IPEN®

The International POPs Elimination Network

Dioxin Sources Among Mexico's Industrial Sectors

NACEC Workshop on Reductions in Environmental Releases of Dioxins, Furans and Hexachlorobenzene: With a Focus on Industrial Sectors in Mexico,

31 January – 1 February, 2007, Monterrey, Nuevo Leon, Mexico

Pat Costner, Science Advisor, IPEN

STOCKHOLM CONVENTION ON PERSISTENT ORGANIC POLLUTANTS

Article 5

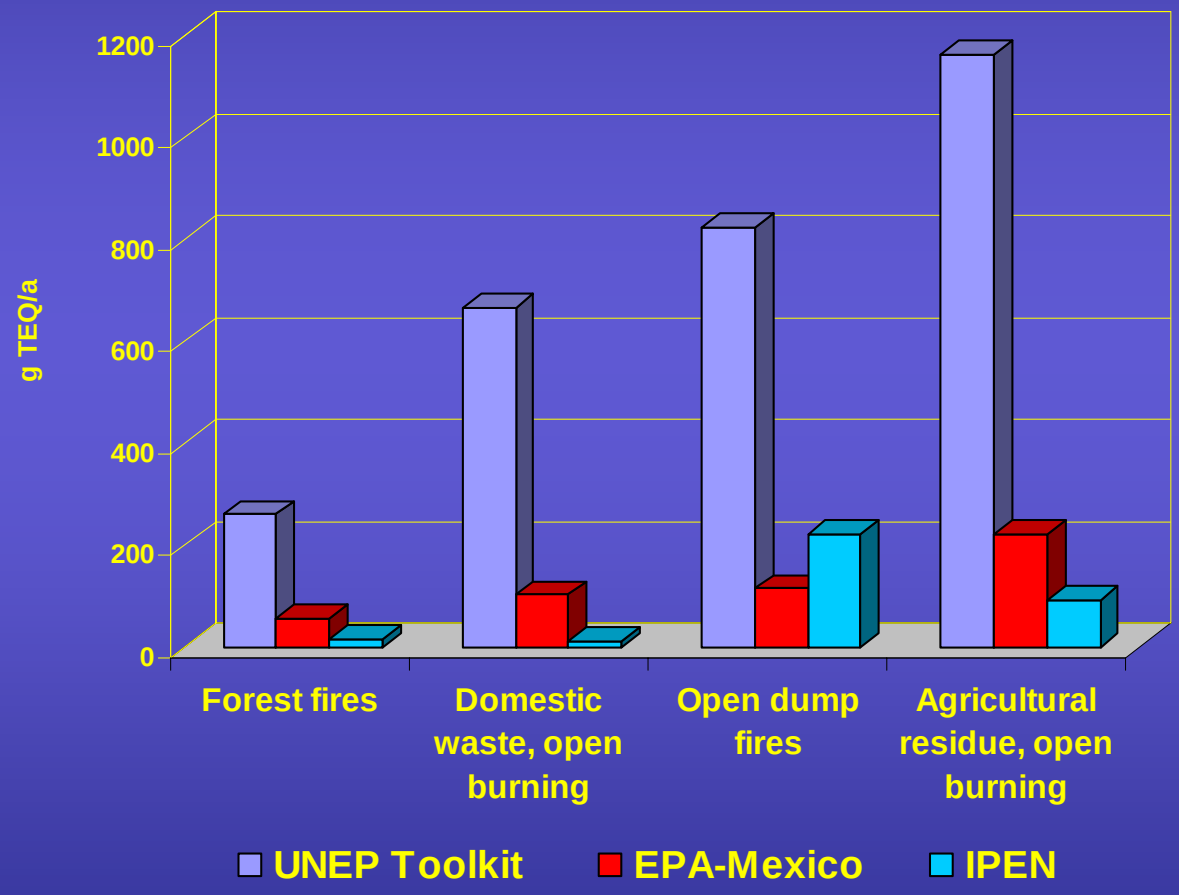
Measures to reduce or eliminate releases from unintentional production

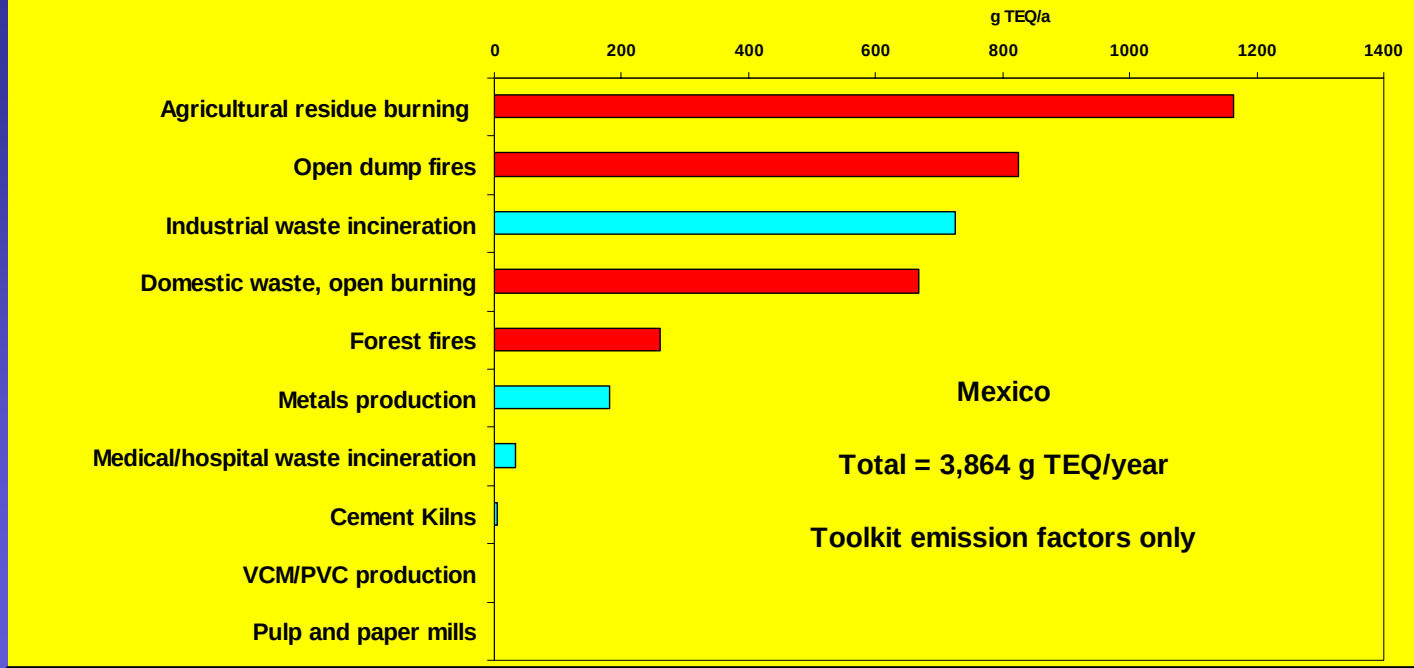
Each Party shall at a minimum take the following measures to reduce the total releases derived from anthropogenic sources of each of the chemicals listed in Annex C, with the goal of their continuing minimization and, where feasible, ultimate elimination:

