Disposal of Pesticides
A "Burning" question?

Tsakhkadzor, Armenia

31st May 2011

Alan Watson C.Eng

Senior Scientific Advisor International POPs Elimination Network

Public Interest Consultants

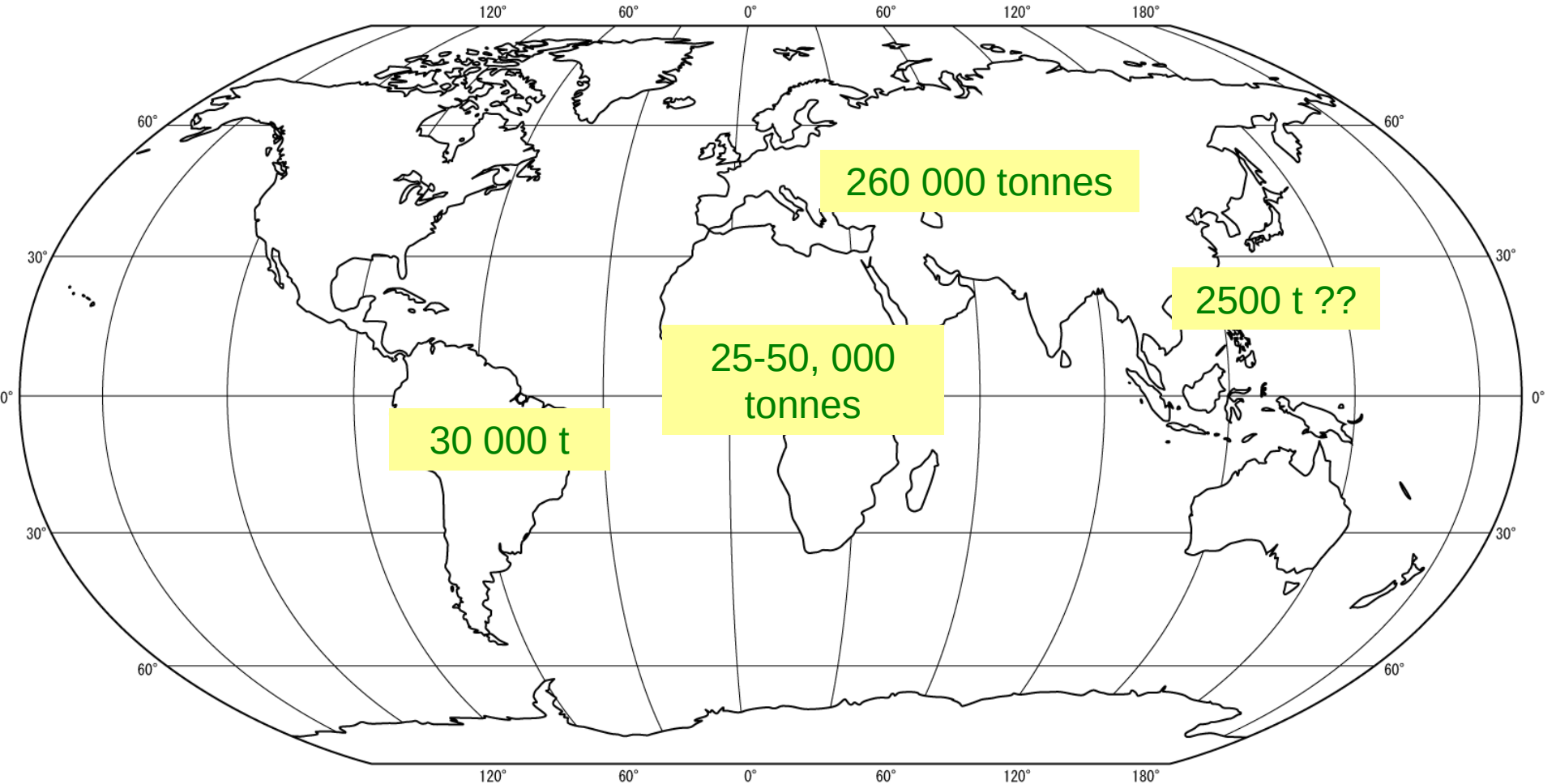
Outline

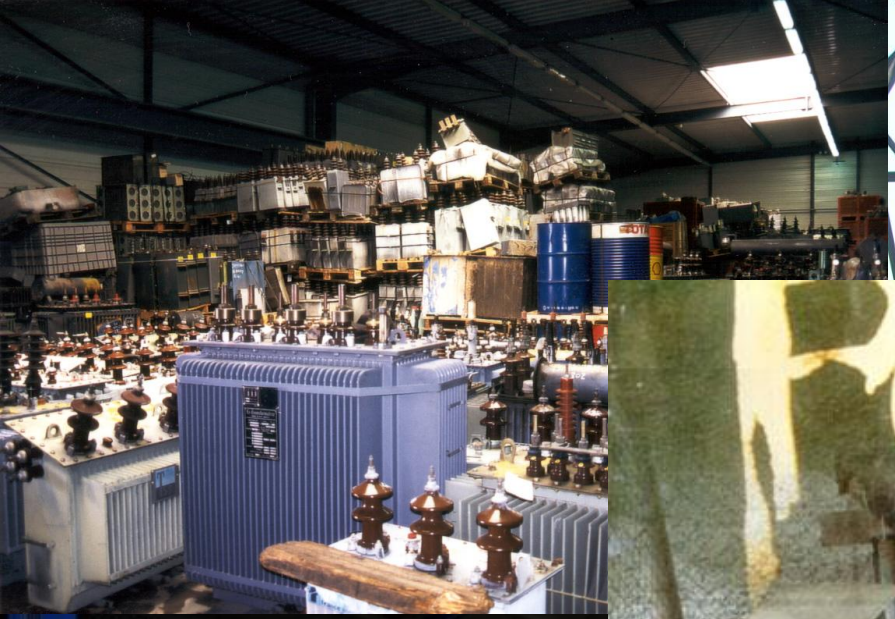
What are:

- the Issues?
- the problems with landfill/Cement Kilns/Incinerators?
- the requirements of alternatives?
- the options to consider?

