Figure 40) are not interpretable.

#### 4.2.2 SABK2

Table 38 provides the individual concentrations data from the soils in the vicinity of the industrial scale kiln SABK2 in comparison to the background soils together with the concentrations in bottom ash and bricks.

Table 38: Results for SABK2, coal fired industrial scale site-				
Distance from kiln	PCDD/PCDF	dl-PCB	HCB	Field code
<i>m</i>	<i>ng WHO<sub>05</sub>-TEQ/kg</i>		<i>ng/kg</i>	
15	0.35	0.048	160	SABK2-1
100	0.41	0.086	280	SABK2- 2
200	0.69	0.054	70	SABK2- 3
300	0.49	0.072	91	SABK2- 4
430	0.50	0.13	140	SABK2- 5
Background 23 km	0.11	0.0015	660	SABK2-Soil Reference
Ash	1.16	< 0.019*	75	SABK2- Bottom ash
Brick	0.036	0.0072	18	SABK2-brick
Ingredient	4.7	1.0*	1000	SABK2- paper pulp
Ingredient	0.45	0.52*	107	SABK2 duff

**Notes:**  
*0-5cm sampled*  
*\*Coplanar PCBs*

Results validated in Oct .2011, middle bound

The situation around the site SABK2 is similar to SABK1, with slightly higher overall concentrations for PCDD/PCDF and dl-PCBs.

PCDD/PCDF were detected in all soils, but remained below 1 ng WHO<sub>2005</sub>-TEQ/kg and did not display a gradient along the SABK2-2 → SABK2-5 transect (Figure 48)

HCB was detected around the kiln as well, but in this case the HCB concentration at the background site was higher

PCDD/PCDF and dl-PCBs and HCB were elevated in the paper pulp used as a raw brick ingredient, and could be detected also in the “duff” ingredient (fine coal).

Also the bottom ash contained detectable amounts of PCDD/PCDF of around 1 ng WHO<sub>2005</sub>-TEQ/kg and traces of HCB.

### 4.2.3 Dididi

Table 39 provides the individual concentrations data from the soils in the vicinity of the informal kiln Dididi in comparison to the background soil, together with the concentrations in bottom ash and a brick sample.

<i>Table 39: Results for Dididi, wood fired informal site</i>				
Distance from kiln	PCDD/PCDF	dl-PCB	HCB	Field code
<i>m</i>	<i>ng WHO<sub>05</sub>-TEQ/kg</i>		<i>ng/kg</i>	
10	0.064	0.0088	19	Dididi soil 1A
10	0.10	0.0060	<17	Dididi soil 2A
10	0.090	0.0034	<17	Dididi soil 3A
10	0.046	0.0038	<17	Dididi soil 4A
Background 6 km	0.060	0.14	<17	Dididi reference soil (439)
Ash	0.059	0.0070	18	Dididi ash (438)
Ash	0.012	0.0062	20	Dididi ash (435)
Brick	0.06	0.053	<17	Dididi basic brick
<b>Notes:</b> <i>0-5 cm sampled</i>				
Results validated in Oct .2011, middle bound				

In the soils around the informal brickmaking site in Dididi no dl-PCBs or HCB were detected.

PCDD/PCDF could be detected near the LODs of the individual congeners at middle bound concentrations around or below 0.1 ng WHO<sub>2005</sub>-TEQ/kg.

The brick sample was negative except for some traces of OCDD, and few PCDD/PCDF congeners were seen in the bottom ash with middle-bound concentration levels not exceeding 0.1 ng WHO<sub>2005</sub>-TEQ/kg

### 4.2.4 Summary South Africa

Table 40 provides data on agglomerated concentrations in the soil in the vicinity of the kilns compared to the background soils.

The concentrations of all compounds (often close to or at the limit of detection) were basically at the level of the background soils; even higher concentrations could be observed in the background for HCBs and dl-PCBs. So far, no significant impact on the nearby environments of the brick production sites in South Africa has been observed.

<i>Table 40: South Africa - Summary soils</i>			
	<b>PCDD/PCDF</b>	<b>dl-PCB</b>	<b>HCB</b>
	<i>ng WHO<sub>05</sub>-TEQ/kg</i>		<i>ng/kg</i>
All soils around the kilns (n= 21)			
Average	0.19	0.033	63
Median	0.10	0.032	19
STD Dev.	0.19	0.025	81
Min.	0.046	0.0034	17
Max.	0.69	0.086	280
Background soils (n=3)			
Average	0.17	0.053	231
Median	0.11	0.015	17
STD Dev.	0.14	0.075	371
Min.	0.060	0.0045	17
Max.	0.33	0.14	660
<b>Notes:</b>			
Results validated in Oct .2011, middle bound			

*Table 41* compares the soil contamination around the coal-fired industrial scale kilns and the virgin-wood-fired informal kiln.

The topsoil concentrations of all compounds were slightly lower at the informal production site. However, the sampling distances from the source were different and the productivity differences between these two types of kiln are so great that no general conclusion on differences between the overall environmental impacts of the two technologies are indicated.

In *Table 42*, the South African results for bottom ash and bricks are summarised.

The average bottom-ash levels were on average close to the levels seen in Mexico (see *Table 36*), when excluding the Abasolo outlier. In the bottom ash, a slight tendency of towards higher concentrations of all compounds was observed in the (few!) ash samples taken from the industrial-scale kilns.

Also, the average concentration levels of PCDD/PCDF and PCBs in bricks were comparable to the situation in Mexico when the Abasolo outliers were excluded from the average. HCB levels appear to be lower in South Africa, but this is mainly due to differences in the limits of detection and the display of middle-bound concentrations.



<b>Table 41: South Africa – Industrial kilns versus informal kilns</b>			
	<b>PCDD/PCDF</b>	<b>dl-PCB</b>	<b>HCB</b>
	<i>ng WHO<sub>05</sub>-TEQ/kg</i>		<i>ng/kg</i>
Soils around industrial kilns SABK1 and SABK2 (n=17)			
Average	0.23	0.043	79
Median	0.14	0.040	29
STD Dev.	0.20	0.022	88
Min.	0.051	0.0060	17
Max.	0.69	0.086	280
Soils around the informal kiln in Dididi (n=4)			
Average	0.075	0.0055	18
Median	0.077	0.0049	17
STD Dev.	0.025	0.0025	1.0
Min.	0.046	0.0034	17
Max.	0.10	0.0088	19
<b>Notes:</b>			
Results validated in Oct .2011, middle bound			

<b>Table 42: South Africa – Summary of bottom ash and bricks</b>			
	<b>PCDD/PCDF</b>	<b>dl-PCB</b>	<b>HCB</b>
	<i>ng WHO<sub>05</sub>-TEQ/kg</i>		<i>ng/kg</i>
All bottom ash (n= 4)			
Average	0.32	0.011	73
Median	0.060	0.010	48
STD Dev.	0.56	0.0059	75
Min.	0.012	0.0062	18
Max.	1.2	0.019	177
All bricks (n=3)			
Average	0.050	0.022	17
Median	0.053	0.0072	17
STD Dev.	0.013	0.027	0.58

Min.	0.036	0.0070	17
Max.	0.060	0.053	18
<b>Notes:</b>			
Results validated in Oct .2011, middle bound			

**Toolkit-relevant Note 4**

The similarity of concentrations in ash and bricks with the Mexican sites, together with the overall lower concentrations in soil, support the assumption that the emission factors obtained in the Mexican kilns can be applied as an upper-bound estimate for brickmaking in South Africa.

It is notable that only marginal differences were observed in the emission factors of the informal kilns and of those operated at an industrial scale.

## 4.3 Kenya

### 4.3.1 KEBK1, KEBK2, KEBK3 and background KEBG

Table 43 provides the individual concentrations data in the soil in the vicinity of the kilns in comparison to the background soils and the concentration data in bottom ash from the area where the informal kilns KEBK1, KEBK2, KEBK3 are situated.

Table 43: Results KEBK1 KEBK2 and KEBK3, wood-fired informal sites				
Distance	PCDD/PCDF	dI-PCB	HCB	Field code
<i>m</i>	<i>ng WHO<sub>05</sub>-TEQ/kg</i>		<i>ng/kg</i>	
KEBK1(Site A)				
Circular 10 m	0.15	0.63	20	Site A 20 m from road
Circular 10 m	0.064	0.0023	<17	Site A near road
Ash	0.075	0.0028	40	Ash from Kiln A
Ash	0.0088	0.0020	<17	2 <sup>nd</sup> Ash from Kiln B
Ash	0.16	0.0026	78	Ash from Kiln B2
KEBK2 (Site B)				
Circular 10 m	0.13	0.0060	20	Site B 20 m from the road
Circular 10 m	0.19	0.0033	21	Site B near the road
Ash	0.13	0.0038	<17	Site B Ash
KEBK3 (Site C)				
Circular 10 m	0.23	0.063	20	Site C Soil
Ash	0.14	0.0051	27	Site C Ash
KEBG1 (background soil)				
Background 1.6 km	0.24	0.0047	<17	Background Soil 1
<b>Notes:</b> <i>0-30 cm sampled</i>				
Validated in Oct .2011, middle bound				

The concentrations of all compounds were comparable to those of the informal kiln in South Africa, often close or below the detection limits.



### 4.3.2 KEBK4, KEBK5, KEBK6 and background KEBG2, KEBG3

Table 44 provides data on individual concentrations in the soil in the vicinity of the kilns in comparison to the background soils and the concentration data in bottom ash from the area where the informal kilns KEBK4, KEBK5, KEBK6 are situated.

Table 44: Results for KEBK4, KEBK5, KEBK6, wood-fired informal sites				
distance	PCDD/PCDF	dl-PCB	HCB	Field code
<i>m</i>	<i>ng WHO<sub>05</sub> -TEQ/kg</i>		<i>ng/kg</i>	
KEBK4 (Site D)				
Circular 10 m	0.10	0.0068	20	Site D soil
Ash	0.12	0.0030	100	Site D Ash
KEBK5 (Site E)				
Circular 1 m	0.076	0.0040	21	Site E soil
Ash	0.24	0.0044	34	Site E Ash
KEBK6 (Site F)				
10 m circular	0.21	0.0058	21	Site F soil
Ash	0.15	0.0037	30	Site F Ash
Background soils				
Background 2 km	0.14	0.0070	<17	Background Soil 2
Background 2 km	0.17	0.0040	<17	Background Soil 3
<b>Notes:</b>				
<i>0-30 cm sampled</i>				
Results validated in Oct .2011, middle bound				

As was the case for the sites KEBK1, KEBK2, KEBK3, concentrations of all compounds were close to or at the detection limit both for soil and bottom ash.

### 4.3.3 Summary Kenya

Table 45 provides data on agglomerated concentrations in the soil in the vicinity of all kilns compared to the background soils.

Table 45: Kenya - Summary soils			
	PCDD/PCDF	dl-PCB	HCB
	<i>ng WHO<sub>05</sub> -TEQ/kg</i>		<i>ng/kg</i>
All soils around the kilns (n=8 circular field blends)			
Average	0.14	0.11	20

Median	0.14	0.060	20
STD Dev.	0.062	0.21	1.3
Min.	0.064	0.0040	17
Max.	0.23	0.63	21
Background soils (n = 3)			
Average	0.18	0.031	17
Median	0.17	0.040	17
STD Dev.	0.051	0.021	0
Min.	0.14	0.0070	17
Max.	0.24	0.047	17
<b>Notes:</b>			
Results validated in Oct .2011, middle bound			

Similar to South Africa, the concentrations in the soils around the production sites are almost identical to those of the background sites, which indicates that the brickmaking had no impact on the POP concentrations in the soil environments.

Given the analytical uncertainties for analyses close to the detection limit, the average PCDD/PCDF and PCB concentrations in soil can be considered as being similar to those from South Africa. HCB concentrations in Kenya are similar to the informal brickmaking site in Dididi in South Africa, but about five times lower than those of the industrial brickmaking sites there.

Table 46 provides data on agglomerated concentrations in bottom ash from all Kenyan kilns.

<i>Table 46: Kenya - Summary bottom ash</i>			
	PCDD/PCDF	dl-PCB	HCB
	<i>ng WHO<sub>05</sub>-TEQ/kg</i>		<i>ng/kg</i>
All bottom ash (n = 8)			
Average	0.13	0.0034	43
Median	0.14	0.0034	32
STD Dev.	0.067	0.0010	30
Min.	0.0088	0.0020	17
Max.	0.24	0.0051	100
<b>Notes:</b>			
Results validated in Oct .2011, middle bound			

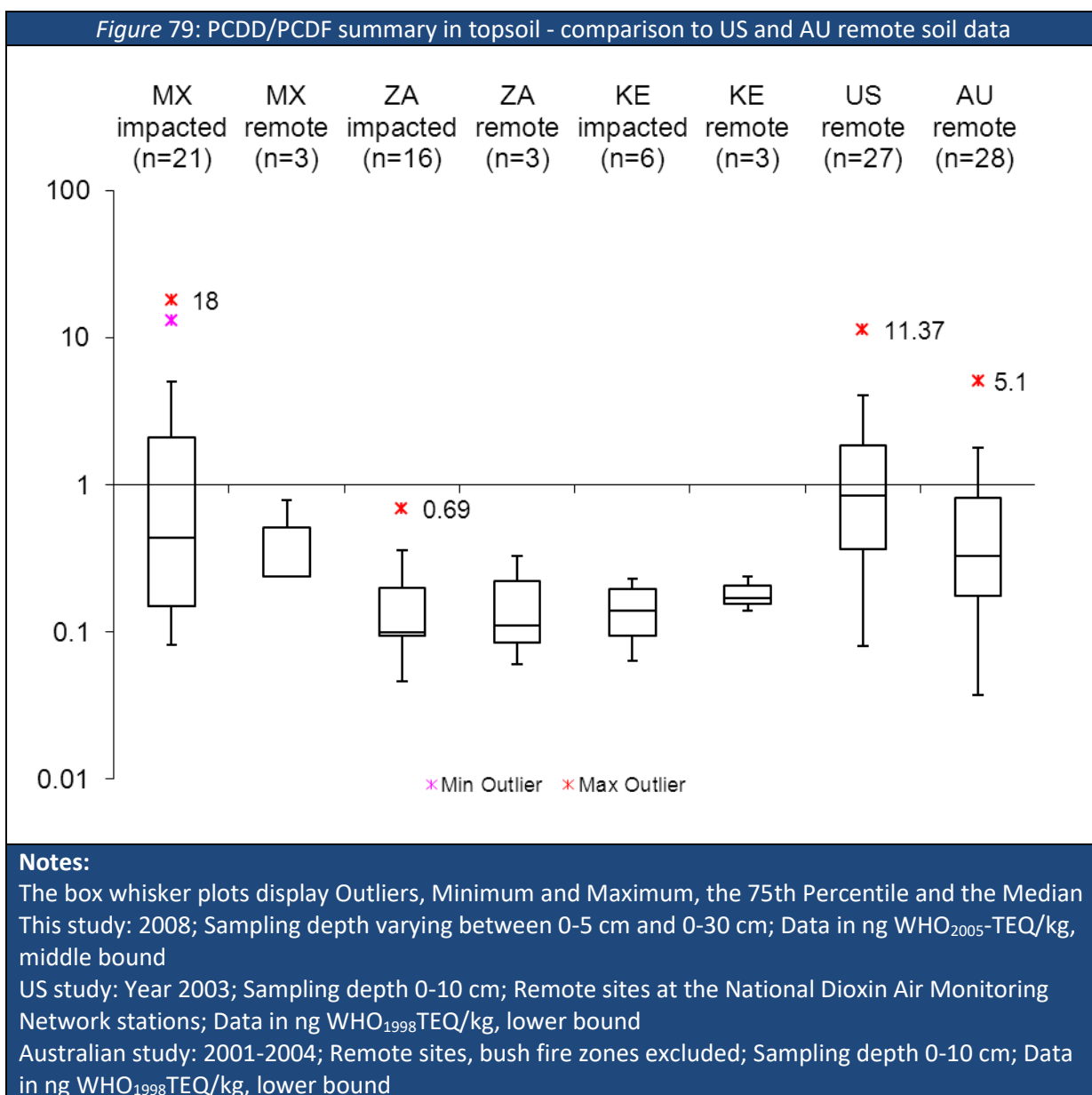
Given the analytical uncertainties in analyses close to the detection limit, the average concentrations in ash can be considered as being similar to those from South Africa and Mexico, if the Abasolo site (the only outlier) is excluded.

### Toolkit-relevant Note 5

The similarity of concentrations to those in the Mexican ash, together with the overall lower concentrations in Kenyan soil, supports the assumption that the emission factors obtained in the Mexican kilns can be applied as an upper-bound estimate for brickmaking in Kenya.

## 4.4 Soil summary and comparison with US and Australian soil surveys

Figure 79 presents an overview of the PCDD/PCDF concentration ranges of all soils analysed in this study, compared with the levels in remote soils from the US (USEPA, 2007) and Australia (Mueller et al., 2004).





The PCBs, which were often near or below the LOD, were generally a small fraction of the total TEQs in soil, and are not discussed further here.

### Background soils

The mean concentrations of the PCDD/PCDF in the background soils of this study were 0.17 ng WHO<sub>2005</sub>-TEQ/kg in South Africa (*ZA remote*), 0.18 ng WHO<sub>2005</sub>-TEQ/kg in Kenya (*KE remote*) and 0.42 ng WHO<sub>2005</sub>-TEQ/kg in Mexico (*MX remote*), with a maximum of 0.78 ng WHO<sub>2005</sub>-TEQ/kg in Mexico.

These concentrations, even though calculated at the middle bound, are around one order of magnitude lower compared to rural/remote soils from taken from all over the US in the vicinity of the National Dioxin Air Monitoring Network, which displayed mean values of 1.7 ng WHO<sub>2005</sub>-TEQ/kg and a maximum of 11 ng WHO<sub>2005</sub>-TEQ/kg at the lower bound (USEPA, 2007).

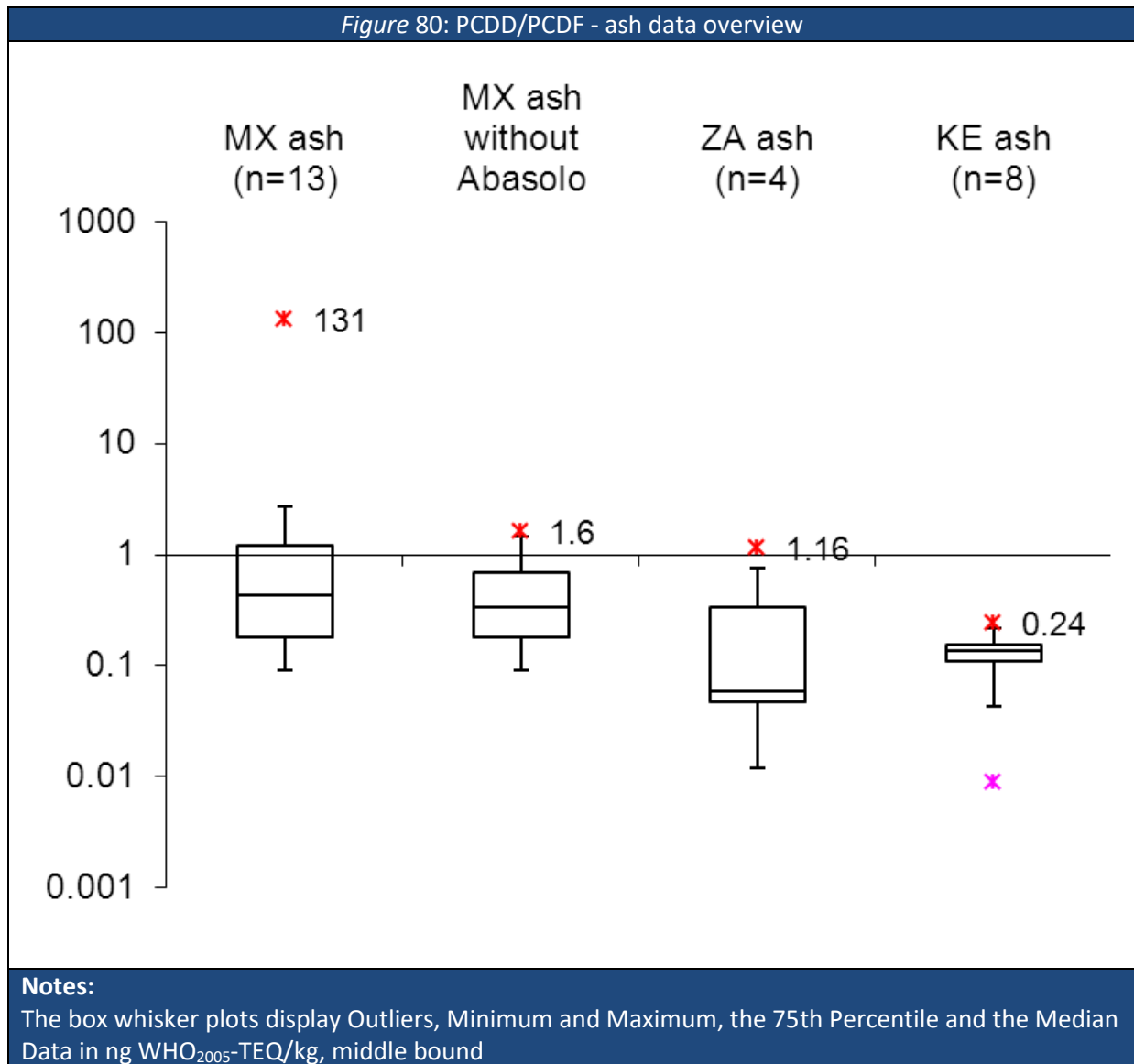
Compared to the situation in Australia, the background soil data from this study fit well into the category of remote soils, where the Australian mean was at 0.24 ng WHO<sub>2005</sub>-TEQ/kg, with maximum levels of around 1 ng WHO<sub>2005</sub>-TEQ/kg, lower bound (Mueller et al., 2004).