(a) Develop an action plan or, where appropriate, a regional or subregional action plan within two years of the date of entry into force of this convention for it, and subsequently implement it as part of its implementation plan specified in Article 7, designed to identify, characterize and address the release of the chemicals listed in Annex C and to facilitate implementation of subparagraphs (b) to (e). The action plan shall include the following elements:

(i) An evaluation of current and projected releases, including the development and maintenance of source inventories and release estimates, taking into consideration the source categories identified in Annex C;

Comparison of Mexico dioxin releases from uncontrolled combustion, using different emission factors




g TEQ/a
0
200
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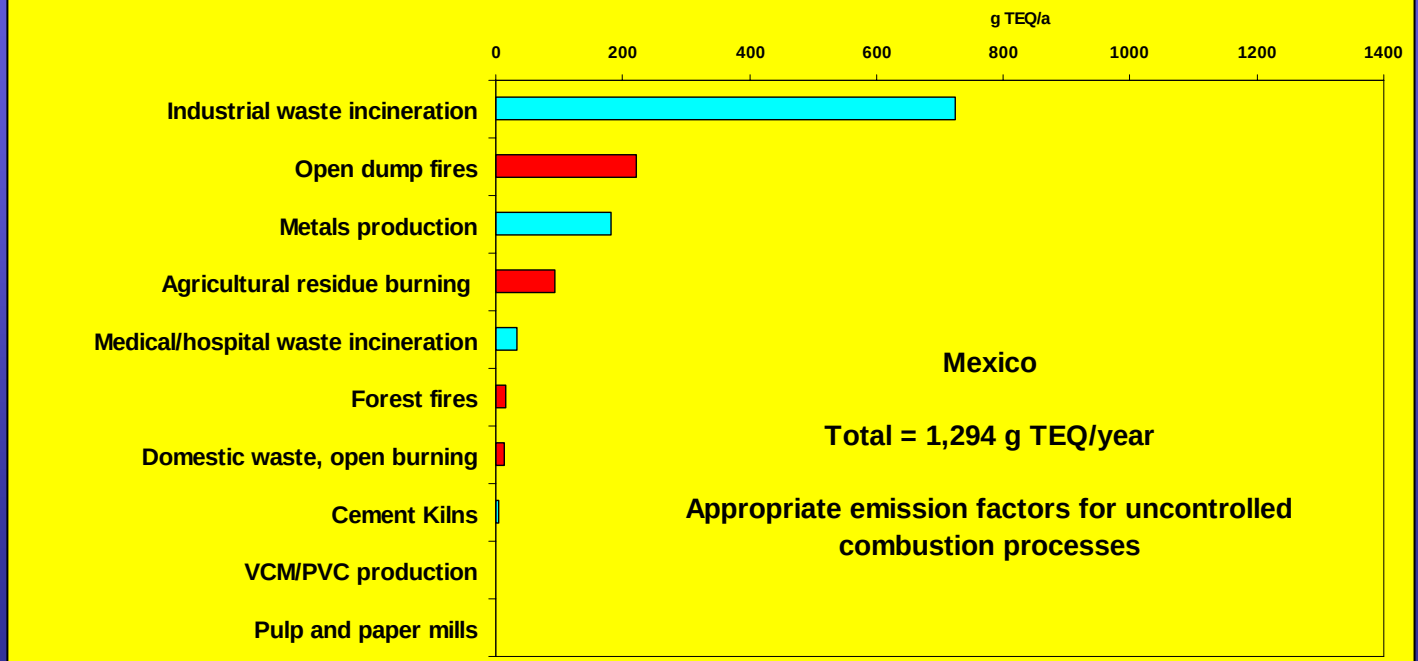
1200
1400
Agricultural residue burning
Open dump fires
Industrial waste incineration
Domestic waste, open burning
Forest fires
Metals production
Medical/hospital waste incineration
Cement Kilns
VCM/PVC production
Pulp and paper mills
Mexico
Total = 3,864 g TEQ/year
Toolkit emission factors only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Metals production
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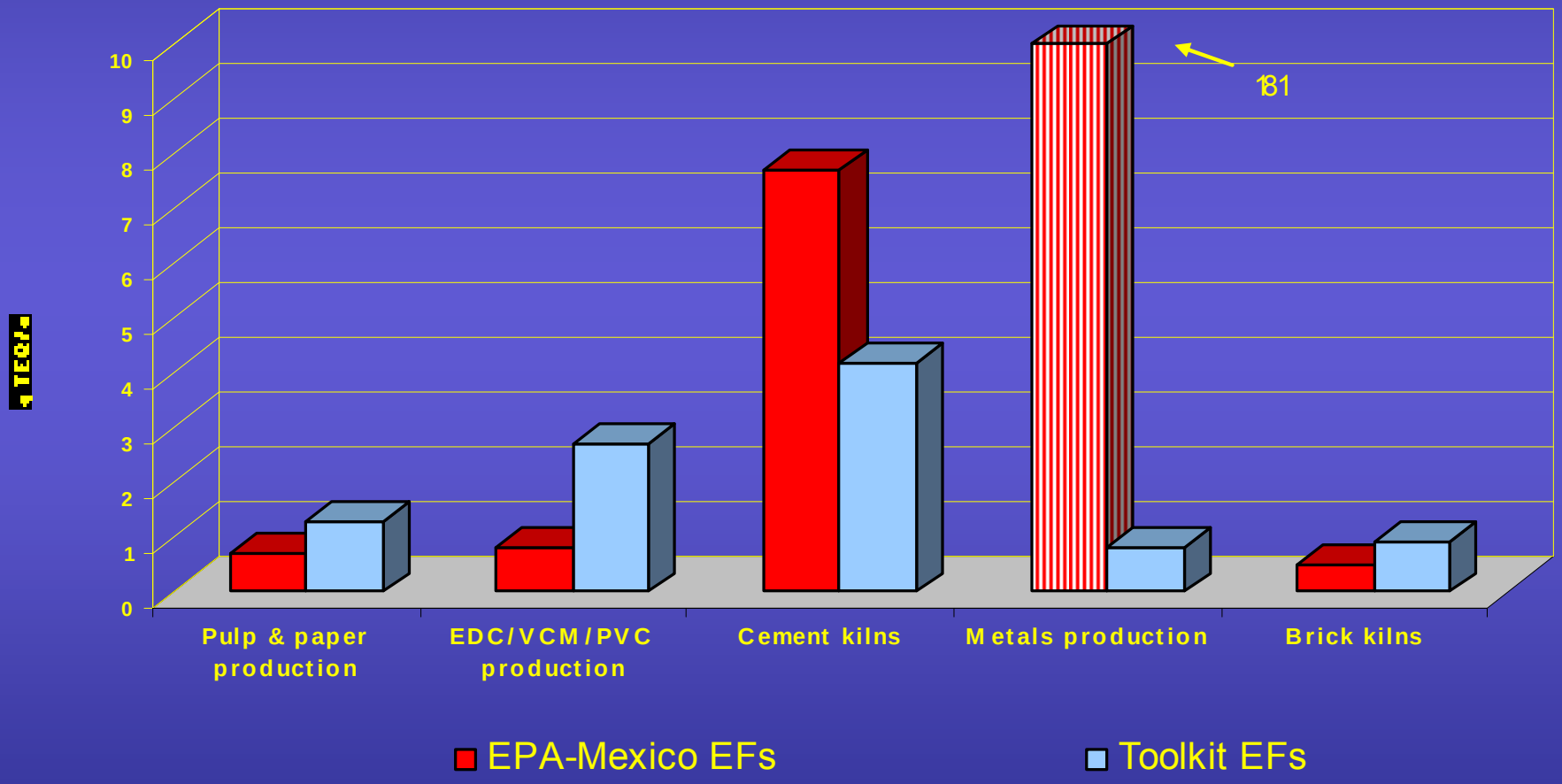
Medical/hospital waste incineration
Forest fires
Domestic waste, open burning
Cement Kilns
VCM/PVC production
Pulp and paper mills
Mexico
Total = 1,294 g TEQ/year
Appropriate emission factors for uncontrolled combustion processes