Stockpiles of POPs Pesticides

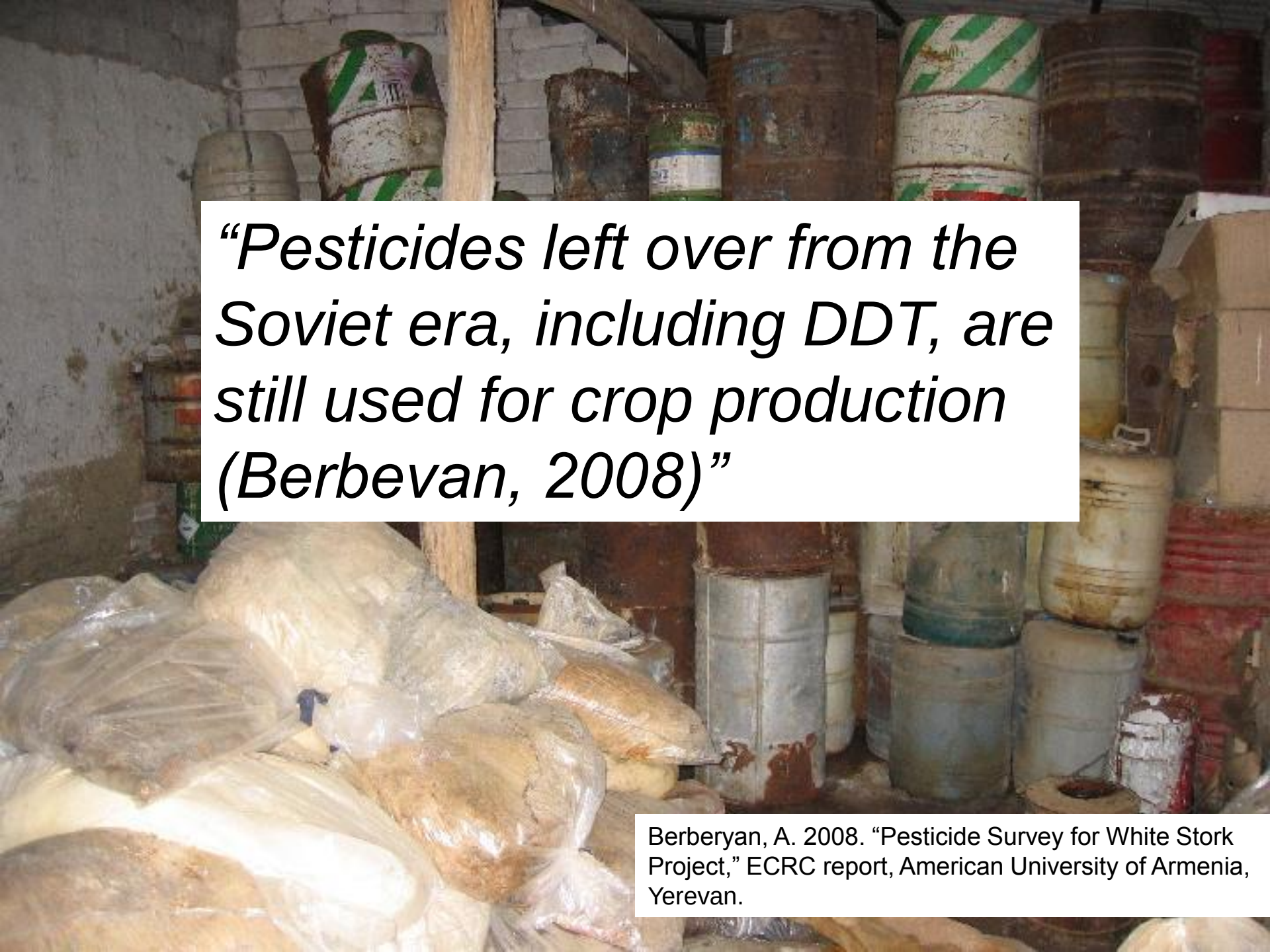
POPs wastes – a global issue






PCB


04/02/2009



“Pesticides left over from the Soviet era, including DDT, are still used for crop production (Berbevan, 2008)”

Berberyan, A. 2008. “Pesticide Survey for White Stork Project,” ECRC report, American University of Armenia, Yerevan.

Berto Collet, Tauw, The Netherlands

Stockholm Obligations

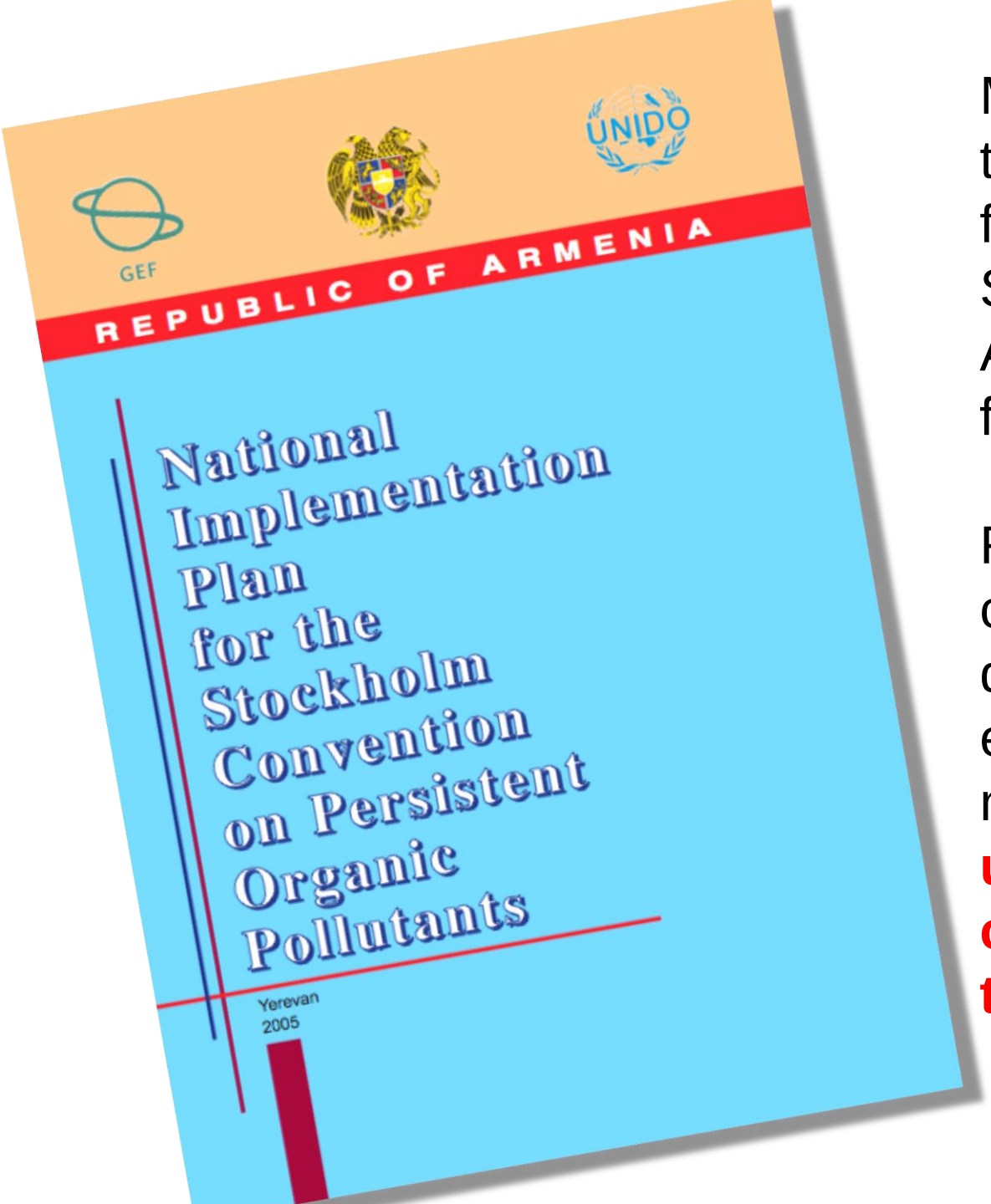
Article 6, 1(d) (ii) requires POPs:

*"Disposed of in such a way that the **POPs content is destroyed or irreversibly transformed** so that they do not exhibit the characteristics of POPs or otherwise disposed of in an environmentally sound manner when destruction of irreversible transformation does not represent the environmentally preferable option"*

Stockholm Convention (2) :

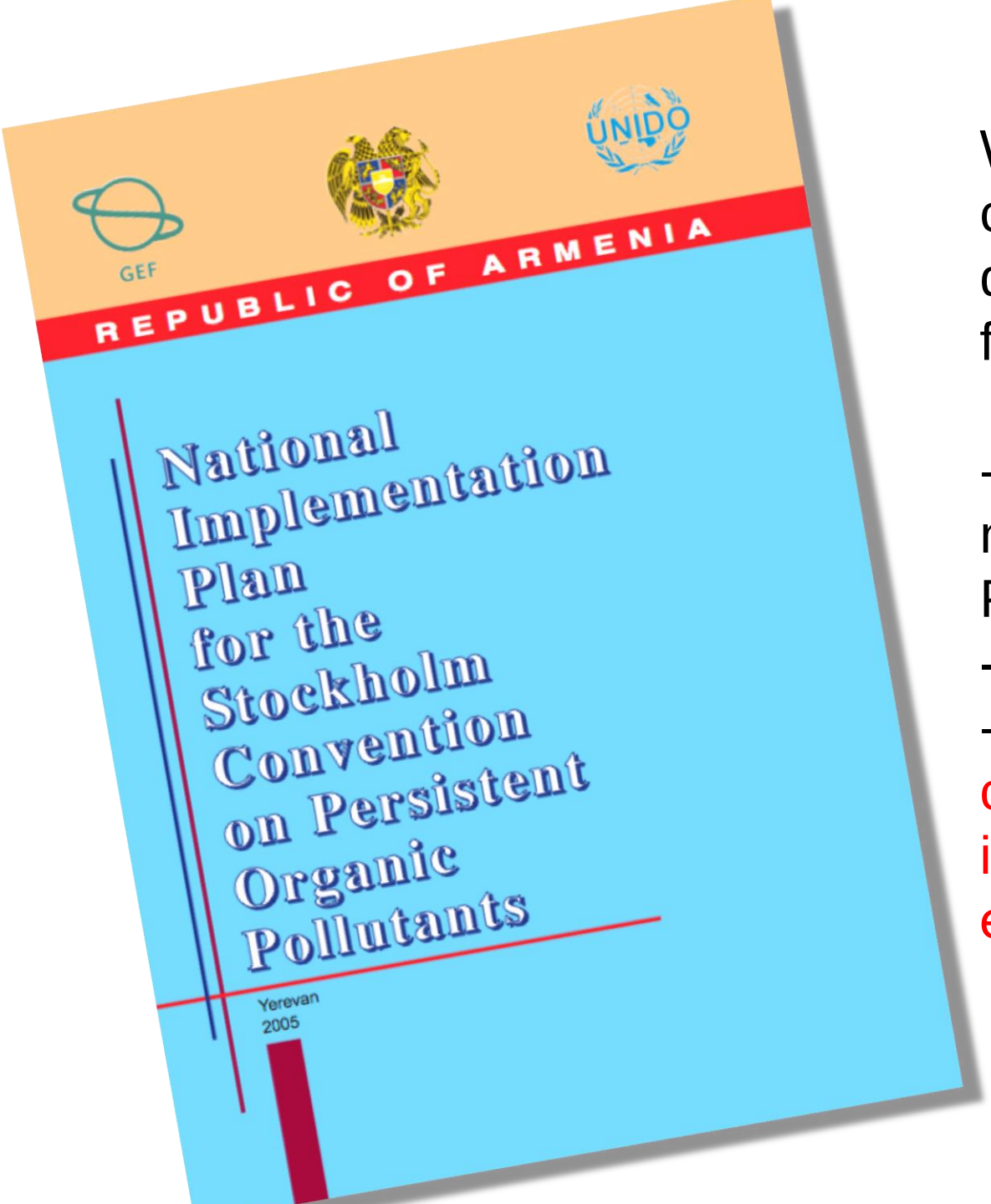
Also, parties must:

"…promote the development and, where it deems appropriate, require the use of substitute or modified materials, products and processes to prevent the **formation** and release of dioxins/furans and other by-product POPs."