### Impacted soils near the brick kilns

While the PCDD/PCDF concentrations in the impacted soils from South Africa (*ZA impacted*) and Kenya (*KE impacted*) were in the same range as the background soils, the Mexican brickmaking sites (*MX impacted*) displayed higher levels. However, as demonstrated by the comparison in *Figure 79* PCDD/PCDF in most of the impacted soils around the Mexican brickmaking sites were still in the range of remote soils in the US.

## 4.5 Bottom ash and brick summary

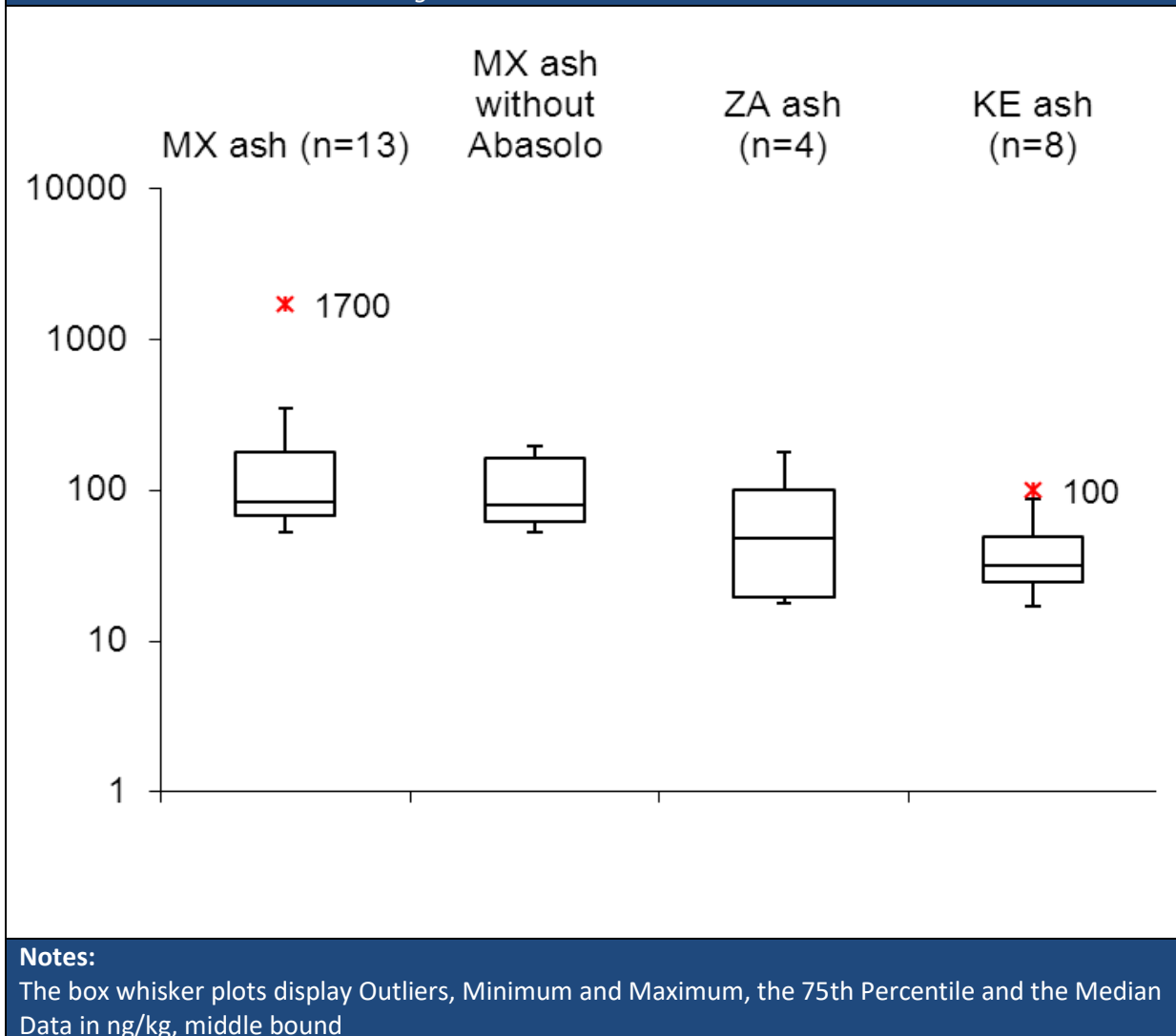
Figure 80 presents an overview of PCDD/PCDF in the bottom ash from Mexico, South Africa and Kenya.



PCDD/PCDFs in the bottom ash from Mexico were mostly below 1 ng WHO<sub>2005</sub>-TEQ/kg, with one outlier (in Abasolo) displaying 131 ng WHO<sub>2005</sub> TEQ/kg. Levels in South Africa and Kenya were generally below 1ng WHO<sub>2005</sub>-TEQ/kg.

Figure 81 presents an overview of HCB in the bottom ashes from Mexico, South Africa and Kenya.

Figure 81: HCB - ash data overview



The situation for HCB displays a similar picture as for PCDD/PCDF. HCB in the bottom ash from Mexico were generally in the range of a few hundred ng/kg, except for one outlier in Abasolo which displayed 1,700 ng/kg. Concentrations in South Africa and Kenya were generally lower, at around or below 100 ng/kg.

Figure 82 presents an overview of PCDD/PCDFs in the brick samples from Mexico and South Africa. No brick samples were available from Kenya.

The range of PCDD/PCDF in the brick samples from Mexico (*MX bricks*) is dominated by the four samples from Abasolo (4 of 7 in total) that displayed concentrations in the range of 10 ng WHO<sub>2005</sub>-TEQ/kg.

If the Abasolo bricks are excluded (*MX bricks without Abasolo*), the concentrations are around 0.1 ng WHO<sub>2005</sub>-TEQ/kg, only slightly higher than the concentrations observed in South Africa.



Figure 82: PCDD/PCDF - brick data overview

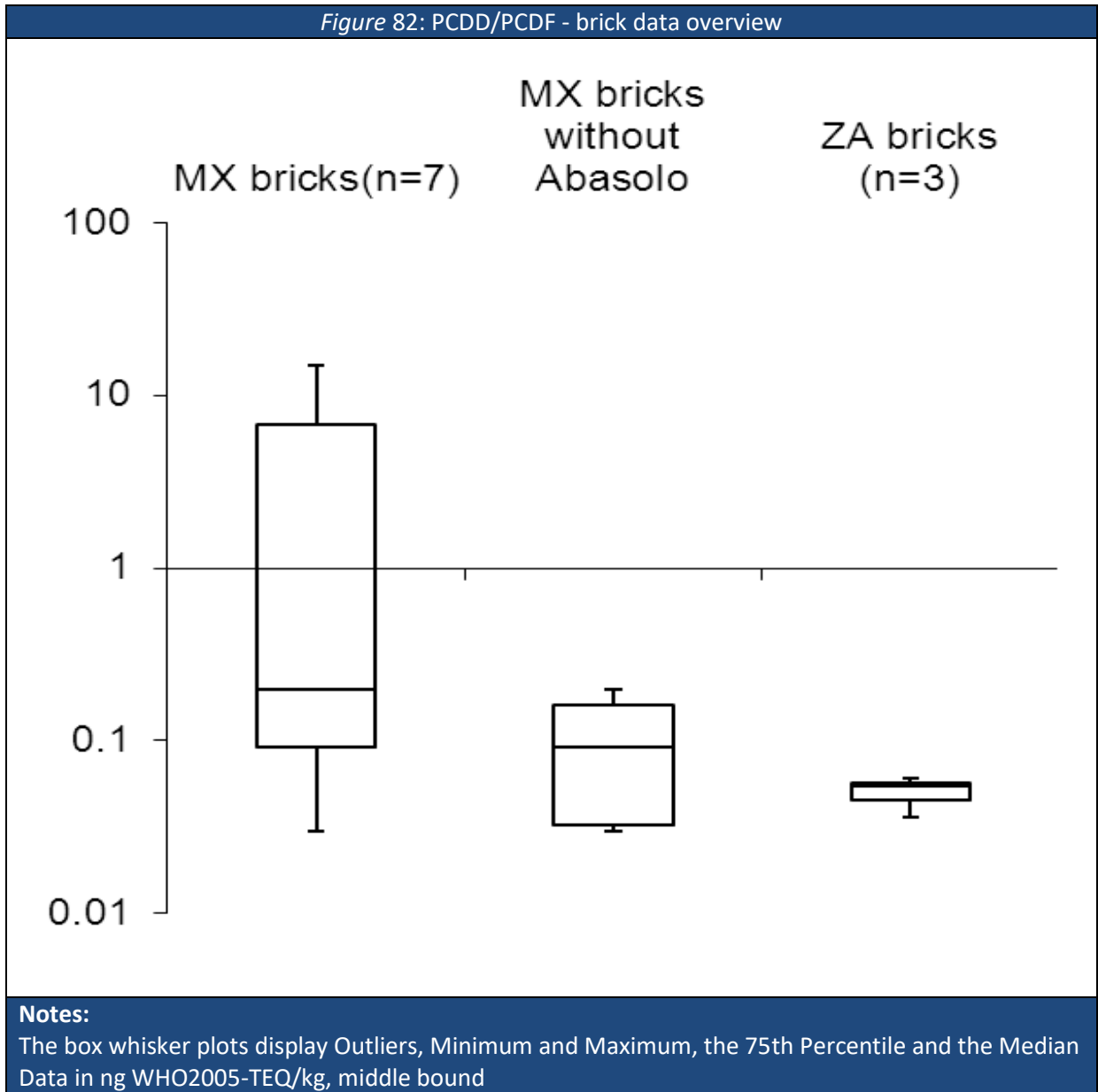
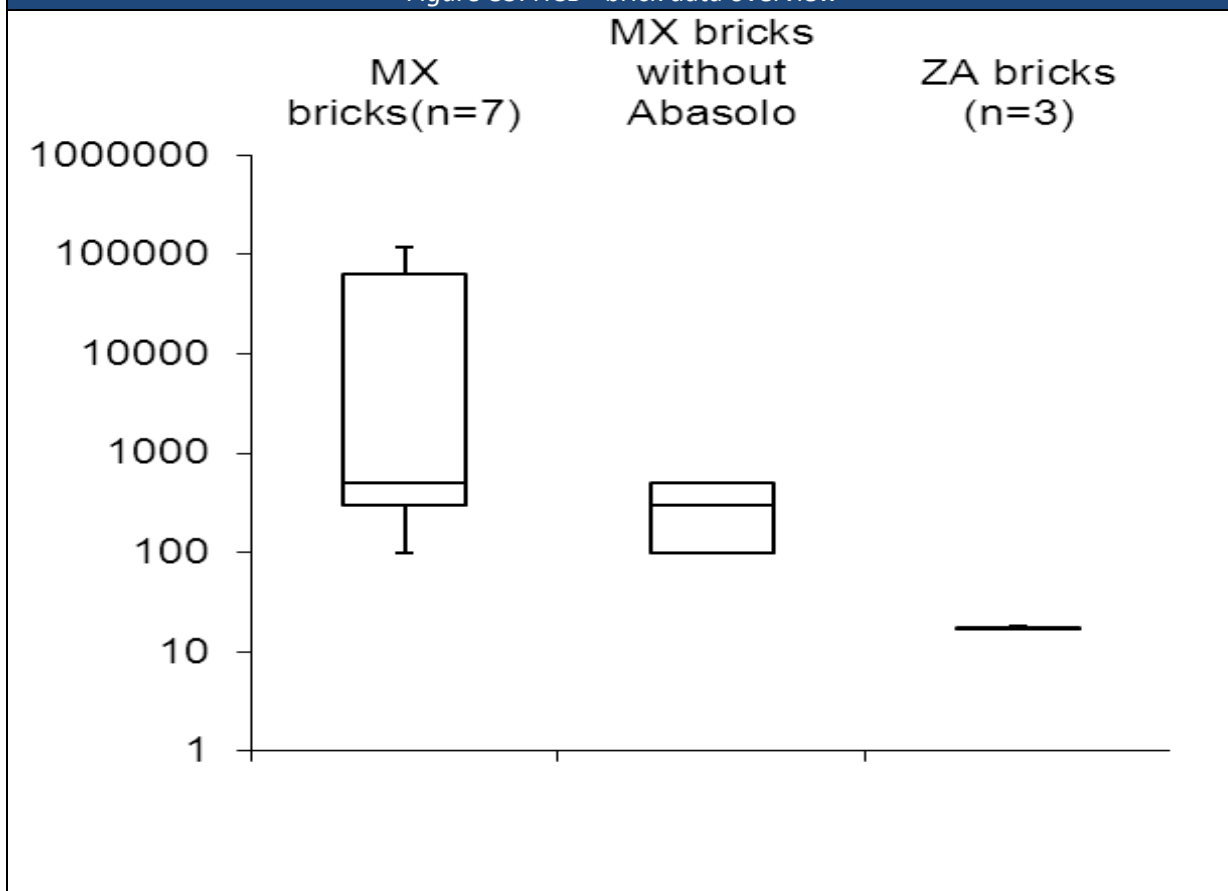


Figure 83 presents an overview of HCB in the brick samples from Mexico and South Africa. No brick samples were available from Kenya.

Figure 83: HCB - brick data overview



**Notes:**

In the case of HCB, the differences between MX without Abasolo and ZA are due to differences in the LOD of the two laboratories involved. Basically, all samples were at or below the LOD. The box whisker plots display Outliers, Minimum and Maximum, the 75th Percentile and the Median Data in ng/kg, middle bound

HCB in bricks display a geographical distribution, as seen for PCDD/PCDF.

**Toolkit-relevant Note 6**

During the emission measurements in Guanajuato, the Emission Factors for HCB were approximately three orders of magnitude higher than for PCDD/PCDF (Note; PCDD/PCDF TEQ versus absolute HCB concentration) (Table 27; Table 28).

A comparable concentration ratio between PCDD/PCDF and HCB was observed in the Mexican bottom ash, supporting the assumption that the POP concentrations in bottom ash and bricks are indicative of the emissions to air.

## 5. Conclusions

The concentrations of unintentionally produced POPs in the soils around the investigated sites in Mexico, Kenya and South Africa were low in comparison to the US and Australia. This observation suggests that emissions of persistent pollutants from brickmaking in developing countries are a minor threat to the environment and health, even when waste-derived fuels are used.

In addition, the contamination of bricks and bottom ash were generally marginal. The stringent German standards for pasture lands were only sporadically exceeded for PCDD/PCDFs, PCBs and HCBs in soils near some Mexican brick kilns, suggesting that all other types of agricultural and urban land use can be considered safe.

The soil transects taken in the vicinity of the investigated kilns in Mexico generally did not result in the clear spatial concentration gradients that could be expected for undisturbed soils under the impact of a point source. This may be due to the high level of urbanisation around the Mexican kilns, resulting in disturbed soils and emissions from other urban and small-scale industrial activities. Since soils “conserve” persistent pollutants for a long time, historical emissions may also play a role.

So far, the concept of assessing the emission source strength of these kilns indirectly through the adjacent contamination gradients in nearby soils, partially failed. Nevertheless, the soil concentration data in urban and remote soils recorded in this study are useful for generating a global view of the environmental impact of brickmaking, and to supplement the fragmentary database on soil contamination in developing countries.

Regarding the initial question with respect to the Toolkit (i.e. whether or not brick production in other developing countries is sufficiently described by the few emission factors to air that were experimentally determined in Salamanca and León), the following observation can be made:

- PCDD/PCDF in bottom ash and bricks from the Mexican sites, except in Abasolo, were rather uniformly distributed among the investigated kilns. WHO<sub>2005</sub>-TEQs were typically about 1 ng/kg, including those from the sites in León and Salamanca, where the air emission factors had previously been determined. So far – presuming that PCDD/PCDF contents of bottom ash and bricks are indicative of emissions to air – the range of emission factors obtained in León and Salamanca appears to be applicable to all investigated sites in Mexico, except for a single outlier in Abasolo.
- South Africa and Kenya displayed similar, though somewhat lower, concentration levels in ash and bricks. This, together with the overall lower levels in the soils in these countries, supports the assumption that the air emission factors obtained from the two Mexican kilns can be applied in South Africa and Kenya as an upper bound estimate of emissions from brickmaking in developing countries and countries in transition.



## 6. Outlook

The reason for the outliers in bricks and bottom ash from Abasolo remains unclear; it would be desirable to conduct emission measurements there. Although the concentrations in bricks and ash from Abasolo do not suggest acute risks for the environment and human health, the reproducibility of high PCDD/PCDF concentrations in the bricks are especially crucial to the emission inventories, since the mass flux of bricks is high compared to those of ash and the combustion gases. This outlier, most probably due to a contamination of brick ingredients, has so far been excluded from the current Toolkit revision. However, considering the small database and geographical coverage of this study, it would be desirable to analyse more bricks and ash from other regions and production technologies, in order to confirm and refine the available emission factors for brickmaking in developing countries. The brickmaking sector, due to its high activity rates, and the fact that secondary fuels often replace traditional fuels, can play a key role in the emission inventories of emerging economies with respect to their increasing demand for building materials.

The objective of the study was not to determine whether co-firing wastes in brick kilns is an adequate waste management method. However, the levels of PCDD/PCDF in soils, ash and bricks observed around the brick kilns using certain waste-derived fuels were low.

This, together with the comparably low PCDD/PCDF emissions to air observed by Maiz et al. (2010) and Garcia-Ubaque et al. (2010) from brick kilns, seem to suggest that co-firing of the waste-derived fuels investigated in this study is not a significant source of PCDD/PCDFs and other unintentional POPs.

By contrast, open burning of municipal solid waste is among the most significant sources of polychlorinated PCDD/PCDFs, as documented in many national inventories prepared pursuant to the Stockholm Convention, in particular for developing countries (Zhang et al., 2011).

The option of co-firing waste in existing structures of the local brick and cement industries of developing countries deserves more scientific attention. Besides investigating a broader range of technologies and fuels, a more extended risk assessment should also consider other pollutants such as black carbon, polyaromatic hydrocarbons, volatile organic compounds, heavy metals (including mercury), particulate matter, etc.

## 7 Acknowledgement

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## A Annex

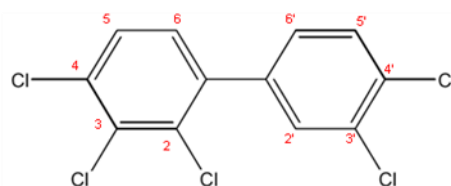
### A.1 Definitions

**Congeners** are related chemicals being part of a family of chemicals. Example: There are 209 congeners of polychlorinated biphenyls (PCB) as well as 135 congeners of polychlorinated dibenzo – p- dioxins and dibenzofurans (PCDD/PCDF)

**Homologues** are a group of compounds with the same chemical formula but (in the case of PCB and PCDD/PCDF) chlorine substitution at different positions. Example: All tetrachlorodibenzo–p-dioxins (TCDDs) are a homologue group within the polychlorinated dibenzo – p- dioxins.

**Isomer** is a single compound out of a homologue group. Example: There are 22 isomers of tertachloro dibenzo-p-dioxin.

**Polychlorinated biphenyls (PCB)** are a class of 209 organic compounds with 1 to 10 chlorine atoms attached to biphenyl, which is a molecule composed of two benzene rings. The chemical formula for PCB is  $C_{12}H_{10-x}Cl_x$ , where  $x = 1-10$ .



2,3,3',4'-TeCB

If the positions 2,2',6 and 6' remain without substitution, the molecule can obtain a coplanar position and the related congeners are referred to as **dioxin-like PCB**.

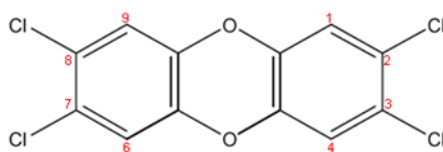
The PCB assume a dioxin-like structure and effect when chlorines occupy

- (a) no more than one of the ortho positions
- (b) Both para positions
- (c) At least two meta positions
- (d) The structure is not hindered from assuming the preferred coplanar configuration

The 14 PCB congeners that display dioxin-like effects are called **dioxin-like PCB**

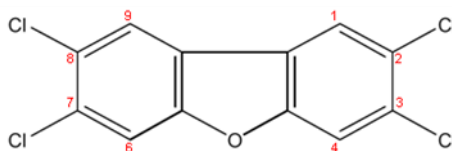
**Polychlorinated dibenzodioxins (PCDD)**, or simply **dioxins**, are a group of polyhalogenated compounds which are significant because they act as environmental pollutants. They are commonly referred to as dioxins for simplicity in scientific publications because every PCDD molecule contains a dioxin skeletal structure. Typically, the *p*-dioxin skeleton is at the core of a PCDD molecule, giving the molecule a dibenzo-*p*-dioxin ring system. Members of the PCDD family have been shown to bio accumulate in humans and

wildlife due to their lipophilic properties, and are known teratogens, mutagens, and suspected human carcinogens.



2,3,7,8-TCDD

**Polychlorinated dibenzofurans (PCDF)** are a group of halogenated organic compounds which are toxic environmental pollutants. They are known teratogens, mutagens, and suspected human carcinogens. PCDF tend to co-occur with polychlorinated dibenzodioxins (PCDD).