Industries addressed in Mexico's dioxin inventories and their estimated dioxin releases

	Estimated releases, g TEQ/yr	
	EPA-Mexico EFs	Toolkit EFs
Brick kilns	0.5	0.9
Metals production	181	0.8
Cement kilns	7.7	4.2
Chemicals production and use		
EDC/VCM/PVC production	0.8	2.7
Pulp & paper production	0.7	1.3

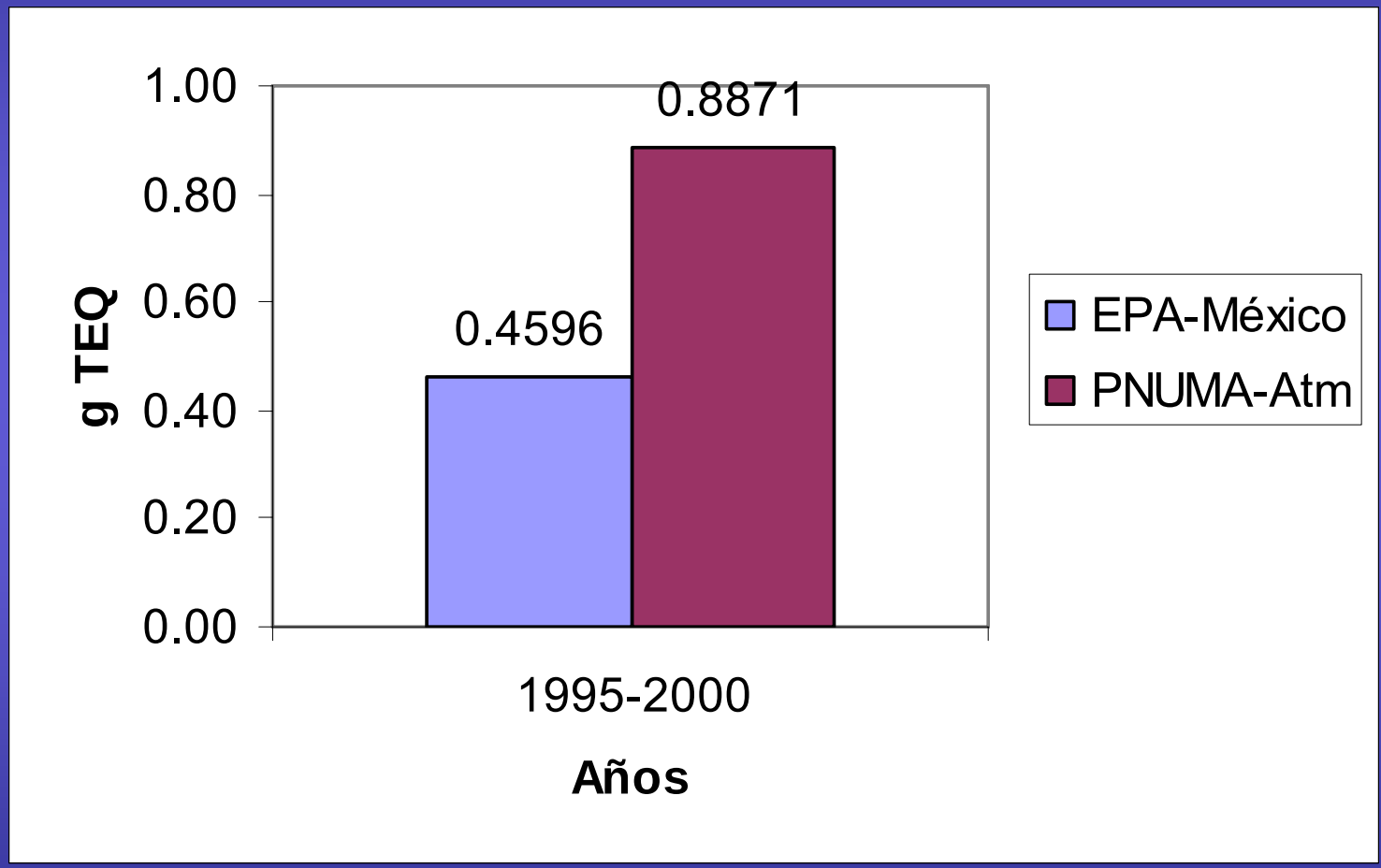
Comparison of Mexico dioxin releases from currently identified industrial sources, using different emission factors