Main strategic trends of the National Action Plan for implementation of Stockholm Convention in Armenia are as follows:….

Replacement of PCB-containing oils and their disposal/ destruction in environmentally sound manner, **preferably using the non-combustion technologies**;



Within the educational campaign it is urgent to draw attention to the following:

-Education, instruction on main aspects relevant to POPs.

-…

- Wide and transparent cooperation with NGOs in the sphere of ecological initiatives….

Treatment Options

1

Tansboundary movement to dedicated hazardous waste treatment plant

2

Local Treatment:

- **Modern Cement Kilns**
- **Alternative methods – non-combustion plant**

3

Only in Exceptional cases:

Specially designed Landfills


Concerned
people
living
downstream
2006


Concerned people living
downstream
April
2010

Swiss Chemical Wastes

[Photo: Newspaper Le Quotidien Jurassien, not dated]

Treatment possibilities

1

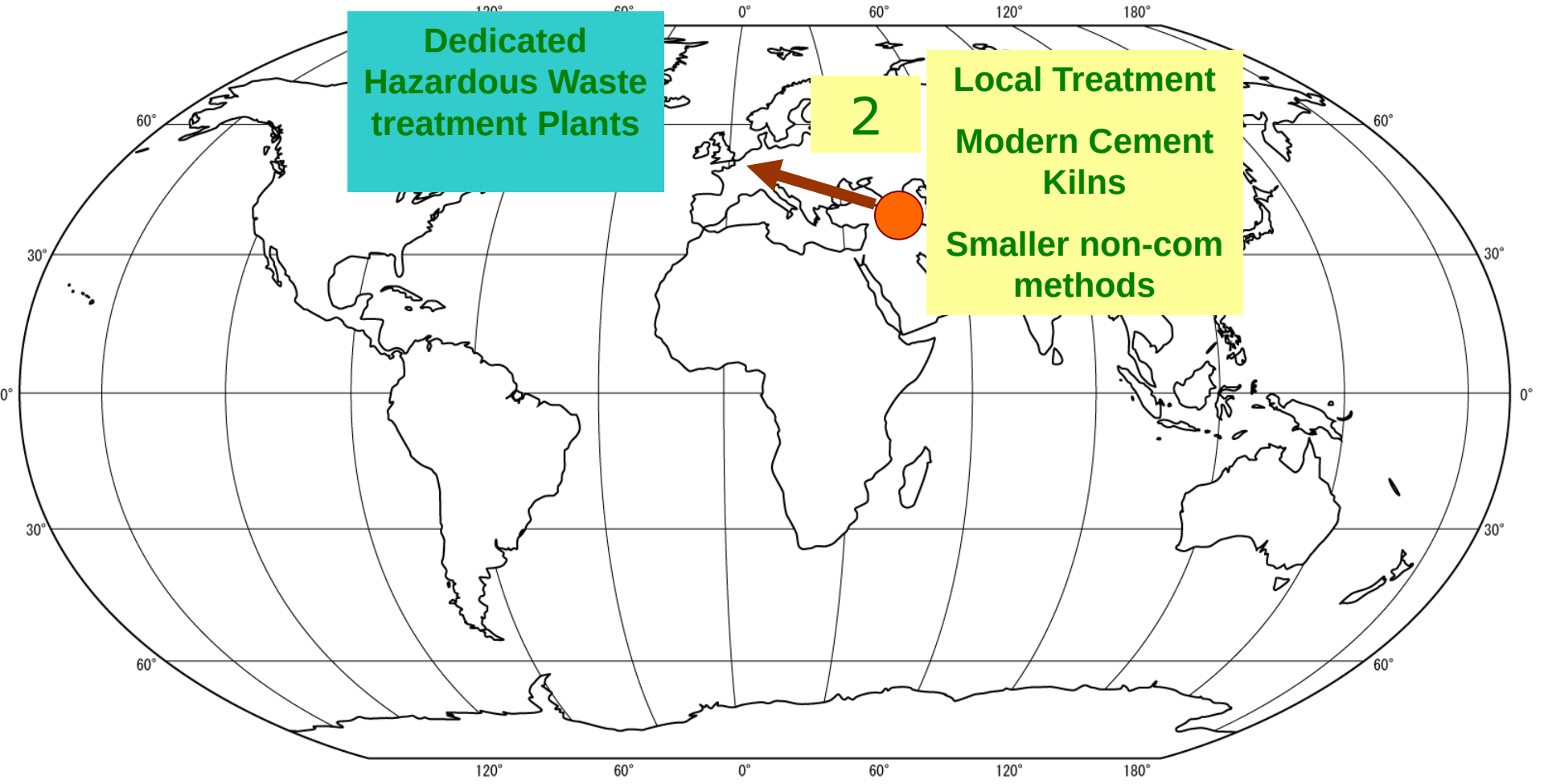
Dedicated Hazardous Waste treatment Plants