2,3,7,8-TCDF

### Toxic equivalent (TEQ)

The TEQ concept has been developed to facilitate risk assessment and regulatory control.

**Toxic equivalent factor (TEQ)** expresses the toxicity of a mixture of dioxins, furans and PCB in terms of the most toxic form of dioxin, 2,3,7,8-TCDD. The toxicity of the individual congeners may vary by orders of magnitude.

The TEQ is calculated based on the Toxic equivalent factors (TEFs) developed for selected congeners of dioxins, furans and PCB. The reference congener is the most toxic dioxin 2,3,7,8-TCDD which per definition has a TEF of one.

Since the toxicity evaluation has slightly changed in the last decades, different TEQs are reported in the literature. The most commonly used are the following:

I-TEQ<sub>DF</sub> (=) Mass of PCDD/PCDF in Toxic Equivalents with respect to 2,3,7,8-TCDD using the International Toxic Equivalent Factors (I-TEFs or NATO-TEFs released by the North Atlantic Treaty Organization (NATO) in 1989.

WHO<sub>98</sub>-TEQ<sub>DFP</sub> (=) Mass of PCDD/PCDF and PCB in Toxic Equivalents with respect to 2,3,7,8-TCDD using the Toxic Equivalent Factors released by the World Health Organisation in 1998.

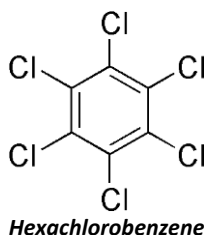
WHO<sub>05</sub>-TEQ<sub>DFP</sub> (=) Mass of PCDD/PCDF and PCB in Toxic Equivalents with respect to 2,3,7,8-TCDD using the Toxic Equivalent Factors revised by the World Health Organisation in 2005.

*Table A1* gives an overview on the commonly used **Toxic Equivalent Factors** released by the different organisations.

<b>Table A1: Toxicity Equivalency Factors (TEFs) of PCDD/Fs and dioxin-like PCBs</b>						
<b>Compound</b>	<b>USEPA 1987</b>	<b>NATO 1989</b>	<b>WHO 1994</b>	<b>WHO 1998</b>	<b>WHO 2005</b>	
<b>Dibenzoparadioxins with chlorine substitution in positions 2,3,7,8</b>						
2,3,7,8-TCDD	1	<b>1</b>	ND	<b>1</b>	1	
1,2,3,7,8-PeCDD	0,5	<b>0,5</b>	ND	<b>1</b>	1	
1,2,3,4,7,8-HxCDD	0,04	<b>0,1</b>	ND	<b>0,1</b>	0,1	
1,2,3,6,7,8-HxCDD	0,04	<b>0,1</b>	ND	<b>0,1</b>	0,1	
1,2,3,7,8,9-HxCDD	0,04	<b>0,1</b>	ND	<b>0,1</b>	0,1	
1,2,3,4,6,7,8-HpCDD	0,001	<b>0,01</b>	ND	<b>0,01</b>	0,01	
1,2,3,4,6,7,8,9-OCDD	0	<b>0,001</b>	ND	<b>0,000 1</b>	0,000 3	
<b>Dibenzofurans with chlorine substitution in positions 2,3,7,8</b>						
2,3,7,8-TCDF	0,1	<b>0,1</b>	ND	<b>0,1</b>	0,1	
1,2,3,7,8-PeCDF	0,1	<b>0,05</b>	ND	<b>0,05</b>	0,03	
2,3,4,7,8-PeCDF	0,1	<b>0,5</b>	ND	<b>0,5</b>	0,3	
1,2,3,4,7,8-HxCDF	0,01	<b>0,1</b>	ND	<b>0,1</b>	0,1	
1,2,3,6,7,8-HxCDF	0,01	<b>0,1</b>	ND	<b>0,1</b>	0,1	
1,2,3,7,8,9-HxCDF	0,01	<b>0,1</b>	ND	<b>0,1</b>	0,1	
2,3,4,6,7,8-HxCDF	0,01	<b>0,1</b>	ND	<b>0,1</b>	0,1	
1,2,3,4,6,7,8-HpCDF	0,001	<b>0,01</b>	ND	<b>0,01</b>	0,01	
1,2,3,4,7,8,9-HpCDF	0,001	<b>0,01</b>	ND	<b>0,01</b>	0,01	
OCDF	0	<b>0,001</b>	ND	<b>0,000 1</b>	0,000 3	
<b>Dioxin-like Polychlorinated Biphenyls</b>						
<b>No. IUPAC</b>	<b>PCBs non-orto substituted</b>					
77	3,3',4,4'-TCB	ND	ND	0,000 5	<b>0,000 1</b>	0,000 1
81	3,4,4',5-TCB	ND	ND	ND	<b>0,000 1</b>	0,000 3
126	3,3',4,4',5-PeCB	ND	ND	0,1	<b>0,1</b>	0,1
169	3,3',4,4',5,5'-HxCB	ND	ND	0,01	<b>0,01</b>	0,03
	<b>PCBs mono-orto substituted</b>	ND	ND			
105	2,3,3',4,4'-PeCB	ND	ND	0,000 1	<b>0,000 1</b>	0,000 03
114	2,3,4,4',5-PeCB	ND	ND	0,000 5	<b>0,000 5</b>	0,000 03
118	2,3',4,4',5-PeCB	ND	ND	0,000 1	<b>0,000 1</b>	0,000 03
123	2',3,4,4',5-PeCB	ND	ND	0,000 1	<b>0,000 1</b>	0,000 03
156	2,3,3',4,4',5-HxCB	ND	ND	0,000 5	<b>0,000 5</b>	0,000 03
157	2,3,3',4,4',5'-HxCB	ND	ND	0,000 5	<b>0,000 5</b>	0,000 03
167	2,3',4,4',5,5'-HxCB	ND	ND	0,000 01	<b>0,000 01</b>	0,000 03
170	2,2',3,3',4,4',5-HpCB	ND	ND	0,000 1	ND	ND
180	2,2',3,4,4',5,5'-HpCB	ND	ND	0,000 01	ND	ND
189	2,3,3',4,4',5,5'-HpCB	ND	ND	0,000 1	<b>0,000 1</b>	0,000 03
<b>Nomenclature:</b>						
ND (=) No data. The TEF is set to zero						
TCDD/F/B (=) Tetrachlorodibenzo-p-dioxin / Tetrachlorodibenzofuran / Tetrachlorobiphenyl						



**Hexachlorobenzene (HCB)**, or **perchlorobenzene**, is a chlorocarbon with the molecular formula  $C_6Cl_6$ . It is a fungicide formerly used as a seed treatment, especially on wheat to control the fungal disease bunt.



Its production and use has been banned globally under the Stockholm Convention on persistent organic pollutants. Since it is formed also as a byproduct of combustion, HCB is also listed in the category of unintentionally released POPs and therefore includes into the Standardized Toolkit.

**Concentration** is the relation between the mass of a compound or a group of compounds with respect to a reference matrix (e.g. the volume of a gas or liquid or the mass of solids such as soil or ashes). In case of emissions to the atmosphere the common reference is the standard volume of gases emitted into the air.

**Emissions** is the mass of a compound or a group of compounds released per unit time

**Emission factor** is the mass of a compound or a group of compounds released per unit of any variable of the process. In this study the reference variable selected was the unit mass of bricks produced.

## **A.2 Field sampling guidelines employed in this study**

## Sampling Guidelines for the Brick Kiln Project

### Part 1: Environmental Monitoring: Kenya, Mexico, South Africa

#### 1 BACKGROUND

In decision SC 3/6 Parties agreed to an open and transparent process to update and further improve the “Standardized Toolkit for Identification and Quantification of Dioxin and Furan Releases”. The process is jointly implemented by the Secretariat of the Stockholm Convention (SSC) and UNEP Chemicals and supported by the Toolkit Expert Group consisting of national representatives from developing and developed country regions, industry and civil society as well as sectoral experts. The Expert Group meets annually.

The second meeting of the Toolkit Expert Group, held 2007 in Geneva, identified priority areas for updating and improving the Toolkit. The Group highlighted the need for screening PCDD/PCDF sources that so far are poorly characterized in the Toolkit. Among the priorities, *brick kilns in developing countries* were given highest priority, since they are typical for many developing countries and so far, no PCDD/PCDF data are available.

Since traditional emission sampling at brick kilns cannot be easily done, the Expert Group agreed that soil samples taken in the neighbourhood of typical brick kilns in developing countries would provide a useful first orientation as to the significance of these sources in developing countries.

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.

Although it is well understood that this study will not generate emission factors for direct use in the Toolkit; this project will be a valuable contribution to further characterize the sources of unintentional POPs in developing countries. However, the presence or absence of measurable concentrations in the close vicinity of potential sources cannot be more than first indicators for future studies of actual emission measurements.

It is proposed that soil samples be taken from locations close to typical brick kilns to study the impact from these kilns on neighboring soils and bottom ash to obtain a first indication as to the dioxin formation potential in the brick making process. Three developing countries, namely Kenya, South Africa, and Mexico will participate in this project.

The soil sampling will follow established protocols to make the results comparable with data from other studies. Soil samples will be taken from undisturbed soils and be taken in the vicinity of these brick kilns according to the four main wind directions and from more distant sites with no visible impact from other human activities (determination of baseline situation).

The samples will be collected by the developing country team, packaged, and sent to the JRC for analysis at an experienced dioxin laboratory.

*Draft: 16.11.2010*



## 2 MATERIALS AND METHODS

### 2.1 Guidelines for the Selection of the Kilns

Sampling sites should be characteristic of a "typical" developing country situation. It should be noted that soil samples reflect the input from long-time exposure; therefore, it should be attempted to **identify sites where relatively stable operational conditions have occurred during the last years**. This means, that the brick kilns should have operated under similar conditions, *e.g.*, predominantly traditional fuels used (preferentially the same) or if frequently contaminated fuel fractions have been used (such as waste oils, industrial waste) for the time period specified.

Each country shall provide photos and characteristics of the targeted kilns before obtaining approval to go ahead with the sampling at the pre-selected kilns.

Also different kinds of brick constituents should be reflected, since not only the fuels, but also the chemical composition (*e.g.*, the chlorine content) of the raw materials may have an impact on the emissions.

### 2.2 Guidelines for Sampling

#### 2.2.1 General Considerations

Representative soil samples at a comparable short distance from brick kilns shall be analysed and compared to background soils from the region.

Both the short distance and the background sampling sites should be selected where undisturbed soils are present in a way that no additional contamination with dioxin/POPs occurs.

Under these conditions the background sampling sites would reflect the baseline atmospheric deposition and the site in the vicinity of the kiln both, of the baseline atmospheric deposition plus the additional deposition arising from the brick processing.

If the kiln is a significant source of POPs emissions it should become visible by a clear concentration gradient between the samples taken nearby and the background sample.

If different types of kilns are sampled in a comparable way, differences in emission due to different processes/fuels should become visible.

The bottom ash samples are another indicator that may be useful to reflect differences in dioxin/POPs formation between different types of kilns and fuels.

#### **Representative soil samples, what does it mean?**

The concentration of POPs in the sample should reflect

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1. The atmospheric deposition from the kiln on a defined surface area, *i.e.*, amount of PCDD/PCDF or POPs per square meter, [PCDD/PCDF] m<sup>-2</sup> or [POP] m<sup>-2</sup>, respectively; and
2. The concentration in the soil sample, *i.e.*, mass of PCDD/PCDF or POPs per kilogram of dry matter soil, [PCDD/PCDF] kg<sup>-1</sup> or [POP] kg<sup>-1</sup>, respectively.

Factors impacting the concentration in the soil sample:

- The physics of the emission that determine the spatial dimension of the deposition (Thus the distance from the source where a sample is taken);
- The availability of undisturbed soil
  - The deposition of process residues may create wrong false positives.
  - Soil erosion or excavation may create bias in the results (wrong negatives);
- Other POPs sources may add to the deposition from the kiln;
- The depth of the sampling respectively the vertical distribution of the POPs in the soil column.

### 2.2.2 Criteria for the Selection of the Soil Sampling Sites

The soil sampling sites close to the kiln shall be selected in a way that

- They are not affected by emissions from products or processes other than atmospheric deposition and emission from the brick kiln under investigation.

The background soil sampling sites shall be selected in a way that

- They are not affected by other inputs such as dioxin-contaminated/POPs-contaminated products/residues (such as ashes) or dioxin-releasing processes.
- They reflect the baseline atmospheric deposition of the region where the kiln is situated.

In other words, river banks, excavation areas, areas of visible deposition of soil or similar should be excluded and not be sampled!

### 2.2.3 How to Take a Soil Sample

#### 2.2.3.1 *Orientation of the Samples*

If you can be sure that the soil sampling site is exclusively affected by the emission/deposition from the kiln, proceed as follows:

In an ideal situation, four soil sampling sites will be assigned according to the four main directions (N, E, S, W) at a distance of approximately 2-3 times of the stack height/exhaust gas exit height from the brick kiln (*Note: the directions and the distances are indicative only; they may need to be adjusted to local conditions. Priority is always on having an undisturbed soil*). The sample collection area should be free from visible inputs other than deposition from the brick kiln (in other words, areas with indications of disposal operation have to be excluded).

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In case that appropriate sites may not be available along the 4 main wind directions, a linear transect will be sampled. In such a case the sampling team shall identify **the closest possible sampling site with undisturbed soil**, preferably in the main wind direction, and take the 5 x 5m composite sample (Fig. 1) there.

The distance of the first sampling site to the emission source shall be “Dist<sub>init</sub>”.

In the following 4 more composite samples shall be taken along the same direction by always doubling the distance between the sampling sites.

The philosophy of this flexible approach regarding the absolute distances from the emission source is the following:

Big installations with an impact also on a longer distance will be surrounded by larger areas of disturbed soils belonging to the production area itself. In such cases the Dist<sub>init</sub> will be longer as will be the whole transect. In such a way the concentration gradient in the soils both around small and big installations can be assessed.

**Example:**

Source → +10m (Sample 1) → +20m (sample 2) → +40m (sample3) → +80m (sample 4) → + 160m (sample 5)

Sample 5 will be considered as background sample.

**Note:** since the orientation of the sampling sites is crucial for the interpretability of the results we recommend to contact the contacts at JRC/UNEP as soon as the sites have been inspected in order to refine the final set-up with respect to the individual local conditions.

At each sampling point, five individual soil sampling points will be identified according to Figure 1.



Figure 1: Scheme for the preparation of a composite sample made up from five individual samples

The following steps should be followed (Note: If site conditions require a modification in the protocol, it will be noted in the field log book. The sample collector will notify the project coordinator of any deviations):

1. Select the location of the sampling point and record the GPS coordinates, if possible;
2. Prepare the site to collect the sample (cut grass and remove leaves) and mark the area;

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3. Collect the individual samples from a surface of 5 cm x 5 cm as shown in Figure 1 down to the adequate depth (as indicated in the chapter “Sampling Depth”);
4. Place the individual sample in a clean (acetone) container or on aluminum foil;
5. Remove rocks, sticks, leaves or other large debris;
6. Continue with the other four individual samples as above;
7. Place the composite soil sample into a 1-liter brown glass jar;
8. Carefully remove any soil from the rim of the bottle, secure the cap, place the label (items to be contained, see below under “Documentation”) and custody seal on the top of the bottle. Wrap, label, and fix the custody seal with clear tape;
9. Wrap glass jar with aluminum foil and place in a polyethylene bag, seal the bag and place label with sample-ID on the outside; protect with clear tape;
10. The samples will be stored at room temperature, not exposed to sunlight!

Preferably the soil should be sampled after a dry period.

### 2.2.3.2 *Sampling Depth*

Important consideration:

PCDD/PCDF and other persistent organic pollutants (POPs) are retained in the upper (humus) layer of the soil when introduced via atmospheric deposition. Their mixing into deeper soil layers occurs through bioturbation (in grass or pasture lands) or through ploughing (in agricultural areas). ]

Mixing leads to a *dilution* of the deposited POPs on the soil surface. Depending on the extent (depth) of mixing the concentrations on the surface will decrease. This means that an identical deposition of POPs to a given surface will result in lower concentrations measured in an agricultural soil when compared to a grassland soil when only the upper 5 cm are measured. This would lead to an underestimation of the deposition/emission from a kiln when only 0-5 cm are measured in a ploughed soil. Please note that with the approach of using sampling depths 0-5 cm for grassland and 0-30 cm for arable soil, data will be comparable to already existing databases.

This problem can be resolved by creating a soil profile for every sampling site.

The soil profile will show whether

- the soil is undisturbed;
- which sampling depth has to be applied to assess the entire deposition of POPs to the surface.

Photo 1 below shows an undisturbed grassland soil, where a sampling depth of 0-5 cm is adequate to reflect the atmospheric deposition on the soil surface.

Photo 2 displays a cultivated soil, where the upper (humus) layer has been mixed down to the ploughing depth. Here the sampling depth should correspond to the ploughing depth.

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However, whenever undisturbed soil is available priority should be given to these sites, since the concentrations will be higher and thus the detection power of the analytical procedure will increase.



Photo 1: Soil profile of undisturbed soil under grass (sampling depth 0-5 cm)



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Photo 2: Soil profile of cultivated land under corn (sampling depth equal to ploughing depth = 30 cm)

#### 2.2.4 How to Take Bottom Ash Samples

Bottom ash samples should be taken from the kiln where the soil samples are taken. They will be taken after a minimum operation time of at least three days with the same fuel composition.

Fresh bottom ash samples will be taken as soon as the ashes have cooled down after extinction of the combustion process (Note: do not sample hot ashes). For the purpose of this project equal volumes/masses of ashes from three operations will be taken (either at the same time on three consecutive days for long-time operations or one sample each at morning, midday, and evening of the same day). Sub-samples will be mixed and homogenized in a metal bowl as described for the soil samples. The individual samples should all have the same fuel used. The samples should not contain large amounts of unburned fuel (in case that alternative fuels are fed).

The sample will be taken with a spate/large spoon and placed in a brown glass jar. There will be one bottom ash sample taken per kiln.

The labeling, transport, storage and shipment of the ash samples will follow the description for the soil samples.

#### 2.2.5 Documentation

A standard format for the protocol is provided in the Annex. We encourage the field teams to add any additional observation that may help for a better understanding of the process itself, its representativeness on a national scale, the land use pattern of the soil sites sampled, and the sampling procedure.

#### 2.2.6 Shipping

Prior to shipment to the dioxin laboratory, the samples will be inspected for breakage and inventoried to assure that chain of custody, sample identification numbers, bottle labels, and field logs are in agreement. Each sample will then be placed in the container within a bed of foam packing to ensure that no breakage will occur. After packing, layers of foam will be placed on top of the bottles so that no movement will occur during shipment. The transport box will then be addressed on the top, front and side panel by giving the full address of the laboratory including phone number.

All nationally collected samples will be shipped from Airport to Airport via give name of airline. If in need for a document by UNEP to facilitate customs declaration, please notify Dr. Heidelore Fiedler to arrange for such paper.

The shipment protocol will include the following information:

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- Notify [redacted] Air Freight, [redacted] City on day of impending shipment to [redacted] Destination City, Italy, the following shipment day.
- Notify Dr. Gunther Umlauf, JRC, via E-mail. Dr. Umlauf will acknowledge receipt of arrangement details via e-mail to the nationally responsible scientist.
- The developing country expert will deliver the sample for shipment to [redacted] Airline .
- Upon return from [redacted] Airline Air Freight, he will fax/email the airfreight confirmation/bill to JRC with a request for acknowledgement.
- Upon receipt of the sample shipment, JRC will acknowledge receipt of the samples to the developing country expert and UNEP Chemicals.

### 2.3 Else

Collect some raw bricks, wrap in aluminum foil and store at a cool, dark place.

In case of high levels of contamination in the vicinity of the brick kiln, the raw material will be analysed as well. It would also be useful to analyse a few bricks especially in cases where waste fuels have been used at a high percentage.

## 3 ANNEX – FIELD PROTOCOL

Regarding sampling (for all samples):	
Title of the project (e.g., Kiln XY);	
Sample ID (Soil XY, Ash XX);	
Date and time of sample collection;	
Name of person who collects the sample (and laboratory/institution on charge of the preparation of the sampling equipments and storage of the collected);	
Analytical parameters to be measured	PCDD/PCDF, dioxin-like PCBs, Indicator PCBs and HCB
GIS co-ordinates of sampling location;	
Any deviation from the standard sampling protocol should be noted.	
... ..for soil samples:	

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Land use	
Sampling depth (in cm);	
Sampling surface (ideally 5 x 5 cm; area in cm <sup>-2</sup> );	
Distance and orientation relative to the kiln (e.g., 1700S, 15 m);	
Reference to Photo of each composite sampling site	
Reference to Photo (or drawing) of the soil profile;	
Reference to Map of the site 1:25,000 or better where the location of the kiln and the respective sampling sites are visible (could be also a GOOGLE EARTH image);	
Reference to Photos from the kiln including detailed photographs of fuel, bricks, etc.;	
Information regarding land use or any other urban impacts in the vicinity (vicinity of roads, other industrial activity, etc.);	
Description of the sampling (tools used, observations...), add photo;	
Other observations;	
Any deviation from the standard sampling protocol should be noted.	
<b>Regarding the brick-making process</b>	
A detailed description of the production process ;	

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Name, address of the brick making oven (GPS coordinates where available);	
Description and photo of the kiln (scale of the kiln, material);	
Type of the fuel (used at the time of the sampling. Note: if different from “typical” uses, this should be noted) and gas volume emitted per hour, if available;	
Origin of the fuel;	
Amount of fuel used per ton of bricks produced;	
Raw materials for the bricks (in percentages);	
Origin of the ingredients;	
Any other information available about the process itself;	
An evaluation about the abundance of this type of process within the national sector of brick production;	
An estimate on the annual production of the individual kiln and for how many years it has been operated.	