Brick kilns

	Rank
Toolkit EFs	11
EPA-Mexico EFs	11
IPEN EFs for uncontrolled combustion	11

Brick kilns



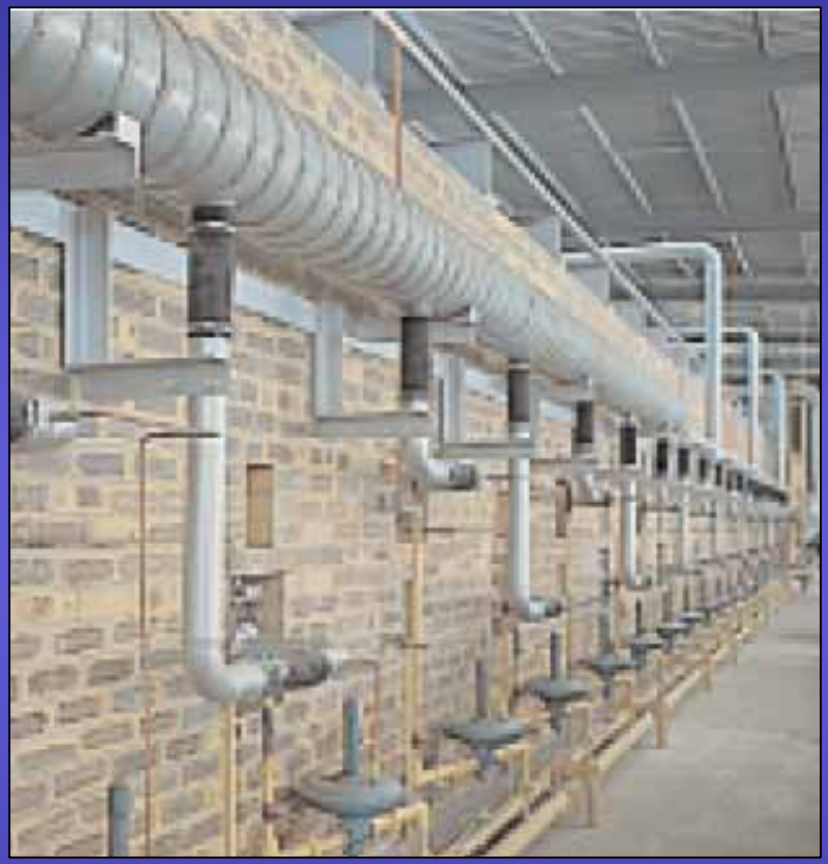
Gráfica 3.4 Estimación de la emisión de PCDD/F por producción de ladrillos en México (1995-2000)

Brick kilns

Materials burned	EPA-Mexico Emission Factors	UNEP Toolkit Emission Factor
Wood & sawdust	2 ng TEQ/kg	
Tires	228 ng TEQ/kg	
Oils	150 pg TEQ/L	
Oil or gas		0.2 μg TEQ/ton of bricks*

*"Tests in Germany showed emissions to air to vary from 0.002 to 0.23 μg TEQ/t of product. All tests were on relatively well-controlled plants.
An emission factor of 0.02 μg TEQ/t of product is to be applied to brick making processes with good control, consistently high temperatures and controls over the fuels used. Higheremissions may occur if poor controls are in place and wastes or poor quality fuels burned; then class 1 [0.2 μg TEQ/t of product]should be applied. " (UNEP Toolkit 2005)