2

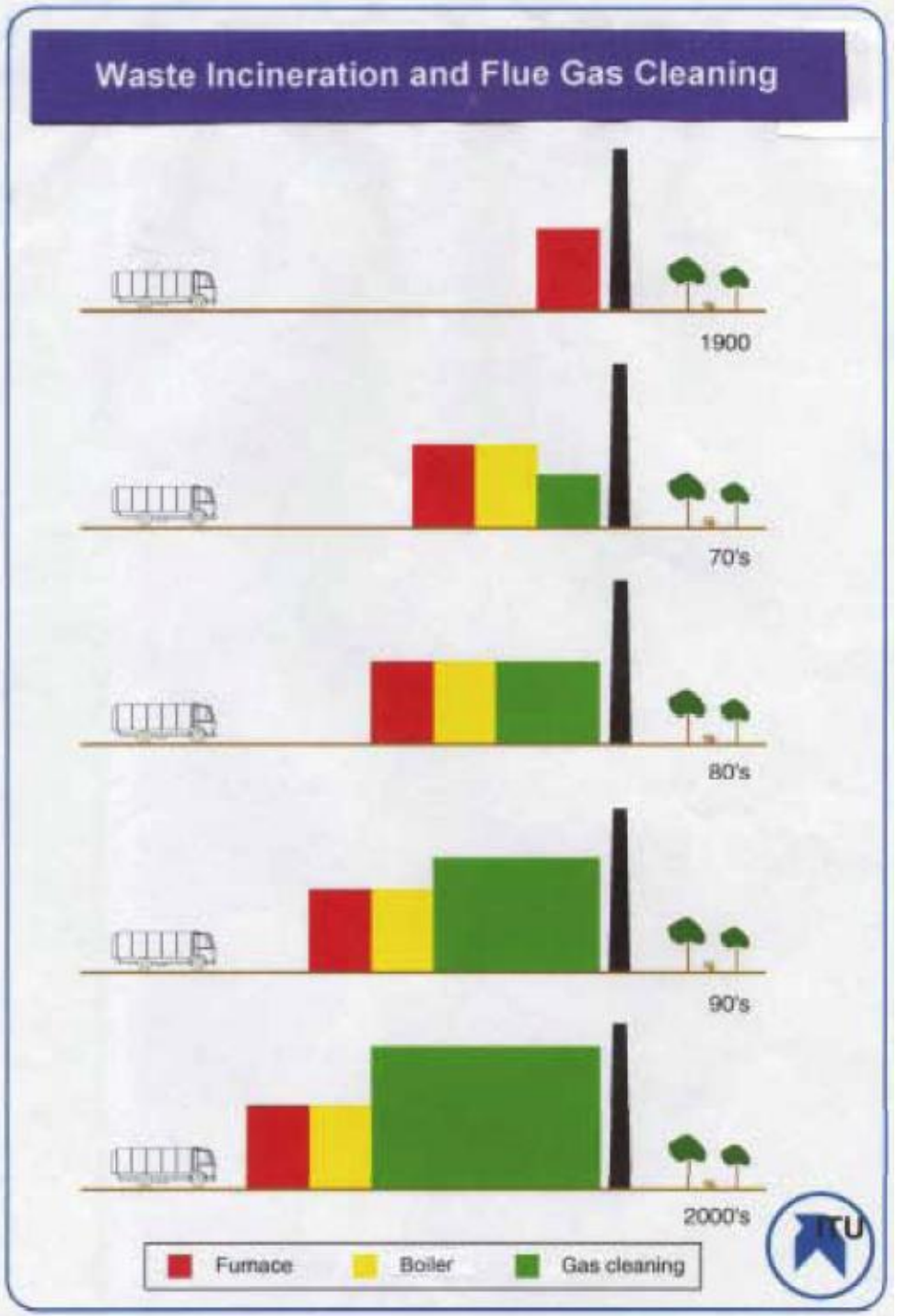
Local Treatment

Modern Cement Kilns

Smaller non-com methods

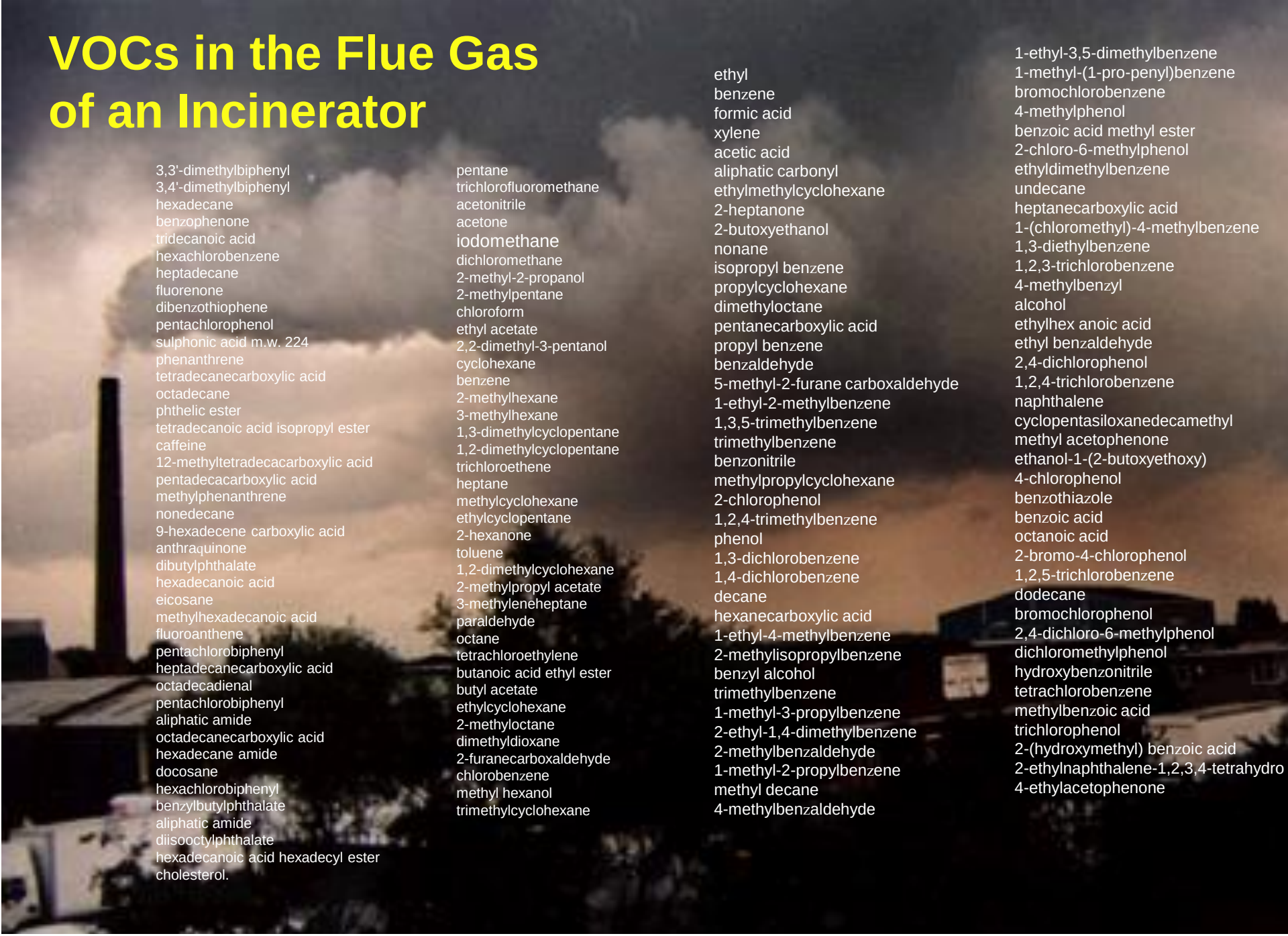



MSC. MARIA LAURA
STOP WASTE TRADE
GREENPEACE
TOP TOXIC TRADE


Waste Incineration and Flue Gas Cleaning
1900
70's
80's
90's
2000's
Furnace
Boiler
Gas cleaning