To be added to the protocol:

- Photo of each composite sampling site
- Photo (or drawing) of the respective soil profile;
- Map of the site 1:25,000 or better where the location of the kiln and the respective sampling sites are visible (could be also a GOOGLE EARTH image);
- Photos from the kiln including detailed photographs of fuel, bricks and their raw materials, *etc.*;

*Draft: 16.11.2010*



- Photos from sampling equipment used.

*Draft: 16.11.2010*

## A.3 Analytical Methods

### A.3.1 JRC protocol

For *PCDD/PCDF*, *PCB* and *HCB* 2g of bottom ash were Soxhlet extracted with toluene for 24 h after being spiked with internal standards (16 <sup>13</sup>C-labelled 2,3,7,8-chlorine-substituted congeners with 400 pg each, except OCDD with 800 pg, 12 <sup>13</sup>C-labelled dl-PCB with 2000 pg each and *HCB* with 50 ng)

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 *PCB* and one containing coplanar *PCB* and *PCDD/PCDF*. The purification method was previously described by Abad et al (2000). *HCB* was analysed in the raw extract adjusted to approx. 200 µL.

Identification and quantification 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.Methods1613 Method and 1668.

*PCDD/PCDF*, and *PCB* were analysed 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 analysed 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.

*HCB* was analysed on double HRGC (Thermo Trace GC Ultra, Thermo Electron, Bremen, Germany), coupled with a DFS high resolution mass spectrometer HRMS (Thermo Electron, Bremen, Germany) operating in the EI-mode at 45 eV with a resolution of 8000/10000. For *HCB* the most two abundant ions of the isotopic molecular cluster were recorded for both native and labelled congeners.

The *HCB* was identified through comparison of retention times of the corresponding standard and the isotopic ratio of the two ions recorded.

*HCB* was separated on a BP-DXN 60 m long with 0.25 mm i.d. (inner diameter) and 0.25 µm films (SGE, Victoria, Australia).

Gas chromatographic conditions were: Split/splitless injector at 250 °C, constant flow at 1.0 ml min<sup>-1</sup> of He, GC-MS interface at 270 °C and a GC program rate: 100 °C with a 1 min. hold, then 10 °C min<sup>-1</sup> to 300 °C and a final hold at 300 °C for 9 min.

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

All solvents used were of nanograde quality.

### A.3.2 Krakow University protocol

## Determination of Polychlorinated Dibenzodioxins and Dibenzofurans (PCDDs and PCDFs), Polychlorinated biphenyls (PCBs) and Hexachlorobenzene (HCB) in bricks from Mexico.

### A. Introduction.

The objective for this study was to determine PCDDs, PCDFs, PCBs and HCB in brick samples obtained in March 2009 from Instituto Nacional de Ecología-Centro Nacional de Investigación y Capacitación Ambiental Av. San Rafael Atlixco No. 186, Universidad Autónoma Metropolitana Iztapalapa, Edificio “W”, Piso 2, Col. Vicentina, Delegación Iztapalapa, Mexico, D.F.

All analytical work has been performed in accredited Laboratory for Trace Organic Analyses (LTOA) at Krakow University of Technology, Krakow (Cracow), Poland. Accreditation number: PCA AB 749 valid until 08.01.2014.

### B. Examined material

**Brick 353/09, Brick 399/09 and Brick 404/09 of average mass of 2 kg each have been delivered to the laboratory in March 2009.**

### C. Description of the procedure

#### 1. Reference substances used in this study:

1. EPA-1613CVS calibration standards solution CS1-CS5 (Wellington Laboratories)
2. DF2 -Labeled compounds clean-up solution prepared from NK-LCS-G (Wellington Laboratories) solution. DF2 contains 15 labeled  $^{13}\text{C}$ - PCDD/Fs at concentration of 0.6 ng/ml each except of OCDD of 1.2 ng/ml.
3. PAR-1 – Matrix Spike Solution prepared from EPA-8290STN (Wellington Laboratories) solution. PAR-1 contains 17 PCDD/Fs at concentrations of 20 - 50-100 ng/ml of individual compounds.
4. EPA-1613ISS – Internal Standard Spiking Solution (Wellington Laboratories)  $^{12}\text{C}^{13}$ -1,2,3,4-TCDD and  $^{12}\text{C}^{13}$ -1,2,3,7,8,9-H<sub>6</sub>CDD – 200 ng/ml in nonane.
5. MBP-CP – coplanar PCB Matrix Spike Solution of  $^{13}\text{C}$ -PCB77,  $^{13}\text{C}$ -PCB126 and  $^{13}\text{C}$ -PCB169 – 10 µg/ml in nonane.
6. WP-LCS – dioxin-like PCBs Internal Standard Solution of:  $^{13}\text{C}$ -PCBs (81, 77, 105, 114, 118, 123, 126, 156, 157, 167, 169,189) of 1 µg/ml in nonane.
- 7.

Standard reference material:



Low dioxin fly ash from local power plant (Krakow) used for internal calibration procedure in the Laboratory. Dioxin concentration: 0.17 pg – WHO<sub>2005</sub> PCDDs/PCDFs TEQ/g

## 2. Sample Preparation

Brick sample of approximately 150 g was crushed in planetary mill, weighed on an analytical balance to ca. 100g with the nearest 0.01 g. A 1 ml of clean-up solution (DF2+ WP-LCS+ ) which contains a set of 15 labeled <sup>13</sup>C- PCDD/PCDF and 12 labeled <sup>13</sup>C- dl-PCB <sup>13</sup>C –HCB internal standards was added into the sample placed in Soxhlet extraction thimble. The extract was evaporated to ca. 1ml in rotary evaporator and introduced into carbon column (1g of active carbon). The column was washed with methanol, dichloromethane and the analyte eluted with boiling toluene. Subsequent clean-up was realized using concentrated sulphuric acid. After sulfuric acid washes, the extract was passing through H<sub>2</sub>SO<sub>4</sub> modified silica gel and NaOH modified silica column. Mono-ortho PCBs and HCB have been collected in the first fraction (2% dichloromethane in hexane) from alumina column. The second fraction from Alumina column (50% dichloromethane/hexane) contained PCDDs/Fs and coplanar PCBs (PCB77, 126 and 169). Finally, both extracts were carefully concentrated up to 20 µl in gentle stream of nitrogen. During final evaporation of solvent, internal standard spiking solution was added to the solution. The final extract was analyzed using GC-MS/MS apparatus according to P/01/02 General Procedure.

## 3. Analytical Method.

The PCDD/Fs, PCBs and HCB analyses were performed by high resolution gas chromatography/ tandem mass spectrometry (HRGC/MS-MS) on a Thermo Scientific GCQ-1100/Trace2000 system equipped with Xcalibur data acquisition and analysis software. Separation was performed on a 30mx0.25mm i.d. DB5MS J&W capillary column of 25µm film and DB17 30mx0.25mm i.d. DB5MS J&W capillary column of 25 µm film. Sample of 2.5µl volume was injected into SSL injector at 260°C. The GC oven was programmed as follows: an initial temperature of 1300C a hold for 3 minutes, then temperature ramp of 50°C/minute to 180°C, then another temperature ramp 2°C/minute to 270°C. Finally, temperature ramp was 20°C/minute to 300°C and held for 5 minutes. In this method primary and secondary (collision dissociated) ion masses were monitored for each analyte and internal standards as follows (data for PCDDs/Fs):

Table 3.

Target Analytes			Internal Standards		
	Primary Ion	Secondary Ion		Primary Ion	Secondary Ion
2,3,7,8-TCDD	322	259	<sup>13</sup> C-2,3,7,8-TCDD	334	270
1,2,3,7,8-PeCDD	365	293	<sup>13</sup> C-1,2,3,7,8-PeCDD	368	304
1,2,3,4,7,8-HxCDD	390	327	<sup>13</sup> C-1,2,3,4,7,8-HxCDD	402	338
1,2,3,6,7,8-HxCDD	390	327	<sup>13</sup> C-1,2,3,6,7,8-HxCDD	402	338
1,2,3,7,8,9-HxCDD	390	327	<sup>13</sup> C-1,2,3,7,8,9-HxCDD	402	338
1,2,3,4,6,7,8-HpCDD	424	361	<sup>13</sup> C-1,2,3,4,6,7,8-	436	372

			HpCDD		
OCDD	460	397	<sup>13</sup> C-OCDD	472	408
2,3,7,8-TCDF	306	243	<sup>13</sup> C-2,3,7,8-TCDF	318	254
1,2,3,7,8-PeCDF	340	277	<sup>13</sup> C-1,2,3,7,8-PeCDF	352	288
2,3,4,7,8-PeCDF	340	277	<sup>13</sup> C-2,3,4,7,8-PeCDF	352	288
1,2,3,4,7,8-HxCDF	374	311	<sup>13</sup> C-1,2,3,4,7,8-HxCDF	386	322
1,2,3,6,7,8-HxCDF	374	311	<sup>13</sup> C-1,2,3,6,7,8-HxCDF	386	322
2,3,4,6,7,8-HxCDF	374	311	<sup>13</sup> C-2,3,4,6,7,8-HxCDF	386	322
1,2,3,7,8,9-HxCDF	374	311	<sup>13</sup> C-1,2,3,7,8,9-HxCDF	386	322
1,2,3,4,6,7,8-HpCDF	408	345	1,2,3,4,6,7,8-HpCDF	420	356
1,2,3,4,7,8,9-HpCDF	408	345	<sup>13</sup> C-1,2,3,4,7,8,9-HpCDF	420	356
OCDF	444	381	<sup>13</sup> C-1,2,3,4-TCDD	334	270

#### 4. Quantification and Result Calculation

For all analytes, calibration of GC-MS-MS was performed by using five-point calibration by injecting of 1µl standard solution containing analytes of interest at five different concentrations over the calibration range.

The concentration of the target analyte in the sample was determined by comparing the integrated area of the target analyte peak in selected-ion chromatogram of the quantitation mass to the of the internal standard. The concentration of the target analyte (pg/g) in brick sample were calculated by the following equations.

$$Concentration = \frac{M_{C13} * A_{pn} / A_{pC13}}{RRf * m_p}$$

where  $A_{pn}$  and  $A_{pC13}$  are areas of analytical signals for target analyte and respected internal standard, RRf is the relative response factor of the target analyte (see table 2),  $m_p$  is the sample mass (in grams).

#### 5. Specificity

In the work gas chromatographic separation and double fragmentation mass spectrometric detection (GC-MS/MS) was used. The method is of high specificity and gives not interfered signals in the determination of all of the seventeen PCDDs and PCDFs and twelve dioxin-like PCBs.

#### 6. Linearity

Linear range of detector response was individually calculated using standard solutions EPA CS1-5 (see Reference Substances #1).

In *Figures 1 and 2* linear ranges for 2,3,7,8-TCDF and 2,3,7,8-TCDD is presented respectively.

Reporting:

*WHO-TEQ* according the 1998 TEFs, *n.n.* corresponds to non-detected, < corresponds to the blank,

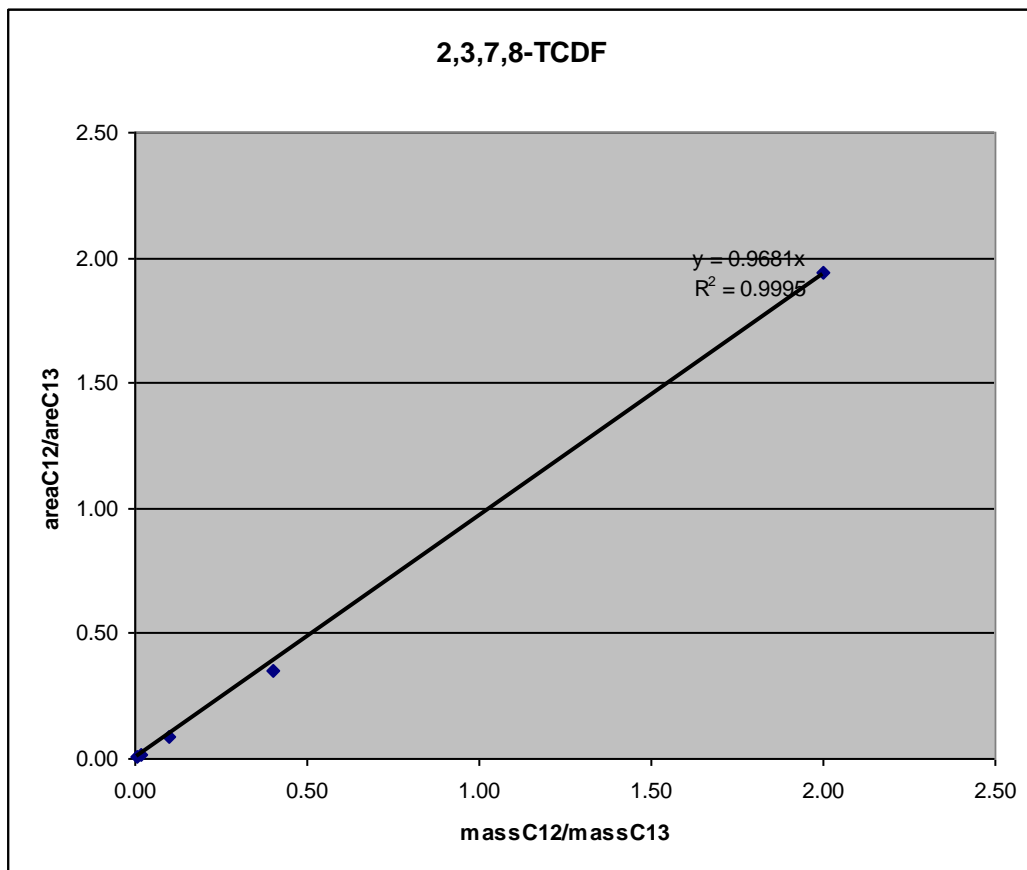


Fig.1 Calibration curve for 2,3,7,8-TCDF



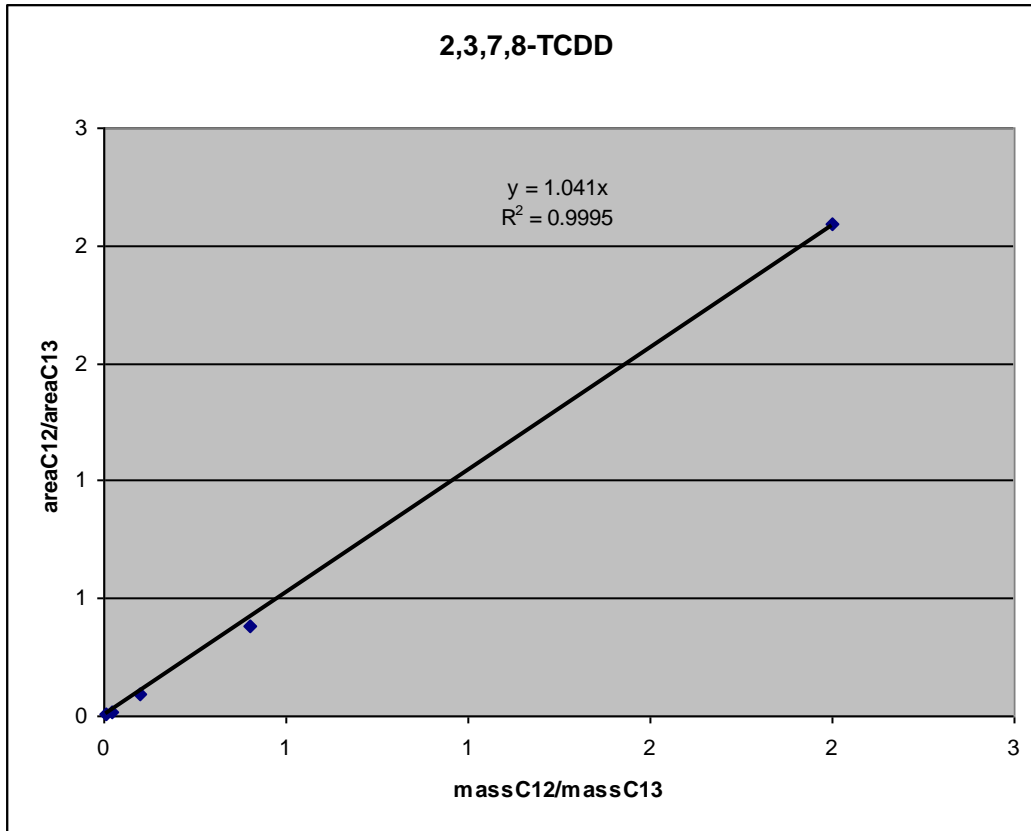


Fig.2 Calibration curve for 2,3,7,8-TCDD

## A 4 Results

### A 4.1 Analytical results as provided by UBA Vienna

Kenya	0912 5668	0912 5669	0912 5670	0912 5671	0912 5672
	Site A , Soil-20m from road	Site A , Soil-near the road	Site A , Ash-From Kiln A	Site A , 2 <sup>nd</sup> Ash-From Kiln B	Site A , Ash-From Kiln B2
Parameter	ng/kg	ng/kg	ng/kg	ng/kg	ng/kg
2,3,7,8-TCDD	n.n.	n.n.	n.n.	n.n.	n.n.
1,2,3,7,8-PCDD	n.n.	n.n.	n.n.	n.n.	0.096
1,2,3,4,7,8-HxCDD	n.n.	n.n.	n.n.	n.n.	n.n.
1,2,3,6,7,8- HxCDD	n.n.	n.n.	n.n.	n.n.	n.n.
1,2,3,7,8,9- HxCDD	n.n.	0.1	0.048	n.n.	n.n.
1,2,3,4,6,7,8- HeCDD	0.26	0.37	0.26	n.n.	0.3
OCDD	1.1	2.5	1	0.34	0.42
2,3,7,8-TCDF	0.23	n.n.	0.056	n.n.	0.13
1,2,3,7,8-PCDF	0.22	0.04	0.04	n.n.	n.n.
2,3,4,7,8-PCDF	n.n.	n.n.	0.04	n.n.	n.n.
1,2,3,4,7,8-HxCDF	n.n.	n.n.	n.n.	n.n.	n.n.
1,2,3,6,7,8- HxCDF	n.n.	n.n.	n.n.	n.n.	n.n.
2,3,4,6,7,8- HxCDF	n.n.	n.n.	n.n.	n.n.	n.n.
1,2,3,7,8,9- HxCDF	0.2	n.n.	n.n.	n.n.	n.n.
1,2,3,4,6,7,8-HeCDF	n.n.	0.14	0.11	n.n.	n.n.
1,2,3,4,7,8,9-HeCDF	n.n.	n.n.	n.n.	n.n.	0.088
OCDF	0.072	0.25	n.n.	n.n.	n.n.
TEQ (I-TEF)	0.2/0.13/0.058	0.1/ 0.61/ 0.02	0.1/ 0.069/ 0.037	0.014/ 0.0074/ 0.00034	0.16/0.11/ 0.065
TEQ - PCDD/F (WHO)	0.24/ 0.15/ 0.057	0.11/ 0.064/ 0.017	0.11/ 0.075/ 0.036	0.017/ 0.0088/ 0.000034	0.2/ 0.16/ 0.11
PCB 77	7.6	< 1,5	< 1,5	n.n.	1.5
PCB 81	4.1	< 0,56	< 0,56	n.n.	< 0,56
PCB 126	4	< 0,27	n.n.	n.n.	< 0,27
PCB 169	< 0.3	n.n.	n.n.	n.n.	n.n.
PCB 105	220	< 3,4	< 3,4	n.n.	4.5
PCB 114	6.5	n.n.	n.n.	n.n.	< 0,52
PCB 118	450	< 10	< 10	n.n.	< 10
PCB 123	8.7	< 1,1	< 1,1	n.n.	< 1,1
PCB 156	230	< 2,8	< 2,8	n.n.	< 2,8
PCB 157	79	< 0,49	n.n.	n.n.	< 0,49
PCB 167	120	< 1,5	< 1,5	n.n.	< 1,5
PCB 189	14	< 0,61	< 0,61	n.n.	< 0,61
TEQ - PCB (WHO)	0.63/ 0.63/ 0.63	0.0045/ 0.0023/ 0.000	0.057/ 0.0028/ 0.000	0.0040/ 0.0020/ 0.000	0.0045/ 0.0026/ 0.000
PCB 28	< 66	n.n.	< 66	n.n.	< 66
PCB 52	51	< 26	< 26	< 26	26
PCB 101	250	< 37	< 37	n.n.	< 37
PCB 138	1900	< 47	< 47	n.n.	< 47
PCB 153	1200	< 39	< 39	n.n.	< 39
PCB 180	230	< 22	< 22	n.n.	< 22
hexachlorobenzene	20	< 17	40	< 17	78
<b>Note:</b> #Upper bound –UB (non detects =100 % LOD), <b>medium bound –MB</b> (non detects = 50 % LOD), lower bound-LB (non detects = 0)					