Brick kilns

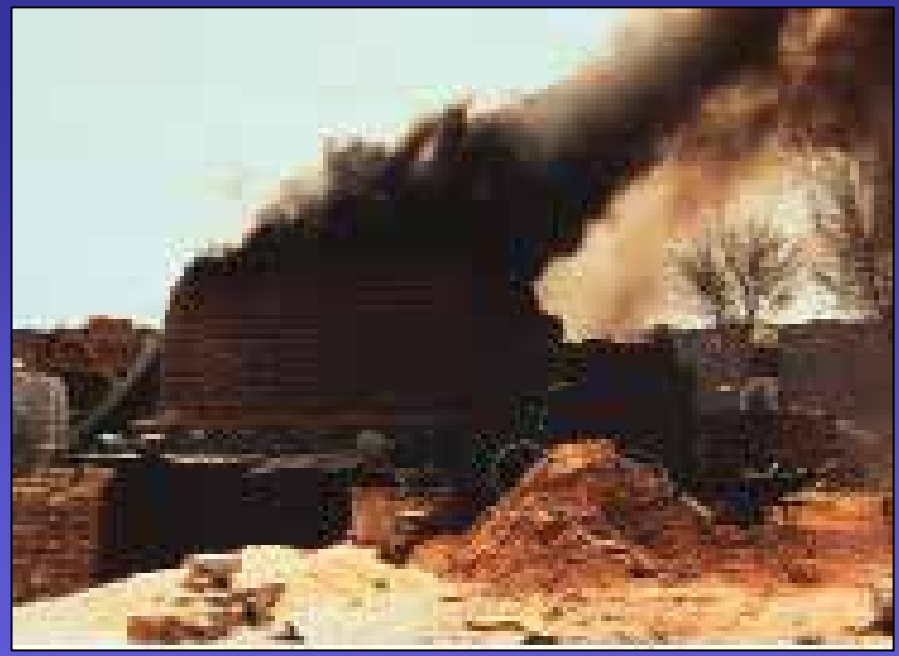


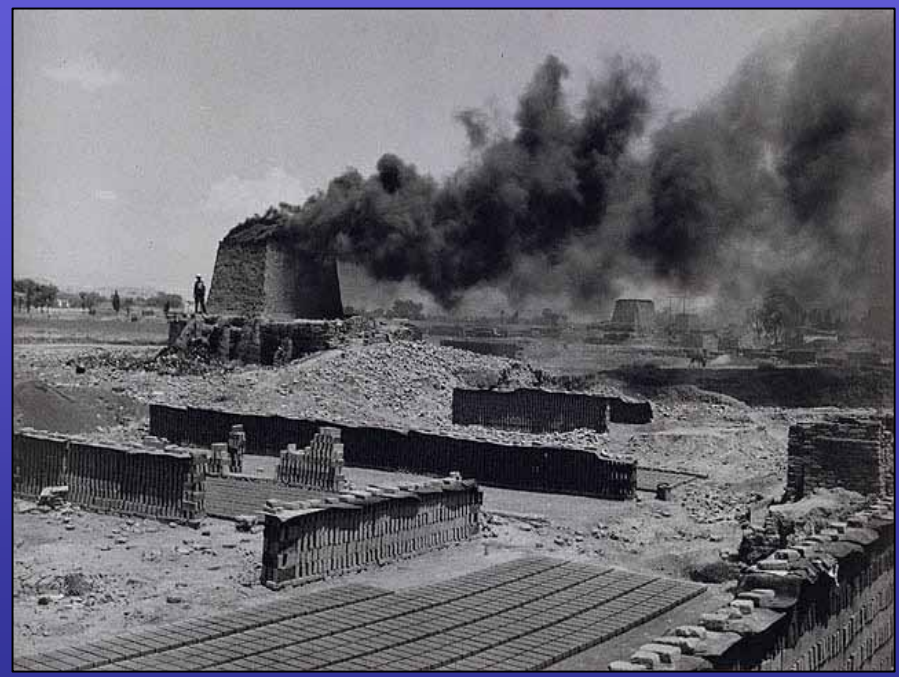
A typical tunnel kiln, a long kiln in which the green bricks are transported stacked on kiln cars past stationary heat sources. Such systems are commonly fired with gas or oil.

"These kilns near Torreon, Mexico fire about 25,000 bricks at once. Since all of the trees and biomass have already been cut down, they now rely on garbage and trash for fuel."
Goyer, K., 2006. Kilns and Brick Making. kgoyer@comcast.net

Brick kilns

According to Mexico's inventory, the materials burned in brick kilns include waste wood, sawdust, heavy fuel oil (combustóleo), other oils, diesel fuel, domestic waste, tires and, in modern kilns, natural gas and L.P.G.

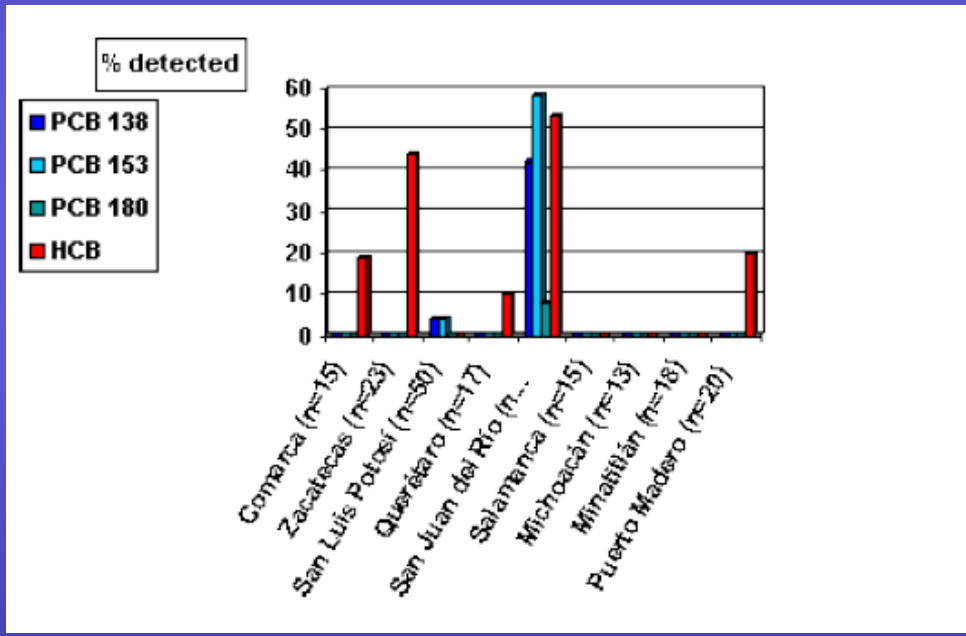




Brick kilns

Yarto et al., 2005. Persistent organic pollutants in children in contaminated sites of Mexico. Presented at Dioxin 2005, Toronto, Canada, 22-25 August 2005.

"Three of the five sites where Hexachlorobenzene was found have brick kiln production activities. HCB was detected in 50% of the children studied from the San Nicolas site. This was also the only site where measurable levels of PCB's (138, 153 and 180) were observed. Exposure to these compounds is probably due to the use of polluted oil as fuel in brick kilns or to the use of wood previously treated with this substance."



Brick kilns

The methods and materials used for firing brick kilns, in conjunction with sparse but compelling evidence of associated contamination, suggest that

1) emission factors for brick kilns in Mexico are considerably larger than those of the UNEP Toolkit and US EPA, and

2) dioxin releases from brick kilns are currently underestimated.