DE vs DRE

VOCs in the Flue Gas of an Incinerator



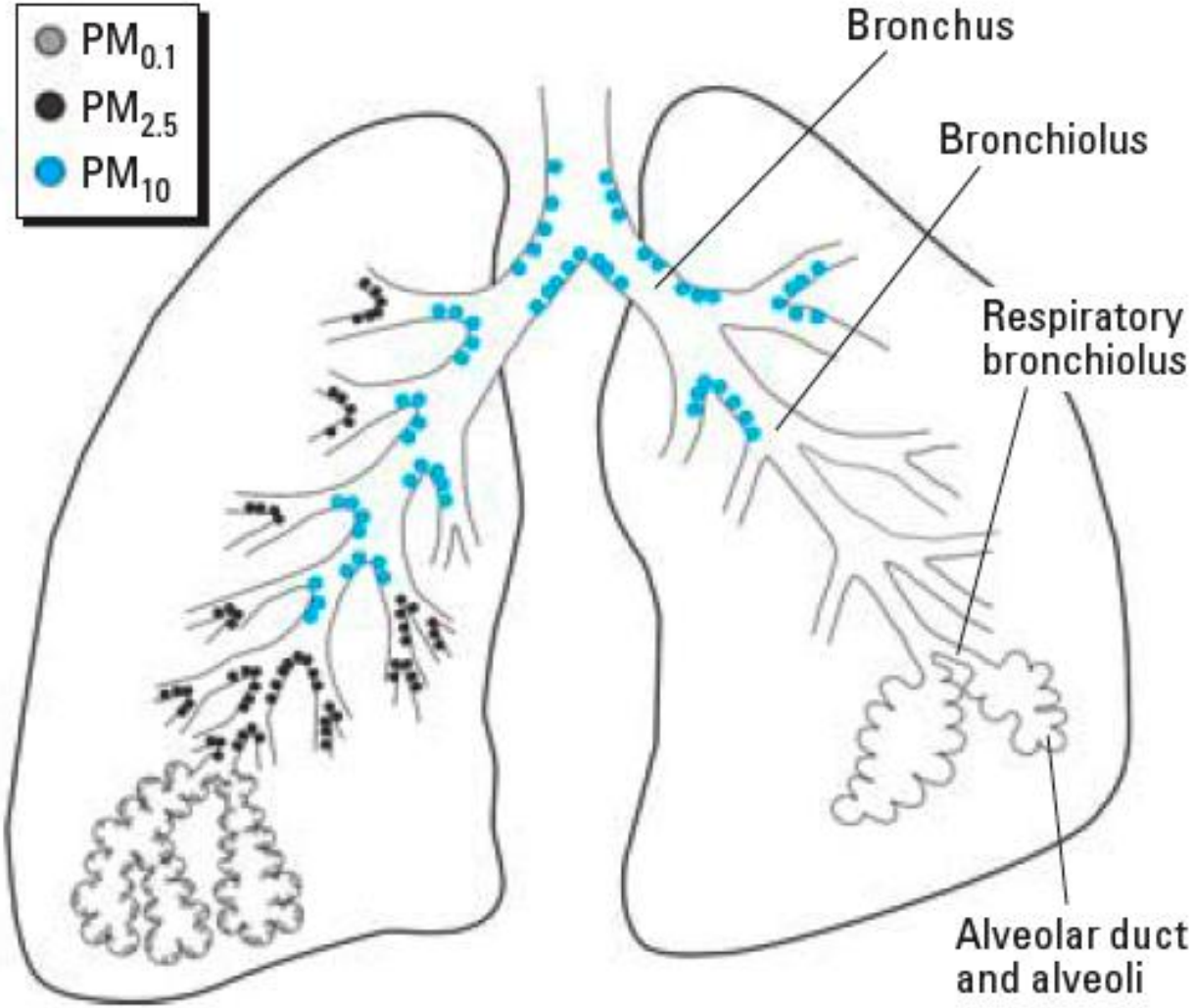
3,3'-dimethylbiphenyl
3,4'-dimethylbiphenyl
hexadecane
benzophenone
tridecanoic acid
hexachlorobenzene
heptadecane
fluorenone
dibenzothiophene
pentachlorophenol
sulphonic acid m.w. 224
phenanthrene
tetradecanecarboxylic acid
octadecane
phthelic ester
tetradecanoic acid isopropyl ester
caffeine
12-methyltetradecacarboxylic acid
pentadecacarboxylic acid
methylphenanthrene
nonedecane
9-hexadecene carboxylic acid
anthraquinone
dibutylphthalate
hexadecanoic acid
eicosane
methylhexadecanoic acid
fluoroanthene
pentachlorobiphenyl
heptadecanecarboxylic acid
octadecadienal
pentachlorobiphenyl
aliphatic amide
octadecanecarboxylic acid
hexadecane amide
docosane
hexachlorobiphenyl
benzylbutylphthalate
aliphatic amide
diisooctylphthalate
hexadecanoic acid hexadecyl ester
cholesterol.