Kenya	0912 5673	0912 5674	0912 5675	0912 5676	0912 5677	0912 5678
	Site B , Soil- 20m from road	Site B , Soil- near the road	Site B , 1 <sup>st</sup> Ash Sample Kiln B	Site C , Soil Sample	Site C , Ash Sample	Site D , Soil Sample
Parameter	ng/kg	ng/kg	ng/kg	ng/kg	ng/kg	ng/kg
2,3,7,8-TCDD	n.n.	n.n.	n.n.	n.n.	0.088	n.n.
1,2,3,7,8-PCDD	n.n.	0.048	n.n.	n.n.	n.n.	n.n.
1,2,3,4,7,8-HxCDD	0.072	0.04	n.n.	0.04	n.n.	n.n.
1,2,3,6,7,8- HxCDD	0.14	0.32	0.096	0.14	n.n.	0.13
1,2,3,7,8,9- HxCDD	0.25	0.38	0.18	0.11	n.n.	0.14
1,2,3,4,6,7,8- HeCDD	0.38	0.6	1.1	0.27	0.25	0.13
OCDD	2.4	3.2	7.4	1.8	1.1	1.5
2,3,7,8-TCDF	0.032	0.032	n.n.	0.13	0.21	n.n.
1,2,3,7,8-PCDF	0.1	0.14	0.08	0.15	n.n.	n.n.
2,3,4,7,8-PCDF	n.n.	0.048	n.n.	0.056	n.n.	n.n.
1,2,3,4,7,8-HxCDF	n.n.	0.04	n.n.	n.n.	n.n.	0.15
1,2,3,6,7,8- HxCDF	n.n.	0.04	0.048	0.064	n.n.	n.n.
2,3,4,6,7,8- HxCDF	n.n.	n.n.	n.n.	n.n.	n.n.	n.n.
1,2,3,7,8,9- HxCDF	0.44	n.n.	0.53	1.2	0.12	0.17
1,2,3,4,6,7,8-HeCDF	0.16	0.19	0.31	0.14	n.n.	0.14
1,2,3,4,7,8,9-HeCDF	n.n.	0.04	n.n.	n.n.	n.n.	n.n.
OCDF	0.17	0.54	0.19	0.14	n.n.	0.056
TEQ (I-TEF), UB/ MB/ LB#	0.15/ <b>0.13</b> / 0.11	0.18/ <b>0.17</b> / 0.15	0.15/ <b>0.13</b> / 0.11	0.25/ <b>0.23</b> / 0.21	0.15/ <b>0.14</b> / 0.12	0.15/ <b>0.10</b> / 0.063
TEQ - PCDD/F (WHO), UB/ MB/ LB#	0.16/ <b>0.13</b> / 0.10	0.20/ <b>0.19</b> / 0.17	0.15/ <b>0.13</b> / 0.10	0.25/ <b>0.23</b> / 0.21	0.16/ <b>0.14</b> / 0.12	0.15/ <b>0.10</b> / 0.062
PCB 77	< 1.5	< 1,5	< 1.5	3.5	< 1.5	< 1,5
PCB 81	< 0.56	< 0,56	n.n.	< 0,56	< 0.56	< 0,56
PCB 126	n.n.	< 0,27	< 0.27	< 0,27	n.n.	n.n.
PCB 169	n.n.	n.n.	n.n.	n.n.	n.n.	n.n.
PCB 105	< 3.4	< 3,4	< 3.4	6.2	< 3.4	< 3,4
PCB 114	< 0.52	n.n.	n.n.	0.64	< 0.52	n.n.
PCB 118	< 10	< 10	< 10	13	< 10	< 10
PCB 123	< 1.1	< 1,1	n.n.	< 1,1	n.n.	< 1,1
PCB 156	< 2.8	< 2,8	< 2.8	< 2,8	< 2.8	4.1
PCB 157	< 0.49	n.n.	< 0.49	< 0,49	< 0.49	< 0,49
PCB 167	< 1.5	< 1,5	< 1.5	< 1,5	< 1.5	< 1,5
PCB 189	< 0.61	n.n.	< 0.61	< 0,61	n.n.	< 0,61
TEQ - PCB (WHO), UB/ MB/ LB#	0.012/ <b>0.006</b> / 0.000	0.066/ <b>0.0033</b> / 0.000	0.0076/ <b>0.0038</b> / 0.000	0.010/ <b>0.063</b> / 0.0026	0.010/ <b>0.0051</b> / 0.000	0.012/ <b>0.0068</b> / 0.0021
PCB 28	< 66	< 66	n.n.	< 66	< 66	< 66
PCB 52	< 26	< 26	n.n.	< 26	< 26	< 26
PCB 101	< 37	< 37	< 37	< 37	n.n.	< 37
PCB 138	< 47	< 47	< 47	< 47	n.n.	< 47
PCB 153	< 39	< 39	< 39	< 39	n.n.	< 39
PCB 180	< 22	< 22	< 22	< 22	n.n.	< 22
hexachlorobenzene	20	21	< 17	20	27	20

**Note:** #Upper bound (non detects =100 % LOD),medium bound (non detects = 50 % LOD)/lower bound (non detects = 0)



Kenya	0912 5679	0912 5680	0912 5681	0912 5682	0912 5683	0912 5684
	Site D , Ash Sample	Site E , Soil Sample	Site E , Ash Sample	Site F , Soil Sample	Site F , Ash Sample	Background soil sample 1
Parameter	ng/kg	ng/kg	ng/kg	ng/kg	ng/kg	ng/kg
2,3,7,8-TCDD	n.n.	n.n.	0.048	n.n.	n.n.	0.1
1,2,3,7,8-PCDD	n.n.	n.n.	0.04	0.032	n.n.	n.n.
1,2,3,4,7,8-HxCDD	n.n.	n.n.	n.n.	0.048	n.n.	n.n.
1,2,3,6,7,8- HxCDD	n.n.	0.032	n.n.	0.18	n.n.	n.n.
1,2,3,7,8,9- HxCDD	0.072	n.n.	n.n.	0.26	n.n.	n.n.
1,2,3,4,6,7,8- HeCDD	0.22	n.n.	0.072	1.6	0.072	2.1
OCDD	0.64	0.63	0.86	8.7	0.39	15
2,3,7,8-TCDF	0.3	n.n.	0.97	n.n.	0.66	0.14
1,2,3,7,8-PCDF	0.08	n.n.	0.064	0.096	n.n.	n.n.
2,3,4,7,8-PCDF	n.n.	n.n.	0.072	0.048	n.n.	n.n.
1,2,3,4,7,8-HxCDF	n.n.	n.n.	0.04	0.056	n.n.	n.n.
1,2,3,6,7,8- HxCDF	n.n.	n.n.	n.n.	0.1	n.n.	0.04
2,3,4,6,7,8- HxCDF	n.n.	n.n.	n.n.	0.1	n.n.	0.072
1,2,3,7,8,9- HxCDF	n.n.	n.n.	n.n.	0.48	n.n.	0.19
1,2,3,4,6,7,8-HeCDF	0.2	n.n.	0.048	0.33	n.n.	0.58
1,2,3,4,7,8,9-HeCDF	n.n.	n.n.	n.n.	0.056	0.12	n.n.
OCDF	n.n.	n.n.	0.5	0.84	n.n.	1.1
TEQ (I-TEF), UB/ MB/ LB#	0.16/ <b>0.11</b> / 0.046	0.14/ <b>0.07</b> / 0.0038	0.22/ <b>0.22</b> / 0.21	0.22/ <b>0.21</b> / 0.20	0.20/ <b>0.13</b> / 0.068	0.27/ <b>0.23</b> / 0.19
TEQ - PCDD/F (WHO), UB/ MB/ LB#	0.19/ <b>0.12</b> / 0.045	0.15/ <b>0.076</b> / 0.0033	0.24/ <b>0.24</b> / 0.23	0.21/ <b>0.21</b> / 0.20	0.23/ <b>0.15</b> / 0.068	0.30/ <b>0.24</b> / 0.17
PCB 77	< 1,5	< 1.5	1.5	1.6	1.9	3.2
PCB 81	< 0,56	n.n.	< 0,56	< 0,56	< 0,56	< 0,56
PCB 126	< 0,27	n.n.	n.n.	< 0,27	n.n.	n.n.
PCB 169	n.n.	n.n.	n.n.	< 0,3	n.n.	< 0,3
PCB 105	< 3,4	< 3.4	< 3,4	4.8	< 3,4	3.6
PCB 114	< 0,52	n.n.	n.n.	< 0,52	< 0,52	< 0,52
PCB 118	< 10	< 10	< 10	< 10	< 10	< 10
PCB 123	< 1,1	n.n.	< 1,1	< 1,1	n.n.	< 1,1
PCB 156	< 2,8	< 2.8	< 2,8	3.8	n.n.	< 2,8
PCB 157	< 0,49	< 0.49	< 0,49	< 0,49	< 0,49	< 0,49
PCB 167	n.n.	< 1.5	< 1,5	1.6	n.n.	< 1,5
PCB 189	< 0,61	< 0.61	< 0,61	< 0,61	n.n.	< 0,61
TEQ - PCB (WHO), UB/ MB/ LB#	0.061/ <b>0.0030</b> / 0.000	0.0080/ <b>0.0040</b> / 0.000	0.0086/ <b>0.0044</b> / 0.000	0.0091/ <b>0.0058</b> / 0.0036	0.0072/ <b>0.0037</b> / 0.0019	0.088/ <b>0.0047</b> / 0.0007
PCB 28	< 66	< 66	< 66	< 66	< 66	n.n.
PCB 52	< 26	< 26	< 26	< 26	< 26	n.n.
PCB 101	< 37	n.n.	< 37	< 37	< 37	< 37
PCB 138	< 47	n.n.	< 47	< 47	n.n.	< 47
PCB 153	< 39	< 39	< 39	44	n.n.	< 39
PCB 180	< 22	n.n.	< 22	24	n.n.	< 22
hexachlorobenzene	100	21	34	21	30	< 17

**Note:** #Upper bound (non detects =100 % LOD),medium bound (non detects = 50 % LOD)/lower bound (non detects = 0)

Kenya	0912 5685	0912 5686
	Background soil sample 2	Background soil sample 3
Parameter	ng/kg	ng/kg
2,3,7,8-TCDD	n.n.	n.n.
1,2,3,7,8-PCDD	n.n.	n.n.
1,2,3,4,7,8-HxCDD	n.n.	n.n.
1,2,3,6,7,8- HxCDD	n.n.	0.08
1,2,3,7,8,9- HxCDD	0.16	0.18
1,2,3,4,6,7,8- HeCDD	0.3	1.1
OCDD	1.1	8.3
2,3,7,8-TCDF	n.n.	0.072
1,2,3,7,8-PCDF	n.n.	0.13
2,3,4,7,8-PCDF	n.n.	n.n.
1,2,3,4,7,8-HxCDF	n.n.	0.04
1,2,3,6,7,8- HxCDF	n.n.	0.048
2,3,4,6,7,8- HxCDF	n.n.	0.04
1,2,3,7,8,9- HxCDF	n.n.	0.79
1,2,3,4,6,7,8-HeCDF	0.18	0.32
1,2,3,4,7,8,9-HeCDF	n.n.	n.n.
OCDF	n.n.	0.52
TEQ (I-TEF), UB/ MB/ LB#	0.21/ <b>0.14</b> / 0.022	0.15/ <b>0.16</b> / 0.17
TEQ - PCDD/F (WHO), UB/ MB/ LB#	0.25/ <b>0.14</b> / 0.021	0.15/ <b>0.17</b> / 0.18
PCB 77	3.2	2.9
PCB 81	< 0,56	< 0,56
PCB 126	n.n.	n.n.
PCB 169	n.n.	< 0,3
PCB 105	5.6	4.7
PCB 114	< 0,52	n.n.
PCB 118	< 10	< 10
PCB 123	< 1,1	< 1,1
PCB 156	3.6	< 2,8
PCB 157	< 0,49	< 0,49
PCB 167	< 1,5	< 1,5
PCB 189	< 0,61	< 0,61
TEQ - PCB (WHO), UB/ MB/ LB#	0.0114/ <b>0.0070</b> /0.0027	0.072/ <b>0.0040</b> / 0.00076
PCB 28	n.n.	n.n.
PCB 52	< 26	< 26
PCB 101	< 37	< 37
PCB 138	< 47	< 47
PCB 153	< 39	< 39
PCB 180	< 22	< 22
hexachlorobenzene	< 17	< 17
<b>Note:</b> #Upper bound (non detects =100 % LOD),medium bound (non detects = 50 % LOD)/lower bound (non detects = 0)		

South Africa	0911 5007	0911 5008	0911 5009	0911 5010	0911 5011	0911 5012
	SABK1-1 soil	SABK1-2 soil	SABK1-3 soil	SABK1-4 soil	SABK1-5 soil	SABK1-6 soil
Parameter	ng/kg	ng/kg	ng/kg	ng/kg	ng/kg	ng/kg
2,3,7,8-TCDD	n.n.	n.n.	n.n.	n.n.	n.n.	n.n.
1,2,3,7,8-PCDD	n.n.	n.n.	n.n.	n.n.	n.n.	n.n.
1,2,3,4,7,8-HxCDD	n.n.	n.n.	n.n.	n.n.	n.n.	n.n.
1,2,3,6,7,8- HxCDD	0.16	0.14	0.37	0.31	n.n.	n.n.
1,2,3,7,8,9- HxCDD	0.24	0.38	0.6	0.6	0.17	0.22
1,2,3,4,6,7,8-HeCDD	n.n.	0.21	0.34	0.15	0.17	n.n.
OCDD	1.3	1	1.3	1.2	0.91	0.48
2,3,7,8-TCDF	0.048	n.n.	n.n.	n.n.	n.n.	0.032
1,2,3,7,8-PCDF	0.096	n.n.	0.04	0.032	0.064	n.n.
2,3,4,7,8-PCDF	0.056	n.n.	n.n.	n.n.	0.064	n.n.
1,2,3,4,7,8-HxCDF	0.12	n.n.	n.n.	n.n.	0.072	n.n.
1,2,3,6,7,8- HxCDF	0.08	n.n.	0.048	0.1	n.n.	n.n.
2,3,4,6,7,8- HxCDF	0.056	n.n.	n.n.	n.n.	n.n.	n.n.
1,2,3,7,8,9- HxCDF	0.15	0.26	0.15	n.n.	0.1	n.n.
1,2,3,4,6,7,8-HeCDF	0.39	0.11	0.14	n.n.	0.15	n.n.
1,2,3,4,7,8,9-HeCDF	n.n.	n.n.	n.n.	n.n.	n.n.	n.n.
OCDF	0.42	n.n.	n.n.	n.n.	n.n.	n.n.
TEQ (I-TEF), UB/ MB/ LB#	0.15/ <b>0.14</b> / 0.12	0.11/ <b>0.098</b> / 0.082	0.16/ <b>0.14</b> / 0.12	0.14/ <b>0.12</b> / 0.11	0.12/ <b>0.096</b> / 0.074	0.072/ <b>0.049</b> / 0.026
TEQ - PCDD/F (WHO), UB/ MB/ LB#	0.16/ <b>0.14</b> / 0.12	0.12/ <b>0.10</b> / 0.081	0.17/ <b>0.15</b> / 0.12	0.15/ <b>0.13</b> / 0.10	0.13/ <b>0.10</b> / 0.073	0.077/ <b>0.051</b> / 0.025
PCB 77	< 1.5	< 1.5	n.n.	1.6	< 1.5	< 1.5
PCB 81	n.n.	n.n.	n.n.	< 0.56	n.n.	n.n.
PCB 126	n.n.	n.n.	n.n.	n.n.	n.n.	n.n.
PCB 169	n.n.	n.n.	n.n.	n.n.	n.n.	n.n.
PCB 105	< 3.4	< 3.4	n.n.	< 3.4	< 3.4	< 3.4
PCB 114	n.n.	n.n.	n.n.	n.n.	n.n.	n.n.
PCB 118	< 10	< 10	< 10	< 10	< 10	< 10
PCB 123	n.n.	< 1.1	< 1.1	< 1.1	n.n.	n.n.
PCB 156	< 2.8	< 2.8	< 2.8	< 2.8	< 2.8	< 2.8
PCB 157	< 0.49	n.n.	n.n.	n.n.	< 0.49	n.n.
PCB 167	< 1.5	< 1.5	< 1.5	< 1.5	< 1.5	n.n.
PCB 189	n.n.	< 0.61	< 0.61	< 0.61	< 0.61	< 0.61
TEQ - PCB (WHO), UB/ MB/ LB#	0.044/ <b>0.022</b> / 0.000	0.082/ <b>0.041</b> / 0.000	0.064/ <b>0.032</b> / 0.000	0.079/ <b>0.040</b> / 0.0002	0.054/ <b>0.027</b> / 0.000	0.069/ <b>0.035</b> / 0.000
PCB 28	n.n.	n.n.	n.n.	n.n.	n.n.	n.n.
PCB 52	< 26	< 26	n.n.	< 26	n.n.	n.n.
PCB 101	< 37	< 37	< 37	< 37	< 37	n.n.
PCB 138	< 47	< 47	< 47	< 47	< 47	< 47
PCB 153	< 39	< 39	< 39	< 39	< 39	< 39
PCB 180	< 22	< 22	< 22	< 22	< 22	< 22
hexachlorobenzene	200	35	22	< 17	18	< 17

**Note:** #Upper bound (non detects =100 % LOD),medium bound (non detects = 50 % LOD)/lower bound (non detects = 0)



South Africa No	0911 5013	0911 5014	0911 5015	0911 5016	0911 5017	0911 5018
	SABK1-7 soil	SABK1-8 soil	SABK1-9 reference soil	Dididi soil 1A	Dididi soil 2A	Dididi soil 3A
Parameter	ng/kg	ng/kg	ng/kg	ng/kg	ng/kg	ng/kg
2,3,7,8-TCDD	0.04	n.n.	n.n.	n.n.	0.024	n.n.
1,2,3,7,8-PCDD	n.n.	n.n.	n.n.	n.n.	0.032	n.n.
1,2,3,4,7,8-HxCDD	0.056	n.n.	0.12	n.n.	n.n.	n.n.
1,2,3,6,7,8- HxCDD	0.15	0.2	0.16	n.n.	n.n.	0.04
1,2,3,7,8,9- HxCDD	0.13	0.35	0.16	n.n.	n.n.	n.n.
1,2,3,4,6,7,8-HeCDD	0.2	0.18	2	0.048	0.088	0.25
OCDD	0.58	0.7	5.7	0.46	0.38	0.67
2,3,7,8-TCDF	n.n.	n.n.	0.14	0.14	n.n.	0.18
1,2,3,7,8-PCDF	n.n.	n.n.	0.12	n.n.	n.n.	n.n.
2,3,4,7,8-PCDF	n.n.	n.n.	0.28	0.064	0.048	0.08
1,2,3,4,7,8-HxCDF	n.n.	0.048	0.22	n.n.	0.096	0.08
1,2,3,6,7,8- HxCDF	n.n.	0.048	0.18	0.048	0.04	0.072
2,3,4,6,7,8- HxCDF	n.n.	n.n.	0.3	n.n.	n.n.	n.n.
1,2,3,7,8,9- HxCDF	0.088	0.11	n.n.	n.n.	n.n.	n.n.
1,2,3,4,6,7,8-HeCDF	0.12	0.13	0.58	0.12	0.14	0.25
1,2,3,4,7,8,9-HeCDF	n.n.	n.n.	0.17	n.n.	n.n.	n.n.
OCDF	n.n.	n.n.	0.66	n.n.	0.056	0.2
TEQ (I-TEF), UB/ MB/ LB#	0.10/ <b>0.095</b> / 0.086	0.11/ <b>0.093</b> / 0.079	0.35/ <b>0.33</b> / 0.31	0.072/ <b>0.062</b> / 0.053	0.088/ <b>0.084</b> / 0.08	0.098/ <b>0.090</b> / 0.083
TEQ - PCDD/F (WHO), UB/ MB/ LB#	0.11/ <b>0.098</b> / 0.086	0.11/ <b>0.096</b> / 0.079	0.36/ <b>0.33</b> / 0.30	0.76/ <b>0.64</b> / 0.053	0.10/ <b>0.10</b> / 0.096	0.10/ <b>0.091</b> / 0.082
PCB 77	n.n.	n.n.	2.4	n.n.	< 1.5	< 1.5
PCB 81	n.n.	n.n.	< 0.56	n.n.	n.n.	n.n.
PCB 126	n.n.	n.n.	n.n.	n.n.	< 0.27	n.n.
PCB 169	n.n.	n.n.	n.n.	n.n.	n.n.	n.n.
PCB 105	n.n.	< 3.4	5.9	n.n.	< 3.4	< 3.4
PCB 114	n.n.	n.n.	n.n.	n.n.	n.n.	< 0.52
PCB 118	< 10	< 10	< 10	n.n.	< 10	< 10
PCB 123	< 1.1	< 1.1	< 1.1	n.n.	n.n.	n.n.
PCB 156	< 2.8	< 2.8	n.n.	n.n.	< 2.8	n.n.
PCB 157	< 0.49	n.n.	< 0.49	n.n.	n.n.	< 0.49
PCB 167	< 1.5	< 1.5	< 1.5	n.n.	n.n.	< 1.5
PCB 189	< 0.61	n.n.	< 0.61	n.n.	n.n.	< 0.61
TEQ - PCB (WHO), UB/ MB/ LB#	0.0064/ <b>0.0032</b> / 0.000	0.012/ <b>0.0060</b> / 0.000	0.0082/ <b>0.0045</b> / 0.00083	0.018/ <b>0.0088</b> / 0.000	0.012/ <b>0.0060</b> / 0.000	0.0069/ <b>0.0034</b> / 0.000
PCB 28	n.n.	n.n.	n.n.	n.n.	n.n.	n.n.
PCB 52	n.n.	n.n.	n.n.	n.n.	n.n.	n.n.
PCB 101	< 37	< 37	< 37	n.n.	n.n.	< 37
PCB 138	< 47	< 47	< 47	n.n.	n.n.	< 47
PCB 153	< 39	< 39	< 39	n.n.	n.n.	< 39
PCB 180	< 22	< 22	< 22	n.n.	n.n.	< 22
hexachlorobenzene	< 17	< 17	n.n.	19	< 17	< 17