Metals Production

	Rank
Toolkit EFs	6
EPA-Mexico EFs	9
IPEN EFs for uncontrolled combustion	3

Metals Production

Mexico's dioxin inventory includes only the production of steel from scrap iron. 14,213 tons of steel were produced in 1999, some 18 percent by "acerias". (1) However, there is far greater production of ferrous and nonferrous metals taking place in Mexico that is not yet included in the inventory.

Metals Production in Mexico	Tons per year	Ref	Toolkit EFs (air) , μg/ton
Steel from scrap	14,213	1	0.01 - 10
Crude steel, total	8,500,000	4	0.01 - 10
Secondary aluminum	42 smelters, some as large as 72,000 tpy	2	1 - 350
Primary copper	1,122,000	1	.01 - .03
Secondary copper	5,000	3	5 – 800 [24.451 Yu]
Primary lead	360,000	1	[3.14 Yu]
Secondary lead	"large" sector (one of facilities produces 75,000 tpy)	1	0.5 - 80
Primary zinc	380,000	1	[0.166 Yu]
Secondary zinc	240,000	1	0.3 – 1,000

1. Acosta y Associados, 2001. Preliminary Atmospheric Emissions Inventory of Mercury in Mexico. Final Report. Prepared for Commission for Environmental Cooperation. No. 3.2.1.04
2. Light Metal Age: http://www.lightmetalage.com/producers.php.
3. IndexMundi, Country Facts: Mexico. http://www.indexmundi.com/mexico
4. Iron & Steel Statistics Bureau, 2005. WORLD STEEL REVIEW.. http:// www.issb.co.uk
Yu, et al., 2006. Emission of PCDD/Fs and dioxin-like from metallurgy industries in S. Korea. Chemosphere 62 (2006) 494–501.

Metals Production in Mexico

Cantidades en toneladas métricas

ESTABLECIMIENTO	SECTOR	ESTADO	DIOXINAS
xxxx S.A. de C.V.	Metalurgica (incluye la siderurgica)	Coahuila	0.3400

Registro de Emisiones y Transferencia de Contaminantes (RETC)

Cement Kilns

	Rank
Toolkit EFs	8
EPA-Mexico EFs	4
IPEN EFs for uncontrolled combustion	8

Cement kilns

"*There are 31 cement plants in Mexico, 28 of which are operated by three cement manufacturing group: Cementos Apasco, Cementos Mexicanos y Cementos Cruz Azul. 25 of the Mexican cement plants are authorized to burn "alternate" fuels, including hazardous waste equaling from 5 percent up to 30 percent of the total heat input required by the process. A number of the cement plants located in Mexico have taken advantage of this authorization, burning both waste combustible liquid and solid hazardous waste.*"

Acosta y Associados, 2001. Preliminary Atmospheric Emissions Inventory of Mercury in Mexico. Final Report. Prepared for Commission for Environmental Cooperation. No. 3.2.1.04

TABLE 4.10 AUTHORIZED CEMENT PLANTS TO BURN ALTERNATE FUELS

PLANT	STATE	CITY	%*
Cementos Apasco, S.A. de C.V.	Coahuila	Ramos Arizpe	10-30
Cementos Apasco, S.A. de C.V.	Veracruz	Ixtaczoquitlán	10-30
Cementos Apasco, S.A. de C.V.	Guerrero	Acapulco	10-30
Cementos Apasco, S.A. de C.V.	Edo. De México	Apaxco	10-30
Cooperativa La Cruz Azul	Hidalgo	Tula de allende	10-30
Cooperativa La Cruz Azul	Oaxaca	Lagunas	10-30
Cementos Mexicanos, S.A. de C.V.	Coahuila	Torreón	10-25
Cementos Mexicanos,S.A. de C.V.	Hidalgo	Huichapan	10-30
Cementos Guadalajara, S.A. de C.V.	B.C.	Ensenada	5
Cementos Maya, S.A. de C.V.	Yucatán	Mérida	5
Cementos Portland Moctezuma	Morelos	Juitepec	25
Cementos Apasco, S.A. de C.V.	Colima	Tecomán	10-30
Cementos de Chihuahua, S.A. de C.V.	Chihuahua	Samalayuca	5
Cementos del Yaqui, S.A. de C.V.	Sonora	La Colorada	5
Cemento Portland Nacional, S.A. de C.V.	Sonora	Hermosillo	5
Cooperativa La Cruz Azul, S.C.L.	Hidalgo	Tula de Allende	5
Cementos del Yaqui, S.A. de C.V.	Edo. De México	Tlanepantla	5
Preconcreto de Alta Resistencia, S.A. de C.V.	Jalisco	Tlaquepaque	5
Cementos Mexicanos, S.A. de C.V.	S.L.P	Tamulín	5
Cementos Tolteca, S.A. de C.V.	Puebla	Tepeaca	5
Cementos Mexicanos, S.A. de C.V.	N. L.	Monterrey	5
Cementos Apasco, S.A. de C.V.	Tabasco	Macuspana	5
Cementos Tolteca, S.A. de C.V.	Jalisco	Zapotiltic	5
Cemento Portland Blanco de México, S.A. de C.V.	Hidalgo	Atotonilco de tula	5
Cementos Tolteca, S.A. de C.V.	Hidalgo	Atotonilco de tula	5
Cementos Mexicanos, S.A. de C.V.	S.L.P.	Valles	5

* % of energy requirements replaced by alternate fuels

Figure 1.1. Distribution of cement kilns

Source: National Association of Cement Producers (Canacem)

Cement kilns

Cantidades en toneladas métricas

ESTABLECIMIENTO	SECTOR	ESTADO	DIOXINAS
xxxxxxx S.A. de C.V.	Cemento	Colima	30.6056

It should be noted that these are only preliminary draft values and can in no way be assumed to reflect reality.

Registro de Emisiones y Transferencia de Contaminantes (RETC)
http://app1.semarnat.gob.mx/retc/index.php

Lime kilns

	Rank
Toolkit EFs	Not included in inventory
EPA-Mexico EFs	
IPEN EFs for uncontrolled combustion	

Lime kilns

Lime kilns are not yet included in Mexico's dioxin inventory.