pentane
trichlorofluoromethane
acetonitrile
acetone
iodomethane
dichloromethane
2-methyl-2-propanol
2-methylpentane
chloroform
ethyl acetate
2,2-dimethyl-3-pentanol
cyclohexane
benzene
2-methylhexane
3-methylhexane
1,3-dimethylcyclopentane
1,2-dimethylcyclopentane
trichloroethene
heptane
methylcyclohexane
ethylcyclopentane
2-hexanone
toluene
1,2-dimethylcyclohexane
2-methylpropyl acetate
3-methyleneheptane
paraldehyde
octane
tetrachloroethylene
butanoic acid ethyl ester
butyl acetate
ethylcyclohexane
2-methyloctane
dimethyldioxane
2-furanecarboxaldehyde
chlorobenzene
methyl hexanol
trimethylcyclohexane

ethyl
benzene
formic acid
xylene
acetic acid
aliphatic carbonyl
ethylmethylcyclohexane
2-heptanone
2-butoxyethanol
nonane
isopropyl benzene
propylcyclohexane
dimethyloctane
pentanecarboxylic acid
propyl benzene
benzaldehyde
5-methyl-2-furane carboxaldehyde
1-ethyl-2-methylbenzene
1,3,5-trimethylbenzene
trimethylbenzene
benzonitrile
methylpropylcyclohexane
2-chlorophenol
1,2,4-trimethylbenzene
phenol
1,3-dichlorobenzene
1,4-dichlorobenzene
decane
hexanecarboxylic acid
1-ethyl-4-methylbenzene
2-methylisopropylbenzene
benzyl alcohol
trimethylbenzene
1-methyl-3-propylbenzene
2-ethyl-1,4-dimethylbenzene
2-methylbenzaldehyde
1-methyl-2-propylbenzene
methyl decane
4-methylbenzaldehyde

1-ethyl-3,5-dimethylbenzene
1-methyl-(1-pro-penyl)benzene
bromochlorobenzene
4-methylphenol
benzoic acid methyl ester
2-chloro-6-methylphenol
ethyldimethylbenzene
undecane
heptanecarboxylic acid
1-(chloromethyl)-4-methylbenzene
1,3-diethylbenzene
1,2,3-trichlorobenzene
4-methylbenzyl
alcohol
ethylhex anoic acid
ethyl benzaldehyde
2,4-dichlorophenol
1,2,4-trichlorobenzene
naphthalene
cyclopentasiloxanedecamethyl
methyl acetophenone
ethanol-1-(2-butoxyethoxy)
4-chlorophenol
benzothiazole
benzoic acid
octanoic acid
2-bromo-4-chlorophenol
1,2,5-trichlorobenzene
dodecane
bromochlorophenol
2,4-dichloro-6-methylphenol
dichloromethylphenol
hydroxybenzonitrile
tetrachlorobenzene
methylbenzoic acid
trichlorophenol
2-(hydroxymethyl) benzoic acid
2-ethylnaphthalene-1,2,3,4-tetrahydro
4-ethylacetophenone

Jay, K. and L. Stieglitz (1995). "Identification and quantification of volatile organic components in emissions of waste incineration plants." Chemosph



Ultra Fine Particle Penetration into the lungs

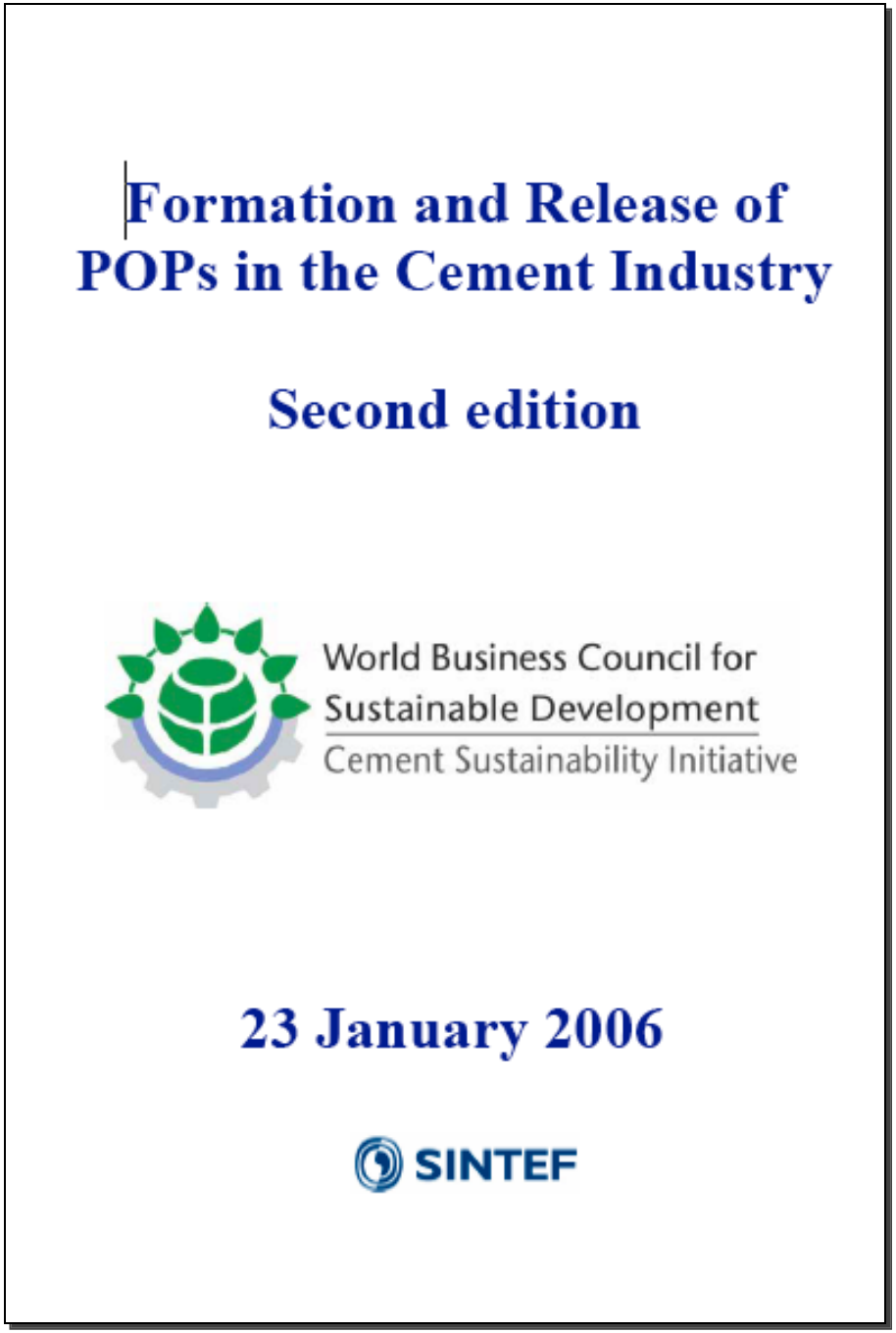
Cormier, S. A., S. Lomnicki, et al. (2006). "Origin and health impacts of emissions of toxic by-products and fine particles from combustion and thermal treatment of hazardous wastes and materials." Environ Health Perspect **114(6): 810-7.**

Dioxin Issues Remain….