**Note:** #Upper bound (non detects =100 % LOD),medium bound (non detects = 50 % LOD)/lower bound (non detects = 0)

South Africa No	0911 5019	09 11 5020	0911 5021	0911 5022	0911 5023	09 11 5024	09 11 5025
	Dididi soil 4A	SABK2-1 soil	SABK2-2 soil	SABK2-3 soil	SABK2-4 soil	SABK2-5 soil	SABK2 reference soil
Parameter							
2,3,7,8-TCDD	n.n.	n.n.	n.n.	n.n.	n.n.	n.n.	n.n.
1,2,3,7,8-PCDD	n.n.	n.n.	0.12	0.12	0.056	n.n.	n.n.
1,2,3,4,7,8-HxCDD	n.n.	0.088	0.064	n.n.	n.n.	0.088	n.n.
1,2,3,6,7,8- HxCDD	n.n.	0.26	0.18	0.29	0.23	0.18	0.12
1,2,3,7,8,9- HxCDD	n.n.	0.3	0.18	0.29	0.27	0.27	0.11
1,2,3,4,6,7,8- HeCDD	n.n.	0.91	0.84	0.65	0.57	0.86	0.26
OCDD	0.46	4.6	5.2	2.7	2.1	3.8	1.3
2,3,7,8-TCDF	0.18	0.29	0.34	n.n.	0.17	0.28	0.072
1,2,3,7,8-PCDF	0.064	0.22	0.14	0.49	0.14	0.1	0.056
2,3,4,7,8-PCDF	n.n.	0.14	0.18	0.16	0.19	0.25	0.08
1,2,3,4,7,8-HxCDF	n.n.	0.26	0.32	0.2	0.26	0.33	0.088
1,2,3,6,7,8- HxCDF	0.056	0.2	0.18	0.2	0.18	0.21	0.064
2,3,4,6,7,8- HxCDF	n.n.	0.14	0.22	0.11	0.13	0.21	n.n.
1,2,3,7,8,9- HxCDF	n.n.	0.92	0.26	3.3	1.9	1.8	n.n.
1,2,3,4,6,7,8-HeCDF	0.096	0.65	0.66	0.59	0.48	0.99	0.27
1,2,3,4,7,8,9-HeCDF	n.n.	0.13	n.n.	0.096	0.11	0.17	n.n.
OCDF	n.n.	0.55	0.9	0.41	0.28	0.6	0.3
TEQ (I-TEF)	0.028/ <b>0.043</b> / 0.057	0.35/ <b>0.35</b> / 0.36	0.35/ <b>0.36</b> / 0.37	0.62/ <b>0.63</b> / 0.64	0.46/ <b>0.47</b> / 0.48	0.49/ <b>0.50</b> / 0.50	0.095/ <b>0.11</b> / 0.12
TEQ - PCDD/F (WHO)	0.028/ <b>0.046</b> / 0.064	0.34/ <b>0.35</b> / 0.36	0.41/ <b>0.41</b> / 0.42	0.68/ <b>0.69</b> / 0.70	0.48/ <b>0.49</b> / 0.50	0.49/ <b>0.50</b> / 0.51	0.094/ <b>0.11</b> / 0.12
PCB 77	< 1.5	13	23	3.5	3.6	5.7	< 1.5
PCB 81	n.n.	0.71	1.4	< 0.56	< 0.56	< 0.56	n.n.
PCB 126	n.n.	0.39	0.71	0.49	0.67	1.2	< 0.27
PCB 169	n.n.	n.n.	n.n.	n.n.	< 0.3	n.n.	n.n.
PCB 105	< 3.4	15	28	8.3	7.3	9.3	< 3.4
PCB 114	n.n.	0.69	1.4	< 0.52	n.n.	< 0.52	n.n.
PCB 118	< 10	21	40	12	11	14	< 10
PCB 123	n.n.	< 1.1	1.1	< 1.1	< 1.1	n.n.	n.n.
PCB 156	< 2.8	5.4	7.9	4.5	3.8	4.3	< 2.8
PCB 157	n.n.	0.86	1.3	0.49	0.53	n.n.	< 0.49
PCB 167	< 1.5	2	2.9	< 1.5	< 1.5	2.7	< 1.5
PCB 189	< 0.61	0.73	0.86	< 0.61	< 0.61	n.n.	< 0.61
TEQ - PCB (WHO)	0.00/ <b>0.0038</b> / 0.0076	0.048/ <b>0.048</b> / 0.048	0.086/ <b>0.086</b> / 0.086	0.054/ <b>0.054</b> / 0.054	0.071/ <b>0.072</b> / 0.072	0.13/ <b>0.13</b> / 0.13	0.00/ <b>0.0015</b> / 0.0030
PCB 28	n.n.	110	220	n.n.	< 66	n.n.	n.n.
PCB 52	n.n.	56	92	< 26	< 26	< 26	n.n.
PCB 101	< 37	42	56	< 37	< 37	< 37	< 37
PCB 138	< 47	58	70	61	< 47	54	< 47
PCB 153	< 39	50	60	72	39	50	< 39
PCB 180	< 22	31	36	36	25	34	< 22
hexachlorobenzene	< 17	160	280	70	91	140	660

**Note:** #Upper bound (non detects =100 % LOD),medium bound (non detects = 50 % LOD)/lower bound (non detects = 0)

South Africa	1011 5966	1011 5965	1011 5964	1011 5968	1011 5969	1011 5967
	Dididi Brick,	SABK1-Brick	SABK2 Brick	438 Dididi Ash	435 Dididi ash	439 Dididi reference soil
Parameter	ng/kg	ng/kg	ng/kg	ng/kg	ng/kg	ng/kg
2,3,7,8-TCDD	n.n.	n.n.	n.n.	n.n.	n.n.	n.n.
1,2,3,7,8-PCDD	n.n.	n.n.	n.n.	n.n.	n.n.	n.n.
1,2,3,4,7,8-HxCDD	n.n.	n.n.	n.n.	n.n.	n.n.	n.n.
1,2,3,6,7,8- HxCDD	n.n.	n.n.	n.n.	n.n.	n.n.	0.11
1,2,3,7,8,9- HxCDD	n.n.	n.n.	n.n.	n.n.	n.n.	0.11
1,2,3,4,6,7,8-HeCDD	n.n.	n.n.	n.n.	n.n.	n.n.	n.n.
OCDD	n.n.	0.17	0.61	0.16	n.n.	0.67
2,3,7,8-TCDF	n.n.	n.n.	n.n.	n.n.	0.54	n.n.
1,2,3,7,8-PCDF	n.n.	n.n.	n.n.	n.n.	0.15	n.n.
2,3,4,7,8-PCDF	n.n.	n.n.	n.n.	n.n.	n.n.	n.n.
1,2,3,4,7,8-HxCDF	n.n.	n.n.	n.n.	n.n.	n.n.	n.n.
1,2,3,6,7,8- HxCDF	n.n.	n.n.	n.n.	n.n.	n.n.	n.n.
2,3,4,6,7,8- HxCDF	n.n.	n.n.	n.n.	n.n.	n.n.	n.n.
1,2,3,7,8,9- HxCDF	n.n.	n.n.	n.n.	n.n.	n.n.	n.n.
1,2,3,4,6,7,8-HeCDF	n.n.	n.n.	n.n.	0.1	n.n.	n.n.
1,2,3,4,7,8,9-HeCDF	n.n.	n.n.	n.n.	n.n.	n.n.	n.n.
OCDF	0.17	n.n.	1.7	0.54	0.42	0.14
TEQ (I-TEF)	0.00017/ <b>0.05</b> / 0.1	0.00017/ <b>0.045</b> / 0.089	0.0023/ <b>0.033</b> / 0.063	0.0017/ <b>0.047</b> / 0.093	0.062/ <b>0.11</b> / 0.16	0.023/ <b>0.052</b> / 0.082
TEQ - PCDD/F (WHO)	0.000017/ <b>0.06</b> / 0.12	0.000017/ <b>0.055</b> / 0.11	0.00023/ <b>0.036</b> / 0.072	0.0011/ <b>0.059</b> / 0.12	0.062/ <b>0.12</b> / 0.17	0.022/ <b>0.06</b> / 0.099
PCB 77	< 1,5	< 1,5	2.3	< 1,5	< 1,5	< 1,5
PCB 81	< 0,56	n.n.	0.58	< 0,56	0.74	1.3
PCB 126	n.n.	n.n.	n.n.	n.n.	n.n.	1.3
PCB 169	n.n.	n.n.	n.n.	n.n.	< 0,3	1.1
PCB 105	4.7	< 3,4	5.3	< 3,4	< 3,4	< 3,4
PCB 114	< 0,52	n.n.	< 0,52	< 0,52	< 0,52	0.72
PCB 118	< 10	< 10	< 10	< 10	< 10	< 10
PCB 123	n.n.	n.n.	n.n.	n.n.	< 1,1	n.n.
PCB 156	< 2,8	< 2,8	3.2	< 2,8	< 2,8	< 2,8
PCB 157	< 0,49	n.n.	< 0,49	< 0,49	n.n.	1.1
PCB 167	< 1,5	< 1,5	< 1,5	< 1,5	< 1,5	< 1,5
PCB 189	< 0,61	< 0,61	< 0,61	n.n.	< 0,61	1.5
TEQ - PCB (WHO)	0.00047/ <b>0.0053</b> / 0.010	0.00/ <b>0.0070</b> / 0.014	0.0034/ <b>0.0072</b> / 0.012	0.00/ <b>0.0070</b> / 0.014	0.000074/ <b>0.0062</b> / 0.012	0.14/ <b>0.14</b> / 0.14
PCB 28	< 66	n.n.	< 66	< 66	< 66	< 66
PCB 52	31	< 26	< 26	< 26	< 26	< 26
PCB 101	< 37	n.n.	< 37	< 37	< 37	< 37
PCB 138	< 47	n.n.	< 47	< 47	< 47	< 47
PCB 153	< 39	< 39	< 39	< 39	< 39	< 39
PCB 180	< 22	< 22	< 22	< 22	< 22	< 22
hexachlorobenzene	< 17	< 17	18	18	20	< 17

**Note:** #Upper bound (non detects =100 % LOD),medium bound (non detects = 50 % LOD)/lower bound (non detects = 0)

Mexico	0911 5026	0911 5027	0911 5028	09 11 5029	09 11 5030	09 11 5031
	Salamanca 1 / 2556 soil	Salamanca 1 / 2558 soil	Salamanca 2 / 2571 soil	Salamanca 2 / 2574 soil	Salamanca 2 / 2576 soil	Salamanca 2 / 2577 soil
Parameter	ng/kg	ng/kg	ng/kg	ng/kg	ng/kg	ng/kg
2,3,7,8-TCDD	n.n.	n.n.	n.n.	n.n.	n.n.	n.n.
1,2,3,7,8-PCDD	0.064	0.16	0.34	n.n.	n.n.	n.n.
1,2,3,4,7,8-HxCDD	n.n.	0.08	0.9	0.2	0.16	0.096
1,2,3,6,7,8- HxCDD	n.n.	0.27	2	0.42	0.17	0.14
1,2,3,7,8,9- HxCDD	0.048	0.32	1.2	0.26	0.25	0.19
1,2,3,4,6,7,8-HeCDD	2.1	6.7	40	9.8	2.8	2.4
OCDD	27	61	420	180	49	48
2,3,7,8-TCDF	n.n.	0.86	0.38	0.12	0.16	0.096
1,2,3,7,8-PCDF	n.n.	n.n.	0.17	0.14	0.088	n.n.
2,3,4,7,8-PCDF	n.n.	0.27	0.34	0.13	n.n.	0.056
1,2,3,4,7,8-HxCDF	n.n.	0.24	3.9	1	0.19	0.15
1,2,3,6,7,8- HxCDF	n.n.	0.2	0.73	0.26	0.12	0.064
2,3,4,6,7,8- HxCDF	0.08	0.16	0.67	0.26	0.096	0.048
1,2,3,7,8,9- HxCDF	0.08	n.n.	0.26	n.n.	0.056	n.n.
1,2,3,4,6,7,8-HeCDF	n.n.	1.5	12	4.4	0.44	0.43
1,2,3,4,7,8,9-HeCDF	n.n.	0.096	1	0.32	0.04	n.n.
OCDF	n.n.	2.1	37	8.4	0.54	0.42
TEQ (I-TEF), UB/ MB/ LB#	0.1/ <b>0.12</b> / 0.15	0.58/ <b>0.58</b> /0.57	2.3/ <b>2.4</b> / 2.4	0.67/ <b>0.66</b> / 0.66	0.22/ <b>0.21</b> / 0.21	0.19/ <b>0.19</b> / 0.18
TEQ - PCDD/F (WHO), UB/ MB/ LB#	0.11/ <b>0.13</b> / 0.15	0.61/ <b>0.60</b> / 0.60	2.1/ <b>2.1</b> / 2.1	0.50/ <b>0.50</b> / 0.49	0.18/ <b>0.17</b> / 0.16	0.15/ <b>0.15</b> / 0.14
PCB 77	< 1,5	5.7	3.6	2.5	2	< 1.5
PCB 81	< 0,56	0.82	0.7	< 0.56	< 0.56	n.n.
PCB 126	< 0,27	1.3	0.91	0.64	< 0.27	0.37
PCB 169	n.n.	< 0.3	< 0.3	< 0.3	n.n.	n.n.
PCB 105	< 3,4	20	9.4	5.6	6.4	< 3.4
PCB 114	< 0,52	0.86	< 0,52	< 0.52	< 0.52	n.n.
PCB 118	< 10	36	15	< 10	< 10	< 10
PCB 123	< 1,1	2.2	< 1,1	< 1.1	< 1.1	n.n.
PCB 156	< 2,8	14	6.1	< 2.8	< 2.8	< 2.8
PCB 157	< 0,49	3.1	0.71	0.55	< 0.49	< 0.49
PCB 167	< 1,5	5.2	2.4	< 1.5	1.6	< 1.5
PCB 189	< 0,61	2.7	0.76	< 0.61	n.n.	1
TEQ - PCB (WHO), UB/ MB/ LB#	0.0045/ <b>0.0023</b> / 0.000	0.15/ <b>0.15</b> / 0.15	0.10/ <b>0.10</b> / 0.10	0.065/ <b>0.065</b> / 0.065	0.0045/ <b>0.0027</b> / 0.0009	0.037/ <b>0.037</b> / 0.037
PCB 28	< 66	n.n.	< 66	< 66	n.n.	n.n.
PCB 52	< 26	< 26	< 26	< 26	< 26	n.n.
PCB 101	< 37	61	< 37	< 37	< 37	< 37
PCB 138	< 47	190	65	< 47	< 47	< 47
PCB 153	< 39	120	50	< 39	< 39	< 39
PCB 180	< 22	130	38	24	< 22	45
hexachlorobenzene	24	100	130	220	190	51

**Note:** #Upper bound (non detects =100 % LOD),medium bound (non detects = 50 % LOD)/lower bound (non detects = 0)



Mexico	09 11 5032	0911 5033	0911 5034	0911 5035	0911 5036	0911 5037
	Salamanca 4 / 2592 soil	Abasolo 1 / 2628 soil	Abasolo 1 / 2630 soil	Abasolo 1 / 2632 soil	Abasolo 1 / 2634 soil	Abasolo 1 / 2636 soil
Parameter	ng/kg	ng/kg	ng/kg	ng/kg	ng/kg	ng/kg
2,3,7,8-TCDD	0.016	0.024	0.15	n.n.	0.32	0.13
1,2,3,7,8-PCDD	n.n.	n.n.	n.n.	n.n.	2.5	0.57
1,2,3,4,7,8-HxCDD	n.n.	0.056	n.n.	n.n.	1.5	0.99
1,2,3,6,7,8- HxCDD	0.18	0.45	0.42	0.25	2.2	2.2
1,2,3,7,8,9- HxCDD	0.34	0.94	0.94	0.39	1.7	1.9
1,2,3,4,6,7,8- HeCDD	1	1.2	1.2	0.35	35	48
OCDD	9	14	5.5	2.8	460	390
2,3,7,8-TCDF	0.14	0.2	0.08	n.n.	8.8	2
1,2,3,7,8-PCDF	0.11	n.n.	n.n.	n.n.	12	2
2,3,4,7,8-PCDF	0.14	0.1	0.11	n.n.	7.5	1.5
1,2,3,4,7,8-HxCDF	0.21	0.18	0.18	n.n.	16	5.2
1,2,3,6,7,8- HxCDF	0.13	0.088	0.14	0.04	7.8	2
2,3,4,6,7,8- HxCDF	0.1	0.11	0.11	n.n.	5.4	1.1
1,2,3,7,8,9- HxCDF	0.14	0.14	0.18	0.032	1	0.2
1,2,3,4,6,7,8-HeCDF	0.48	0.39	0.53	0.18	31	11
1,2,3,4,7,8,9-HeCDF	n.n.	n.n.	0.088	n.n.	3.8	1.2
OCDF	0.59	0.6	0.65	0.94	50	10
TEQ (I-TEF)	0.24/ <b>0.24</b> / 0.24	0.33/ <b>0.33</b> / 0.32	0.44/ <b>0.44</b> / 0.43	0.12/ <b>0.098</b> / 0.080	12/ <b>12</b> / 12	3.8/ <b>3.8</b> / 3.8
TEQ - PCDD/F (WHO)	0.24/ <b>0.24</b> / 0.23	0.32/ <b>0.32</b> / 0.31	0.44/ <b>0.44</b> / 0.43	0.12/ <b>0.098</b> / 0.077	12/ <b>12</b> / 12	3.8/ <b>3.8</b> / 3.8
PCB 77	2	< 1.5	n.n.	< 1.5	7.2	1.8
PCB 81	< 0.56	n.n.	n.n.	n.n.	2.4	2.8
PCB 126	0.63	n.n.	n.n.	n.n.	3.2	0.89
PCB 169	n.n.	n.n.	n.n.	n.n.	0.81	< 0.3
PCB 105	5.4	< 3.4	< 3.4	< 3.4	7.9	< 3.4
PCB 114	n.n.	n.n.	n.n.	n.n.	< 0.52	< 0.52
PCB 118	< 10	< 10	< 10	< 10	13	< 10
PCB 123	< 1.1	n.n.	n.n.	n.n.	n.n.	< 1.1
PCB 156	2.9	< 2.8	< 2.8	< 2.8	6.7	< 2.8
PCB 157	0.49	< 0.49	< 0.49	n.n.	1.7	< 0.49
PCB 167	1.6	< 1.5	< 1.5	n.n.	5.3	2.8
PCB 189	< 0.61	n.n.	n.n.	n.n.	3	1.3
TEQ - PCB (WHO)	0.066/ <b>0.066</b> / 0.065	0.0084/ <b>0.0042</b> / 0.000	0.0071/ <b>0.0036</b> / 0.000	0.0093/ <b>0.0047</b> / 0.000	0.34/ <b>0.34</b> / 0.34	0.09/ <b>0.090</b> / 0.090
PCB 28	n.n.	n.n.	n.n.	n.n.	n.n.	n.n.
PCB 52	< 26	< 26	n.n.	< 26	< 26	n.n.
PCB 101	< 37	< 37	n.n.	n.n.	< 37	< 37
PCB 138	< 47	< 47	< 47	n.n.	55	< 47
PCB 153	< 39	< 39	< 39	< 39	47	< 39
PCB 180	< 22	< 22	< 22	< 22	37	< 22
hexachlorobenzene	550	91	50	52	500	290