"There are 80 registered lime plants in Mexico with a total rated capacity of 5,102,323 tons of hydrated lime and one plant with 140,000 tons of quick lime (55, 57). The majority of these plants operate vertical or shaft kilns. Only a few utilize a rotary kiln for intermediary quick lime production. Only Mexicana de Cobre lime plant in Agua Prieta in the state of Sonora produces quick lime as its final product. All others commercialize hydrated lime."

Acosta y Associados, 2001. Preliminary Atmospheric Emissions Inventory of Mercury in Mexico. Final Report. Prepared for Commission for Environmental Cooperation. No. 3.2.1.04

Table 42: Emission factors for lime production

Classification	Emission Factors – µg TEQ/t of Lime Produced				
	Air	Water	Land	Product	Residue
1. No dust control or contaminated, poor fuels	10	NA	ND	ND	ND
2. Lime production using dust abatement	0.07	NA	ND	ND	ND

Chemicals Production

Chemicals production

Cantidades en toneladas métricas

ESTABLECIMIENTO	SECTOR	ESTADO	DIOXINAS
xxxxxx S.A. de C.V.	Quimica	Coahuila	0.0600

It should be noted that these are only preliminary draft values and can in no way be assumed to reflect reality.

Registro de Emisiones y Transferencia de Contaminantes (RETC)
http://app1.semarnat.gob.mx/retc/index.php

Chemicals production

Chlor-Alkali production is not included in Mexico's dioxin inventory

"The formation of dioxins in the chlorate and chlor-alkali industry has decreased significantly since the use of graphite electrodes was abandoned at the end of the 1970s, and with the declining use of the mercury method. The titanium electrodes now employed do contribute to dioxin formation, but to an appreciably lesser extent. The most significant releases of dioxins occur from landfills and contaminated sites associated with the chlor-alkali industry, accompanying particulates released to water and sediments."

Swedish Environmental Protection Agency, 2005. Survey of Unintentionally Produced Substances. Naturvårdsverket, Stockholm, Sweden

Chlor-alkali

"There are five chlor-alkali plants in Mexico with a combined production of 447,000 tons per year of chlorine gas. 147,000 tons of chlorine per year are produced with the mercury cathode technology in three of these plants that utilize the mercury cell production process."

TABLE 4.13 CHLOR-ALKALI PLANTS IN MEXICO

STATE & CITY	PRODUCER	YEAR BUILT	CELL TYPE	CHLORINE PRODUCTION/ Hg CELLS
Jalisco El Salto	Mexichem, S.A. de C.V.	1976	OxyTech DS45 diaph	None
Mexico Santa Clara	Mexichem, S.A. de C.V.	1958	De Nora 14TGL, 14x3F merc Mathiesen E11 merc. '66	18,000
Monterrey Nuevo Leon	Industria Química del Itsmo, S.A.	1958	Mathiesen E8 merc	29,000
Veracruz Coatzacoalcos	Industria Química del Itsmo, S.A.	1967	De Nora 18X4, 18H4'72 merc	100,000
Pajaritos	Cloro de Tehuantepec S.A. de C.V.	1980	Glanor 1144 diaph.	none

Source: The Chlorine Institute (*47*) and INE (*21*) with data from ANIQ (*5*).

Acosta y Associados, 2001. Preliminary Atmospheric Emissions Inventory of Mercury in Mexico. Final Report. Prepared for Commission for Environmental Cooperation. No. 3.2.1.04

Chemical production

Cantidades en toneladas métricas

ESTABLECIMIENTO	SECTOR	ESTADO	1,2-DICLOROBENCENO
xxxxxxxxx S.A. de C.V.	PETROLEO Y PETROQUIMICA	VERACRUZ	0.0008
xxxxxxxxx S.A. de C.V.	PETROLEO Y PETROQUIMICA	TLAXCALA	0.0001

ESTABLECIMIENTO	SECTOR	ESTADO	TETRACLORURO DE CARBONO
xxxxxxxxx S.A. de C.V.	QUIMICA	VERACRUZ	1.0720
xxxxxxxxx S.A. de C.V.	QUIMICA	MEXICO	0.0040

It should be noted that these are only preliminary draft values and can in no way be assumed to reflect reality.

Registro de Emisiones y Transferencia de Contaminantes (RETC)
http://app1.semarnat.gob.mx/retc/index.php

Cantidades en toneladas métricas

ESTABLECIMIENTO	SECTOR	ESTADO	1,4-DICLOROBENCENO
xxxxxxxxx S.A. de C.V.	QUIMICA	NUEVO LEON	250.0990
xxxxxxxxx S.A. de C.V.	CELULOSA Y PAPEL	DISTRITO FEDERAL	0.0003
xxxxxxxxx S.A. de C.V.	QUIMICA	PUEBLA	0.0000
xxxxxxxxx S.A. de C.V.	PETROLEO Y PETROQUIMICA	TLAXCALA	0.0000

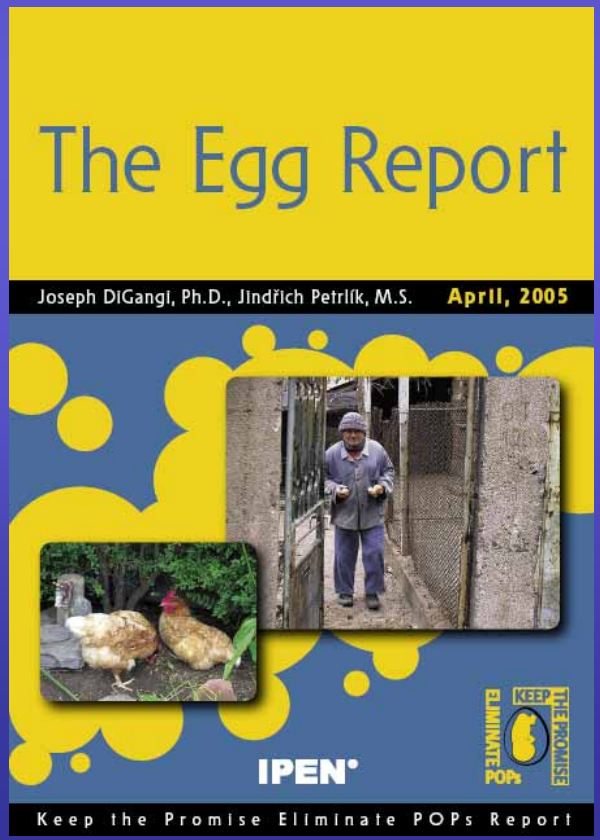
ESTABLECIMIENTO	SECTOR	ESTADO	BIFENILOS POLICLORADOS
xxxxxxxxxx	PETROLEO Y PETROQUIMICA	PUEBLA	0.1500