**Note:** #Upper bound (non detects = 100 % LOD), medium bound (non detects = 50 % LOD)/lower bound (non detects = 0)

Mexico	0911 5038	0911 5039	0911 5040	0911 5041	0911 5042	0911 5043
	León 1 / 2656	León 1 / 2658	León 1 / 2660	León 1 / 2662	León 1 / 2664	León 1 background/ 2666
Parameter	ng/kg	ng/kg	ng/kg	ng/kg	ng/kg	ng/kg
2,3,7,8-TCDD	0.93	0.18	0.13	n.n.	n.n.	0.064
1,2,3,7,8-PCDD	2.4	3.3	0.61	0.064	n.n.	n.n.
1,2,3,4,7,8-HxCDD	1.7	2	0.86	0.26	0.072	0.18
1,2,3,6,7,8- HxCDD	3.3	2.6	1.1	0.37	0.17	0.49
1,2,3,7,8,9- HxCDD	2.6	2.2	0.89	0.39	0.23	0.48
1,2,3,4,6,7,8- HeCDD	50	27	21	3.8	2.9	12
OCDD	600	230	200	75	28	88
2,3,7,8-TCDF	35	9.3	1.7	0.24	0.088	0.48
1,2,3,7,8-PCDF	16	9.8	1.7	0.18	0.04	0.34
2,3,4,7,8-PCDF	10	7.6	2.1	0.22	0.056	0.27
1,2,3,4,7,8-HxCDF	17	17	3.6	0.26	0.32	1.4
1,2,3,6,7,8- HxCDF	13	8.3	2.2	0.23	0.14	0.29
2,3,4,6,7,8- HxCDF	6.7	5.7	2.2	0.18	0.096	0.34
1,2,3,7,8,9- HxCDF	1.3	0.81	0.34	0.21	0.056	0.08
1,2,3,4,6,7,8-HeCDF	45	39	14	0.75	1.2	5.4
1,2,3,4,7,8,9-HeCDF	5.3	4	0.89	0.032	0.056	0.37
OCDF	58	45	11	0.42	1.7	12
TEQ (I-TEF),	18/ 18/ 18	12/ 12/ 12	3.4/ 3.4/ 3.4	0.50/ 0.50/ 0.49	0.23/ 0.22/ 0.22	0.87/ 0.87/ 0.87
TEQ PCDD/F (WHO)	18/ 18/ 18	13/ 13/ 13	3.5/ 3.5/ 3.5	0.46/ 0.46/ 0.45	0.21/ 0.20/ 0.19	0.79/ 0.78/ 0.78
PCB 77	11	12	2.9	1.8	< 1.5	1.5
PCB 81	3.7	2.9	0.74	< 0.56	< 0.56	n.n.
PCB 126	3.3	4.6	1.1	< 0.27	< 0.27	0.31
PCB 169	1	2.9	0.35	n.n.	n.n.	n.n.
PCB 105	11	24	6.5	4	< 3.4	< 3.4
PCB 114	< 0.52	0.88	< 0.52	< 0.52	< 0.52	n.n.
PCB 118	18	35	10	< 10	< 10	< 10
PCB 123	1.2	1.7	< 1.1	n.n.	n.n.	n.n.
PCB 156	7.2	12	4.7	< 2.8	< 2.8	< 2.8
PCB 157	2.2	2.9	0.83	< 0.49	< 0.49	< 0.49
PCB 167	6.4	8.2	2.2	< 1.5	< 1.5	< 1.5
PCB 189	3.4	4.6	1.3	< 0.61	< 0.61	< 0.61
TEQ - PCB (WHO)	0.35/ 0.35/ 0.35	0.50/ 0.50/ 0.50	0.12/ 0.12/ 0.12	0.034/ 0.020/ 0.006	0.025/ 0.0125/ 0.000	0.031/ 0.031/ 0.031
PCB 28	< 66	< 66	n.n.	n.n.	< 66	n.n.
PCB 52	< 26	29	< 26	n.n.	< 26	n.n.
PCB 101	< 37	48	< 37	< 37	< 37	< 37
PCB 138	59	110	< 47	< 47	< 47	< 47
PCB 153	58	80	< 39	< 39	< 39	< 39
PCB 180	44	87	29	< 22	< 22	< 22
hexachlorobenzene	770	1500	2400	23	60	63

**Note:** #Upper bound (non detects = 100 % LOD), medium bound (non detects = 50 % LOD)/lower bound (non detects = 0)

Mexico	0911 5047	0911 5048	0911 5044	0911 5045	0911 5046
	Juventino Rosas 1 / 2611	Juventino Rosas 1 / 2614	Juventino Rosas 1 / 2605	Juventino Rosas 1 / 2607	Juventino Rosas 1 / 2609
Parameter	ng/kg	ng/kg	ng/kg	ng/kg	ng/kg
2,3,7,8-TCDD	n.n.	n.n.	n.n.	n.n.	n.n.
1,2,3,7,8-PCDD	n.n.	0.056	n.n.	0.14	n.n.
1,2,3,4,7,8-HxCDD	n.n.	0.064	n.n.	0.24	0.056
1,2,3,6,7,8- HxCDD	0.11	0.14	n.n.	0.65	0.18
1,2,3,7,8,9- HxCDD	0.2	0.22	n.n.	0.5	n.n.
1,2,3,4,6,7,8- HeCDD	0.91	1.4	3.1	10	1.6
OCDD	11	13	26	91	13
2,3,7,8-TCDF	n.n.	n.n.	0.16	0.38	n.n.
1,2,3,7,8-PCDF	n.n.	n.n.	n.n.	n.n.	n.n.
2,3,4,7,8-PCDF	n.n.	n.n.	n.n.	n.n.	n.n.
1,2,3,4,7,8-HxCDF	0.072	0.096	0.48	1.2	0.21
1,2,3,6,7,8- HxCDF	0.072	0.072	n.n.	0.29	0.12
2,3,4,6,7,8- HxCDF	0.064	0.056	n.n.	0.32	0.032
1,2,3,7,8,9- HxCDF	0.056	n.n.	n.n.	n.n.	n.n.
1,2,3,4,6,7,8-HeCDF	0.22	0.29	1.2	4.5	0.26
1,2,3,4,7,8,9-HeCDF	0.04	0.064	n.n.	0.3	n.n.
OCDF	0.18	0.34	n.n.	10	n.n.
TEQ (I-TEF), UB/ MB/ LB#	0.099/ <b>0.090</b> / 0.080	0.14/ <b>0.13</b> / 0.12	0.19/ <b>0.16</b> / 0.13	0.70/ <b>0.69</b> / 0.68	0.16/ <b>0.13</b> / 0.091
TEQ - PCDD/F (WHO)' UB/ MB/ LB#	0.094/ <b>0.082</b> / 0.070	0.15/ <b>0.15</b> / 0.14	0.18/ <b>0.14</b> / 0.11	0.68/ <b>0.67</b> / 0.66	0.18/ <b>0.13</b> / 0.08
PCB 77	< 1.5	< 1.5	< 1.5	< 1.5	< 1.5
PCB 81	< 0.56	n.n.	< 0.56	< 0.56	< 0.56
PCB 126	n.n.	0.37	0.35	0.33	0.35
PCB 169	n.n.	n.n.	n.n.	n.n.	n.n.
PCB 105	n.n.	3.5	< 3.4	< 3.4	3.9
PCB 114	n.n.	n.n.	< 0.52	< 0.52	< 0.52
PCB 118	< 10	< 10	< 10	< 10	< 10
PCB 123	n.n.	n.n.	n.n.	< 1,1	< 1,1
PCB 156	< 2.8	< 2.8	< 2.8	< 2.8	< 2.8
PCB 157	< 0.49	< 0.49	< 0.49	< 0.49	< 0.49
PCB 167	< 1.5	< 1.5	< 1.5	< 1.5	< 1.5
PCB 189	< 0.61	< 0.61	< 0.61	< 0.61	< 0.61
TEQ - PCB (WHO), UB/ MB/ LB#	0.0050/ <b>0.0025</b> / 0.000	0.038/ <b>0.037</b> / 0.037	0.035/ <b>0.035</b> / 0.035	0.033/ <b>0.033</b> / 0.033	0.036/ <b>0.036</b> / 0.035
PCB 28	n.n.	n.n.	n.n.	n.n.	n.n.
PCB 52	n.n.	n.n.	< 26	n.n.	n.n.
PCB 101	< 37	< 37	< 37	< 37	< 37
PCB 138	< 47	< 47	< 47	< 47	< 47
PCB 153	< 39	< 39	< 39	< 39	< 39
PCB 180	< 22	< 22	< 22	< 22	< 22
hexachlorobenzene	42	32	64	69	44

**Note:** #Upper bound (non detects =100 % LOD),medium bound (non detects = 50 % LOD)/lower bound (non detects = 0)

## A 4.2 Analytical results as provided by the JRC

Data in bold are LOD

Lab. Code:	DP-09-013-080609-1	DP-09-014-080609-2	DP-09-015-080609-3	DP-09-016-080609-4
Sample name:	INE 02549	INE 02564	INE 02584	INE 02598
Type of sample:	Salamanca 1 ASH	Salamanca 2 ASH	Salamanca 3 ASH	Juv. Rosas ASH
Volume sampled:	2	2	2	2
Data analysed:	6/27/2009	6/27/2009	6/27/2009	6/27/2009
				Insufficient Rec
Concentration:	pg/g	pg/g	pg/g	pg/g
<b>2,3,7,8 - PCDD/Fs</b>				
2378-TCDD	0.021	0.038	0.026	0.259
12378-PeCDD	0.051	0.093	0.058	1.471
123478-HxCDD	0.071	0.065	0.031	0.325
123678-HxCDD	0.107	0.307	0.067	0.271
123789-HxCDD	0.047	0.134	0.046	0.819
1234678-HpCDD	1.717	1.583	0.823	2.745
OCDD	3.832	6.569	4.422	19.241
2378-TCDF	0.727	0.771	0.171	0.124
12378-PeCDF	0.964	0.614	0.143	0.732
23478-PeCDF	1.172	0.914	0.150	0.651
123478-HxCDF	2.522	0.801	0.149	0.271
123678-HxCDF	2.423	0.357	0.177	0.481
234678-HxCDF	3.187	0.578	0.239	0.222
123789-HxCDF	0.917	0.126	0.071	0.301
1234678-HpCDF	17.033	1.646	1.206	5.713
1234789-HpCDF	2.863	0.121	0.184	0.879
OCDF	9.227	2.401	2.834	27.206
<b>Upper-bound</b>				
I-TEQ	1.9106	0.9283	0.2616	1.7785
1998 WHO-TEQ	1.9246	0.9668	0.2841	2.4723
2005 WHO-TEQ	1.6734	0.7735	0.2527	2.3368
<b>Middle-bound</b>				
I-TEQ	1.8758	0.8693	0.1737	0.9411
1998 WHO-TEQ	1.8769	0.8845	0.1817	1.2671
2005 WHO-TEQ	1.6258	0.6912	0.1667	1.2039
<b>Lower-bound</b>				
I-TEQ	1.8410	0.8102	0.0859	0.1036
1998 WHO-TEQ	1.8293	0.8022	0.0794	0.0618
2005 WHO-TEQ	1.5782	0.6089	0.0808	0.0711
<b>Total PCDD/Fs</b>				
TCDD	0.552	6.017	0.000	0.000
PeCDD	0.000	6.799	0.000	0.000
HxCDD	0.000	5.469	0.000	0.000
HpCDD	3.776	3.102	1.897	0.000
OCDD	3.832	6.569	4.422	19.241
TCDF	9.080	14.629	0.000	0.000
PeCDF	12.844	7.831	0.000	0.000
HxCDF	20.560	6.471	0.000	0.000
HpCDF	26.599	2.503	2.044	14.267
OCDF	9.227	2.401	2.834	27.206
Total PCDDs	8.16	27.96	6.32	19.24
Total PCDFs	78.31	33.83	4.88	41.47
Total PCDD/Fs	86.47	61.79	11.20	60.71



Lab. Code:	DP-09-017-080609-5	DP-09-018-080609-6	DP-09-019-080609-7
Sample name:	INE 02620	INE 02626	INE 02648
Type of sample:	Abasolo 1ASH	Abasolo1 ASH/Carbon	León 1 ASH
Volume sampled:	2.0	2.0	2.0
Data analysed:	6/27/2009	6/27/2009	6/27/2009
<b>Concentration:</b>	pg/g	pg/g	pg/g
<b>2,3,7,8 - PCDD/Fs</b>			
2378-TCDD	<b>0.060</b>	<b>0.096</b>	<b>0.059</b>
12378-PeCDD	<b>0.143</b>	<b>0.245</b>	<b>0.131</b>
123478-HxCDD	<b>0.123</b>	<b>0.039</b>	<b>0.074</b>
123678-HxCDD	<b>0.419</b>	<b>0.158</b>	<b>0.077</b>
123789-HxCDD	<b>0.214</b>	<b>0.092</b>	<b>0.065</b>
1234678-HpCDD	<b>0.839</b>	2.508	0.713
OCDD	10.195	29.197	4.221
2378-TCDF	0.881	4.633	0.370
12378-PeCDF	<b>0.497</b>	0.899	0.641
23478-PeCDF	<b>0.613</b>	0.966	0.461
123478-HxCDF	<b>0.498</b>	0.612	<b>0.273</b>
123678-HxCDF	<b>0.328</b>	0.485	<b>0.117</b>
234678-HxCDF	<b>0.471</b>	0.405	<b>0.079</b>
123789-HxCDF	<b>0.126</b>	<b>0.113</b>	<b>0.061</b>
1234678-HpCDF	2.014	2.111	0.725
1234789-HpCDF	<b>0.103</b>	0.568	<b>0.069</b>
OCDF	6.508	4.460	1.747
<b>Upper-bound</b>			
I-TEQ	0.8145	1.4852	0.5197
1998 WHO-TEQ	0.8707	1.5771	0.5799
2005 WHO-TEQ	0.7416	1.3726	0.4760
<b>Middle-bound</b>			
I-TEQ	0.4697	1.3561	0.4198
1998 WHO-TEQ	0.4903	1.3869	0.4472
2005 WHO-TEQ	0.4274	1.1824	0.3434
<b>Lower-bound</b>			
I-TEQ	0.1250	1.2270	0.3199
1998 WHO-TEQ	0.1099	1.1967	0.3146
2005 WHO-TEQ	0.1133	0.9922	0.2107
<b>Total PCDD/Fs</b>			
TCDD	1.050	1.811	0.467
PeCDD	0.000	0.000	0.000
HxCDD	0.000	1.851	0.000
HpCDD	0.000	5.907	0.947
OCDD	10.195	29.197	4.221
TCDF	7.505	54.737	6.975
PeCDF	0.000	7.986	3.071
HxCDF	0.000	3.109	0.730
HpCDF	2.680	3.944	1.136
OCDF	6.508	4.460	1.747
Total PCDDs	11.25	38.77	5.63
Total PCDFs	16.69	74.24	13.66
Total PCDD/Fs	27.94	113.00	19.29

Lab. Code:	DP-09-020-080609-8	DP-09-021-080609-9	DP-BLK-080609-10
<b>Sample name:</b>	INE 3338/08	INE 3345/08	Blk
<b>Type of sample:</b>	Salamanca 1ASH	León 1ASH	Blk
<b>Volume sampled:</b>	2.0	2.0	2.0
<b>Data analysed:</b>	6/27/2009	6/27/2009	6/27/2009
<b>Concentration:</b>	pg/g	pg/g	pg/g
<b>2,3,7,8 - PCDD/Fs</b>			
2378-TCDD	0.012	0.037	0.038
12378-PeCDD	0.061	0.151	0.076
123478-HxCDD	0.025	0.026	0.041
123678-HxCDD	0.054	0.029	0.041
123789-HxCDD	0.029	0.043	0.031
1234678-HpCDD	0.203	0.105	0.151
OCDD	2.607	2.179	1.930
2378-TCDF	0.097	0.109	0.059
12378-PeCDF	0.066	0.078	0.043
23478-PeCDF	0.074	0.120	0.057
123478-HxCDF	0.130	0.055	0.144
123678-HxCDF	0.154	0.035	0.095
234678-HxCDF	0.118	0.057	0.103
123789-HxCDF	0.029	0.028	0.022
1234678-HpCDF	0.756	0.481	0.444
1234789-HpCDF	0.097	0.034	0.054
OCDF	1.244	1.840	1.303
<b>Upper-bound</b>			
I-TEQ	0.1600	0.2245	0.1698
1998 WHO-TEQ	0.1871	0.2967	0.2047
2005 WHO-TEQ	0.1718	0.2720	0.1931
<b>Middle-bound</b>			
I-TEQ	0.0857	0.1167	0.0887
1998 WHO-TEQ	0.0975	0.1509	0.1047
2005 WHO-TEQ	0.0903	0.1390	0.0993
<b>Lower-bound</b>			
I-TEQ	0.0114	0.0088	0.0077
1998 WHO-TEQ	0.0079	0.0052	0.0048
2005 WHO-TEQ	0.0087	0.0060	0.0054
<b>Total PCDD/Fs</b>			
TCDD	0.000	0.000	0.000
PeCDD	0.000	0.000	0.000
HxCDD	0.000	0.000	0.000
HpCDD	0.000	0.000	0.000
OCDD	2.607	2.179	1.930
TCDF	0.000	0.000	0.000
PeCDF	0.000	0.000	0.000
HxCDF	0.000	0.000	0.000
HpCDF	0.961	0.878	0.599
OCDF	1.244	1.840	1.303
Total PCDDs	2.61	2.18	1.93
Total PCDFs	2.21	2.72	1.90
Total PCDD/Fs	4.81	4.90	3.83

Lab. Code:	DP-09-073-220410-1	DP-09-074-220410-2	DP-09-075-220410-3
Sample name:	SABK1 Bottom Ash A	SABK1 Duff A	SABK2 Duff
Type of sample:	ASH	Brick ingredient-Coal	Brick ingredient-Coal
Volume sampled:	9.85	10.04	10.04
Data analysed:	6/22/2010	6/22/2010	6/22/2010
<b>Concentration:</b>	pg/g	pg/g	pg/g
<b>2,3,7,8 - PCDD/Fs</b>			
2378-TCDD	0.01	0.01	0.06
12378-PeCDD	0.01	0.02	0.08
123478-HxCDD	0.02	0.01	0.08
123678-HxCDD	0.03	0.01	0.25
123789-HxCDD	0.02	0.02	0.16
1234678-HpCDD	0.16	0.17	2.56
OCDD	0.60	0.87	15.22
2378-TCDF	0.06	0.07	0.20
12378-PeCDF	0.10	0.07	0.23
23478-PeCDF	0.11	0.10	0.28
123478-HxCDF	0.20	0.18	0.56
123678-HxCDF	0.12	0.11	0.41
234678-HxCDF	0.11	0.09	0.47
123789-HxCDF	0.04	0.07	0.15
1234678-HpCDF	0.77	0.68	2.10
1234789-HpCDF	0.15	0.03	0.47
OCDF	2.17	2.22	4.10
<b>Upper-bound</b>			
I-TEQ	0.15	0.13	0.55
1998 WHO-TEQ	0.15	0.14	0.57
2005 WHO-TEQ	0.13	0.12	0.52
<b>Middle-bound</b>			
I-TEQ	0.07	0.07	0.50
1998 WHO-TEQ	0.07	0.07	0.50
2005 WHO-TEQ	0.06	0.06	0.45
<b>Lower-bound</b>			
I-TEQ	0.00	0.00	0.45
1998 WHO-TEQ	0.00	0.00	0.43
2005 WHO-TEQ	0.00	0.00	0.38
<b>Total PCDD/Fs</b>			
TCDD	0.00	0.00	4.54
PeCDD	0.00	0.00	2.47
HxCDD	0.00	0.00	3.08
HpCDD	0.00	0.00	4.94
OCDD	0.60	0.87	15.22
TCDF	0.00	0.00	5.84
PeCDF	0.00	0.00	6.37
HxCDF	0.00	0.00	4.44
HpCDF	0.00	0.00	3.90
OCDF	2.17	2.22	4.10
Total PCDDs	0.00	1.32	30.24
Total PCDFs	0.00	6.33	24.65
Total PCDD/Fs	0.00	7.65	54.89

Lab. Code:	DP-09-076-220410-4	DP-09-077-220410-5	DP-BLK-220410-6
Sample name:	SABK2 Bottom Ash	SABK2 Paper Pulp	BLANK
Type of sample:	Ash	Brick ingredient	BLANK
Volume sampled:	10	10.04	10
Data analysed:	6/22/2010	6/22/2010	6/21/2010
<b>Concentration:</b>	pg/g	pg/g	pg/g
<b>2,3,7,8 - PCDD/Fs</b>			
2378-TCDD	0.06	1.00	<b>0.01</b>
12378-PeCDD	0.39	0.34	<b>0.03</b>
123478-HxCDD	0.20	0.28	<b>0.03</b>
123678-HxCDD	0.57	3.77	<b>0.04</b>
123789-HxCDD	0.37	1.39	<b>0.03</b>
1234678-HpCDD	0.87	36.07	0.22
OCDD	1.14	299.00	0.64
2378-TCDF	1.20	18.15	0.06
12378-PeCDF	0.76	1.00	0.13
23478-PeCDF	0.84	1.06	0.09
123478-HxCDF	0.86	0.74	0.23
123678-HxCDF	0.46	0.31	0.11
234678-HxCDF	0.29	0.42	0.12
123789-HxCDF	0.13	0.26	0.08
1234678-HpCDF	1.06	5.19	0.66
1234789-HpCDF	0.27	0.59	0.21
OCDF	2.14	18.15	2.34
<b>Upper-bound</b>			
I-TEQ	1.15	5.02	0.16
1998 WHO-TEQ	1.34	4.91	0.17
2005 WHO-TEQ	1.16	4.74	0.15
<b>Middle-bound</b>			
I-TEQ	1.15	5.02	0.14
1998 WHO-TEQ	1.34	4.91	0.15
2005 WHO-TEQ	1.16	4.74	0.13
<b>Lower-bound</b>			
I-TEQ	1.15	5.02	0.13
1998 WHO-TEQ	1.34	4.91	0.12
2005 WHO-TEQ	1.16	4.74	0.10
<b>Total PCDD/Fs</b>			
TCDD	19.92	11.89	0.00
PeCDD	14.46	5.85	0.00
HxCDD	7.58	26.80	0.00
HpCDD	1.62	70.78	0.39
OCDD	1.14	299.00	0.64
TCDF	10.44	44.73	0.85
PeCDF	6.66	8.39	0.97
HxCDF	3.40	7.05	1.01
HpCDF	1.80	8.88	1.17
OCDF	2.14	18.15	2.34
Total PCDDs	44.73	414.32	1.03
Total PCDFs	24.44	87.19	6.33
Total PCDD/Fs	69.16	501.51	7.36