ESTABLECIMIENTO	SECTOR	ESTADO	ACIDO 2,4 DICLOROFENOXIACETICO
xxxxxxxxx S.A. de C.V	QUIMICA	TLAXCALA	9.5300

It should be noted that these are only preliminary draft values and can in no way be assumed to reflect reality.

Registro de Emisiones y Transferencia de Contaminantes (RETC)
http://app1.semarnat.gob.mx/retc/index.php

High dioxin levels in eggs of yard chickens are evidence of dioxin releases from chemical production.



Czech Republic	Spolchemie Usti nad Labem; chlorinated solvents manufacturing and incinerator near confluence of two rivers	2X background levels of dioxins 1.5X EU action level for dioxins 0.2X EU HCB limit
India – Eloor	Hindustan Insecticides Ltd.; manufacturing of DDT, lindane and other pesticides; POPs waste stockpile; hazardous waste incinerator; wetland area with direct discharges to creek and tidal inflow and outflow of Periyar River	14X background levels of dioxins 4.6X EU limit for dioxins
Mexico	Pajaritos PEMEX petrochemical complex; Veracruz; VCM production for PVC plastic & incinerators	19X background levels of dioxins 6X EU limit for dioxins 1.5X EU proposed PCB limit
Russia - Gorbatovka	Near "Orgsteklo" Dzerzhinsk; former PCBs production and hazardous waste incinerator, chlorinated hazardous wastes dumpsites	12X background levels of dioxins 4X EU limit for dioxins 4.5X EU proposed PCB limit
Russia - Igumnovo	Near "Kaprolaktam" and "Korund" Dzerzhinsk; pesticides production, chlor alkali plant, PVC plastic and incinerator; near Oka River	44X background levels of dioxins 15X EU limit for dioxins 9X EU proposed PCB limit
USA	Mossville, Lousiana; chlor alkali plants for PVC plastic, coal power plant, oil refinery, and petrochemical plant	6X background levels of dioxins 2X EU limit for dioxins 1.2X EU proposed action level for PCBs

Recommendations

- In preparing the new and/or revising Mexico's dioxin inventory –
  - Consider the IPEN review of emission factors for uncontrolled combustion in developing or revising Mexico's dioxin inventory;
  - Include known sources that are not yet addressed, e.g., various ferrous and nonferrous metal production, lime kilns, chemicals production (e.g, chlor-alkali, chlorobenzenes, 2,4-D);
  - Consider more appropriate emission factors for brick kilns;
  - Compile and/or refine activity data for metals production, in particular secondary aluminum and secondary lead production.

- Encourage and/or require as part of the permitting process, the measurement of dioxin concentrations in releases to air, water, residues and products of industrial sources in Mexico that have significant potential for dioxin releases, e.g., industrial processes that make and/or use chlorine in any form;

- Develop guidelines for calculating industrial release factors for dioxins for reporting releases to the *Registro de Emisiones y Transferencia de Contaminantes* (RETC);

Recommendations, continued

- Solicit financial and technical support for a national biomonitoring program in Mexico of breast milk, eggs, fish, etc. to identify elevated exposures from nearby sources and to establish the overall effectiveness of efforts to prevent and reduce dioxin releases;
- To achieve the goal of *"continuous minimization and, where feasible, ultimate elimination"* of dioxins from brick kilns,

  > establish a program of substitution for this sector, including best practices/techniques, public education, and economic incentives,

  > prohibit the firing of kilns with domestic waste, industrial waste, waste oils, tires and other materials likely to increase dioxin formation, e.g., those that may cause substantial increases in inputs of chlorine in any form and metals.

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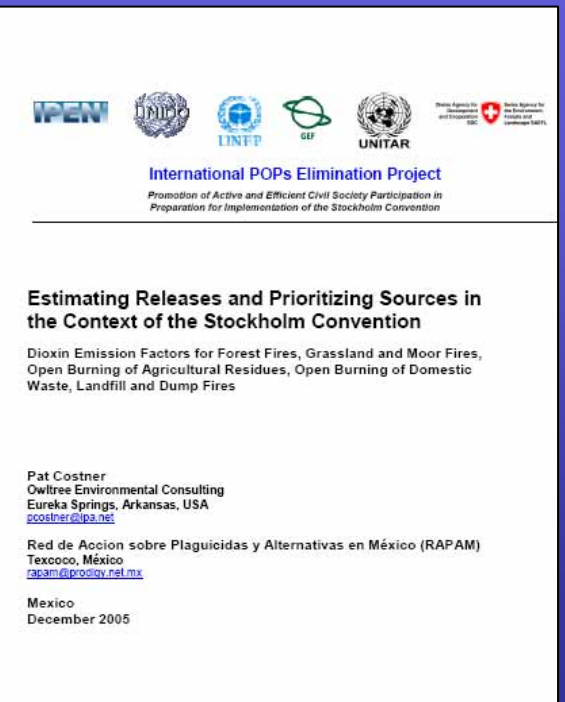
The International POPs Elimination Network

Muchas gracias

Thank you



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International POPs Elimination Project

Promotion of Active and Efficient Civil Society Participation in Preparation for Implementation of the Stockholm Convention

Estimating Releases and Prioritizing Sources in the Context of the Stockholm Convention

Dioxin Emission Factors for Forest Fires, Grassland and Moor Fires, Open Burning of Agricultural Residues, Open Burning of Domestic Waste, Landfill and Dump Fires

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