<b>Lab. Code:</b>	DP-09-102-041109-13	DP-09-103-041109-14	DP-09-104-041109-15
<b>Sample name:</b>	INE 1161/09	INE 403/09	INE 361/09
<b>Type of sample:</b>	Open fire 1-4 ASH	Tequisquiapan ASH	Chiapa ASH
<b>Volume sampled:</b>	2	2	2
<b>Data analysed:</b>	1/13/2010	1/13/2010	1/13/2010
Concentration:	pg/g	pg/g	pg/g
2,3,7,8 - PCDD/Fs			
2378-TCDD	0.06	0.04	0.12
12378-PeCDD	0.05	0.05	0.08
123478-HxCDD	0.05	0.02	0.06
123678-HxCDD	0.04	0.07	0.09
123789-HxCDD	0.04	0.08	0.09
1234678-HpCDD	0.44	0.34	0.83
OCDD	2.50	2.07	2.96
2378-TCDF	0.10	0.13	0.18
12378-PeCDF	0.08	0.03	0.07
23478-PeCDF	0.05	0.09	0.16
123478-HxCDF	0.11	0.06	0.08
123678-HxCDF	0.11	0.07	0.14
234678-HxCDF	0.18	0.10	0.37
123789-HxCDF	0.06	0.03	0.09
1234678-HpCDF	0.26	0.24	0.40
1234789-HpCDF	0.02	0.04	0.06
OCDF	0.66	0.68	1.04
<b>Upper-bound</b>			
I-TEQ	0.19	0.17	0.36
1998 WHO-TEQ	0.21	0.20	0.40
2005 WHO-TEQ	0.20	0.18	0.36
<b>Middle-bound</b>			
I-TEQ	0.10	0.09	0.19
1998 WHO-TEQ	0.11	0.10	0.20
2005 WHO-TEQ	0.10	0.09	0.19
<b>Lower-bound</b>			
I-TEQ	0.01	0.01	0.02
1998 WHO-TEQ	0.01	0.01	0.01
2005 WHO-TEQ	0.01	0.01	0.01
<b>Total PCDD/Fs</b>			
TCDD	0.45	0.00	0.00
PeCDD	0.00	0.00	0.00
HxCDD	0.00	0.00	0.00
HpCDD	0.85	0.68	1.05
OCDD	2.50	2.07	2.96
TCDF	0.00	0.00	0.00
PeCDF	0.00	0.00	0.00
HxCDF	0.00	0.00	0.00
HpCDF	0.34	0.40	0.75
OCDF	0.66	0.68	1.04
Total PCDDs	3.80	2.76	4.01
Total PCDFs	1.00	1.08	1.78
Total PCDD/Fs	4.80	3.83	5.79

Lab. Code:	DP-09-013-080609-1	DP-09-014-080609-2	DP-09-015-080609-3	DP-09-016-080609-4
Sample name:	INE 02549	INE 02564	INE 02584	INE 02598
Type of sample:	Salamanca 1 ASH	Salamanca 2 ASH	Salamanca 3 ASH	Juv. Rosas ASH
Volume sampled:	2	2	2	2
Data analysed:	6/27/2009	6/27/2009	6/27/2009	6/27/2009
Concentration:	pg/g	pg/g	pg/g	pg/g
<b>Non-ortho-substituted PCBs</b>				
PCB-81	2.4810	1.6762	0.7816	<b>1.2278</b>
PCB-77	8.327	5.605	3.702	<b>14.925</b>
PCB-126	1.475	0.703	<b>0.360</b>	0.826
PCB-169	<b>0.2058</b>	<b>0.1320</b>	<b>0.1252</b>	<b>0.3141</b>
<b>Upper-bound</b>				
1998 WHO-TEQ	0.1507	0.0724	0.0377	0.0873
2005 WHO-TEQ	0.1553	0.0754	0.0404	0.0939
<b>Middle-bound</b>				
1998 WHO-TEQ	0.150	0.072	0.019	0.044
2005 WHO-TEQ	0.152	0.073	0.020	0.048
<b>Lower-bound</b>				
1998 WHO-TEQ	0.149	0.071	0.000	0.001
2005 WHO-TEQ	0.149	0.071	0.001	0.001
HCB	<b>67</b>	<b>169</b>	<b>60</b>	<b>53</b>

Lab. Code:	DP-09-017-080609-5	DP-09-018-080609-6	DP-09-019-080609-7	DP-09-020-080609-8
Sample name:	INE 02620	INE 02626	INE 02648	INE 3338/08
Type of sample:	Abasolo 1 ASH	Abasolo 1 ASH/Carbon	León 1 ASH	Salamanca 1 ASH
Volume sampled:	2	2	2	2
Data analysed:	6/27/2009	6/27/2009	6/27/2009	6/27/2009
Concentration:	pg/g	pg/g	pg/g	pg/g
<b>Non-ortho-substituted PCBs</b>				
PCB-81	<b>0.2572</b>	1.2381	<b>0.3123</b>	<b>0.1392</b>
PCB-77	<b>4.672</b>	12.988	2.059	2.119
PCB-126	0.253	1.494	<b>0.262</b>	<b>0.243</b>
PCB-169	<b>0.0468</b>	0.3928	<b>0.0173</b>	<b>0.1266</b>
<b>Upper-bound</b>				
1998 WHO-TEQ	0.0262	0.1547	0.0266	0.0258
2005 WHO-TEQ	0.0272	0.1628	0.0271	0.0283
<b>Middle-bound</b>				
1998 WHO-TEQ	0.013	0.155	0.013	0.013
2005 WHO-TEQ	0.014	0.163	0.014	0.014
<b>Lower-bound</b>				
1998 WHO-TEQ	0.000	0.155	0.000	0.000
2005 WHO-TEQ	0.000	0.163	0.000	0.000
HCB	<b>76</b>	282	<b>76</b>	<b>83</b>

<b>Lab. Code:</b>	DP-09-021-080609-9	DP-BLK-080609-10
<b>Sample name:</b>	INE 3345/08	Blk
<b>Type of sample:</b>	León 1 ASH	Blk
<b>Volume sampled:</b>	2	2
<b>Data analysed:</b>	6/27/2009	6/27/2009

<b>Concentration:</b>	pg/g	pg/g
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**Non-ortho-substituted PCBs**

PCB-81	<b>0.2401</b>	<b>0.1294</b>
PCB-77	2.487	1.628
PCB-126	<b>0.057</b>	<b>0.099</b>
PCB-169	<b>0.0222</b>	<b>0.0152</b>

**Upper-bound**

1998 WHO-TEQ	0.0062	0.0103
2005 WHO-TEQ	0.0067	0.0106

**Middle-bound**

1998 WHO-TEQ	0.003	0.005
2005 WHO-TEQ	0.003	0.005

**Lower-bound**

1998 WHO-TEQ	0.000	0.000
2005 WHO-TEQ	0.000	0.000

HCB	<b>57</b>	195
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<b>Lab. Code:</b>	DP-09-073-220410-1	DP-09-074-220410-2	DP-09-075-220410-3
<b>Sample name:</b>	SABK1 bottom Ash	SABK1 Duff	SABK2 Duff
<b>Type of sample:</b>	ASH	Brick ingredient-Coal	Brick ingredient-Coal
<b>Volume sampled:</b>	9.85	10.04	10.04
<b>Data analysed:</b>	6/22/2010	6/22/2010	6/22/2010

<b>Concentration:</b>	pg/g	pg/g	pg/g
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**Non-ortho-substituted PCBs**

PCB-81	<b>0.19</b>	<b>0.16</b>	22.3
PCB-77	<b>2.1</b>	<b>5.1</b>	429
PCB-126	<b>0.22</b>	<b>0.14</b>	4.6
PCB-169	<b>0.047</b>	<b>0.028</b>	<b>0.21</b>

**Upper-bound**

1998 WHO-TEQ	0.023	0.015	0.508
2005 WHO-TEQ	0.024	0.015	0.517

**Middle-bound**

1998 WHO-TEQ	0.011	0.0073	0.508
2005 WHO-TEQ	0.012	0.0076	0.517

**Lower-bound**

1998 WHO-TEQ	0.000	0.000	0.508
2005 WHO-TEQ	0.000	0.000	0.517

HCB	177	<b>59</b>	107
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<b>Lab. Code:</b>	DP-09-076-220410-4	DP-09-077-220410-5	DP-BLK-220410-6
<b>Sample name:</b>	SABK2 Bottom Ash	SABK2 Paper Pulp	BLANK
<b>Type of sample:</b>	Ash	Brick ingredient	BLANK
<b>Volume sampled:</b>	10.0	10.04	10.0
<b>Data analysed:</b>	6/22/2010	6/22/2010	6/21/2010

<b>Concentration:</b>	pg/g	pg/g	pg/g
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**Non-ortho-substituted PCBs**

PCB-81	<b>0.33</b>	48.0	0.10
PCB-77	<b>5.0</b>	928	3.0
PCB-126	<b>0.37</b>	8.8	0.10
PCB-169	<b>0.043</b>	0.55	0.060

**Upper-bound**

1998 WHO-TEQ	0.038	0.984	0.015
2005 WHO-TEQ	0.039	1.005	0.017

**Middle-bound**

1998 WHO-TEQ	0.019	0.984	0.015
2005 WHO-TEQ	0.019	1.005	0.017

**Lower-bound**

1998 WHO-TEQ	0.000	0.984	0.015
2005 WHO-TEQ	0.000	1.005	0.017

HCB	75	1000	68
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<b>Lab. Code:</b>	DP-09-102-041109-13	DP-09-103-041109-14	DP-09-104-041109-15
	INE 1161/09	INE 403/09	INE 361/09
<b>Sample name:</b>	open fire 1-4 ash	Tequisquiapan Ash	Chiapa Ash
<b>Volume sampled:</b>	2	2	2
<b>Data analysed:</b>	1/13/2010	1/13/2010	1/13/2010

<b>Concentration:</b>	pg/g	pg/g	pg/g
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**Non-ortho-substituted PCBs**

PCB-81	0.46	0.41	0.40
PCB-77	8.20	6.32	6.64
PCB-126	<b>0.26</b>	0.55	0.40
PCB-169	1.71	1.98	1.92

**Upper-bound**

1998 WHO-TEQ	0.04	0.08	0.06
2005 WHO-TEQ	0.08	0.11	0.10

**Middle-bound**

1998 WHO-TEQ	0.03	0.05	0.04
2005 WHO-TEQ	0.07	0.09	0.08

**Lower-bound**

1998 WHO-TEQ	0.02	0.02	0.02
2005 WHO-TEQ	0.05	0.06	0.06

HCB	203	195	178
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Additional ash result from the 04/2008 sampling, extracted from Umlauf et al. 2009:

Sample name:	B lank	Brick 1	Brick 2	Brick 3	Brick 5
Type of sample:	Analytical Blank	Animal dung, garbage w	Tar, preheated	complete trunks and b	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
<b>2,3,7,8 - substituted PCDD/Fs</b>					
2378-TCDD	<b>0.14</b>	<b>0.02</b>	12.29	<b>0.62</b>	<b>0.16</b>
12378-PeCDD	<b>0.17</b>	<b>0.07</b>	17.58	<b>0.52</b>	<b>0.13</b>
123478-HxCDD	<b>0.06</b>	<b>0.10</b>	6.59	0.60	<b>0.11</b>
123678-HxCDD	<b>0.18</b>	<b>0.08</b>	5.82	5.07	<b>0.18</b>
123789-HxCDD	<b>0.09</b>	<b>0.07</b>	5.96	2.33	<b>0.17</b>
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	<b>0.16</b>	1.10	255.52	<b>0.33</b>	<b>0.22</b>
12378-PeCDF	<b>0.12</b>	0.93	114.16	<b>0.37</b>	<b>0.26</b>
23478-PeCDF	<b>0.14</b>	1.29	139.40	<b>0.58</b>	<b>0.33</b>
123478-HxCDF	<b>0.14</b>	0.63	76.07	<b>0.26</b>	<b>0.08</b>
123678-HxCDF	<b>0.10</b>	0.77	78.11	<b>0.32</b>	<b>0.10</b>
234678-HxCDF	<b>0.18</b>	0.64	87.43	<b>0.37</b>	<b>0.16</b>
123789-HxCDF	<b>0.02</b>	<b>0.08</b>	19.27	<b>0.34</b>	<b>0.09</b>
1234678-HpCDF	<b>0.44</b>	1.83	230.52	1.93	1.17
1234789-HpCDF	<b>0.05</b>	<b>0.16</b>	15.71	<b>0.26</b>	<b>0.11</b>
OCDF	1.03	1.28	41.13	4.25	2.82
<b>Upper-bound</b>					
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
<b>Total PCDD/Fs</b>					
TCDD	<b>0.00</b>	<b>0.00</b>	121.72	<b>0.00</b>	<b>0.00</b>
PeCDD	<b>0.00</b>	<b>0.00</b>	101.26	<b>0.00</b>	<b>0.00</b>
HxCDD	<b>0.00</b>	<b>0.00</b>	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	<b>0.00</b>	17.97	3992.00	<b>0.00</b>	<b>0.00</b>
PeCDF	<b>0.00</b>	12.69	1722.12	<b>0.00</b>	<b>0.00</b>
HxCDF	<b>0.00</b>	5.63	759.72	<b>0.00</b>	<b>0.00</b>
HpCDF	<b>0.00</b>	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
<b>Recovery %</b>					
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**

Additional ash result from the 04/2008 sampling, extracted Umlauf et al. 2009:

HCb (pg/g)	150	<150	1700	<150	<150
<b>Sample name:</b>	B lank	Brick 1	Brick 2	Brick 3	Brick 5
<b>Type of sample:</b>	Analytical Blank	animal dung, garbage w	Tar, preheated	complete trunks and l	complete trunks and t
<b>Volume sampled:</b>	2	1.99	2.02	2	2.08
<b>Data analysed:</b>	18/09/08	19/09/08	19/09/08	19/09/08	19/09/08
<b>Concentration:</b>	pg/g	pg/g	pg/g	pg/g	pg/g
<b>Non-ortho-substituted PCBs</b>					
PCB-81	<b>0.1305</b>	<b>0.2350</b>	19.0374	<b>0.4162</b>	<b>0.4699</b>
PCB-77	4.009	4.097	219.407	3.697	2.990
PCB-126	<b>0.114</b>	0.812	94.234	<b>0.402</b>	<b>0.402</b>
PCB-169	<b>0.1667</b>	<b>0.2711</b>	14.4047	<b>0.2254</b>	<b>0.0965</b>
<b>Upper-bound</b>					
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
<b>Recovery %</b>					
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

### A 4.3 Analytical results as provided by Krakow University

sample description	Salamanca 1	Salamanca 5	Chiapa de Corzo
Fuel used	combustole	combustoleo	used car oils
Compound	<b>Brick 3335/08</b>	<b>Brick 3340/08</b>	<b>Brick 353/09</b>
	<b>pg/g</b>	<b>pg/g</b>	<b>pg/g</b>
2,3,7,8-TeCDD	0.0072	0.0052	0.021
1,2,3,7,8-PeCDD	0.0066	0.0054	0.013
1,2,3,4,7,8-HxCDD	0.0113	0.0116	0.012
1,2,3,6,7,8-HxCDD	0.006	0.0038	0.015
1,2,3,7,8,9-HxCDD	0.011	0.0076	0.013
1,2,3,4,6,7,8-HpCDD	0.027	0.103	0.16
OCDD	0.25	0.72	0.47
2,3,7,8-TeCDF	0.0093	0.03	0.058
1,2,3,7,8-PeCDF	0.0099	0.0121	0.067
2,3,4,7,8-PeCDF	0.0143	0.02	0.1
1,2,3,4,7,8-HxCDF	0.0231	0.0339	0.11
1,2,3,6,7,8-HxCDF	0.018	0.013	0.16
1,2,3,7,8,9-HxCDF	0.0164	0.0145	0.049
2,3,4,6,7,8-HxCDF	0.0156	0.021	0.29
1,2,3,4,6,7,8-HpCDF	0.029	0.088	0.64
1,2,3,4,7,8,9-HpCDF	0.0215	0.019	0.091
OCDF	0.028	0.075	0.62
<b>WHO 1998 PCDD/F TEQ</b>	<b>0.034</b>	<b>0.037</b>	<b>0.17</b>
<b>WHO 2005 PCDD/F TEQ</b>	<b>0.030</b>	<b>0.033</b>	<b>0.15</b>
LOD - PCDD/F - TEQ	0.031	0.026	0.018
PCB 77	0.002	0.42	1.67
PCB126	0.011	0.055	0.119
PCB169	0.001	0.02	0.05
PCB 81	0.003	0.04	0.15
PCB105	0.24	1.02	5.02
PCB114	0.063	0.18	0.73
PCB118	0.63	2.27	9.78
PCB123	0.072	0.3	0.41
PCB156	0.07	0.21	0.67
PCB157	0.034	0.086	0.155
PCB167	0.02	0.1	0.33
PCB189	0.003	0.007	0.078
<b>WHO 1998 PCB TEQ</b>	<b>&lt;0,01</b>	<b>&lt;0,01</b>	<b>0.015</b>
<b>WHO 2005 PCB TEQ</b>	<b>&lt;0,01</b>	<b>&lt;0,01</b>	<b>0.014</b>
LOD - PCB - TEQ	0.01	0.01	0.0005
<b>WHO 1998 PCDD/F+PCB TEQ</b>	<b>0.044</b>	<b>0.047</b>	<b>0.18</b>
<b>WHO 2005 PCDD/F+PCB TEQ</b>	<b>0.044</b>	<b>0.047</b>	<b>0.16</b>
	<b>ng/g</b>	<b>ng/g</b>	<b>ng/g</b>
<b>HCB</b>	<b>&lt;0,10</b>	<b>&lt;0,10</b>	<b>&lt; 0,50</b>
LOD - HCB	0.10	0.10	0.50

sample description	Tequisquiapan	Abasolo 1	Abasolo 5	Abasolo 5
Fuel used	residues of oil and automotive additives	combustoleo/wood batchwise	combustoleo/wood batchwise	combustoleo/wood batchwise
Compound	<b>Brick 399/09</b>	<b>Brick 404/09</b>	<b>Brick 317/10</b>	<b>Brick 732/10</b>
	<b>pg/g</b>	<b>pg/g</b>	<b>pg/g</b>	<b>pg/g</b>
2,3,7,8-TeCDD	0.024	0.084	0.054	0.045
1,2,3,7,8-PeCDD	0.007	0.128	0.088	0.05
1,2,3,4,7,8-HxCDD	0.021	0.39	0.325	0.725
1,2,3,6,7,8-HxCDD	0.026	0.675	0.74	1.24
1,2,3,7,8,9-HxCDD	0.025	0.542	0.48	0.65
1,2,3,4,6,7,8-HpCDD	0.24	5.62	11.5	12
OCDD	0.61	14.4	28	36.5
2,3,7,8-TeCDF	0.015	0.342	0.45	0.65
1,2,3,7,8-PeCDF	0.079	0.535	0.89	1.35
2,3,4,7,8-PeCDF	0.14	5.25	12.5	26.4
1,2,3,4,7,8-HxCDF	0.16	2.29	3.6	10.2
1,2,3,6,7,8-HxCDF	0.24	3.46	3.5	11
1,2,3,7,8,9-HxCDF	0.016	0.135	0.28	0.3
2,3,4,6,7,8-HxCDF	0.6	10.8	35.2	35
1,2,3,4,6,7,8-HpCDF	1.28	21.1	99	80
1,2,3,4,7,8,9-HpCDF	0.16	0.16	0.5	0.9
OCDF	1.08	46.8	130	128
<b>WHO 1998 PCDD/F TEQ</b>	<b>0.23</b>	<b>5.0</b>	<b>12</b>	<b>20.3</b>
<b>WHO 2005 PCDD/F TEQ</b>	<b>0.20</b>	<b>4.0</b>	<b>9.5</b>	<b>15.0</b>
LOD - PCDD/F - TEQ	0.013	0.02	0.035	0.05
PCB 77	0.18	0.87	0.5	0.62
PCB126	0.093	3.74	1.15	0.58
PCB169	0.04	0.58	2.45	0.84
PCB 81	0.02	0.2	0.75	0.35
PCB105	1.14	2.46	32	11.8
PCB114	0.09	0.29	2.25	0.4
PCB118	2.2	3.28	17	6.25
PCB123	0.18	0.24	1.4	0.39
PCB156	0.49	1.14	4.4	3.15
PCB157	0.097	0.533	1.1	0.64
PCB167	0.18	0.42	0.85	0.88
PCB189	0.076	1.29	0.65	0.7
<b>WHO 1998 PCB TEQ</b>	<b>0.010</b>	<b>0.38</b>	<b>0.15</b>	<b>0.071</b>
<b>WHO 2005 PCB TEQ</b>	<b>0.011</b>	<b>0.39</b>	<b>0.19</b>	<b>0.084</b>
LOD - PCB - TEQ	0.0005	0.0025	0.0015	0.0015
<b>WHO 1998 PCDD/F+PCB TEQ</b>	<b>0.24</b>	<b>5.4</b>	<b>12.2</b>	<b>20.4</b>
<b>WHO 2005 PCDD/F+PCB TEQ</b>	<b>0.21</b>	<b>4.3</b>	<b>9.7</b>	<b>15.1</b>
	<b>ng/g</b>	<b>ng/g</b>	<b>ng/g</b>	<b>ng/g</b>
<b>HCB</b>	<b>&lt; 0,50</b>	<b>52.5</b>	<b>120</b>	<b>77</b>
LOD - HCB	0.50	1.2	1.5	0.7



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