PCDD/F emissions during start-up could reach 96.9 ng I-TEQ /Nm^3 (nearly 1,000 times the EU limit of 0.1 ng/m^3)

- Gass, Lüder et al. 2002; Nordsieck, Neuer-Etscheidt et al. 2003; Environment Agency 2006; Neuer-Etscheidt, Nordsieck et al. 2006; Tejima, Nishigaki et al. 2007; Wang, Hwang et al. 2007; Wang, Hsi et al. 2007; Chen, Lin et al. 2008

The Cement Industry



Holcim - GTZ

Holcim (www.holcim.com) is a major worldwide supplier of cement and aggregates as well as value-adding activities such as ready-mix concrete and asphalt, with other services.

GTZ (www.gtz.de) is a German government owned corporation for international cooperation for sustainable development with worldwide operations.

Holcim and GTZ (2006). Guidelines on Co-processing Waste Materials in Cement Production - The GTZ-Holcim Public Private Partnership.

FORUM

The Cement Industry as a Scavenger in Industrial Ecology and the Management of Hazardous Substances

Lucas Reijnders

Keywords

biological analogy
forced extraction
hazardous materials
industrial ecology

Summary

The cement industry uses a variety of secondary materials and fuels, thus fulfilling the role of "scavenger" in industrial ecology (IE). The use of wastes in cement production has been advo-

Reijnders, L. (2007). "The Cement Industry as a Scavenger in Industrial Ecology and the Management of Hazardous Substances." Journal of Industrial Ecology **11(3): 15-25**.


Ararat Cement Kiln

Ambient Dust Levels

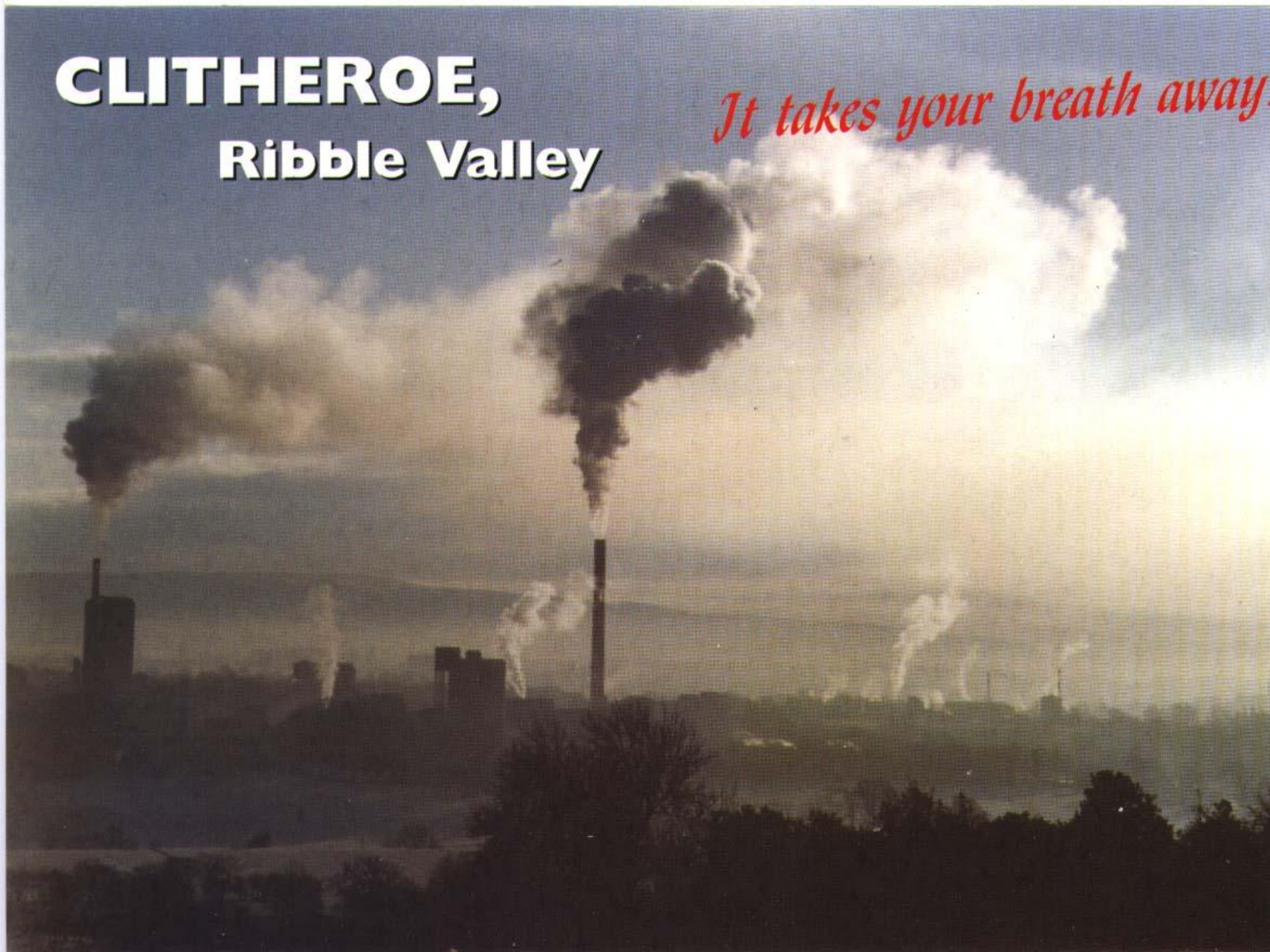
- Hrazdan 3.8 X
- Ararat 5.4 X

Maximum permissible concentration

Arka News Agency 16/06/2008

Mozambique

Mauricio Sulilia in front of the cement factory that LIVANINGO stopped becoming a toxic waste incinerator.
Photo: Paul Weinberg/OxfamAUS


CLITHEROE,
Ribble Valley
It takes your breath away

Cemex - Rugby, UK

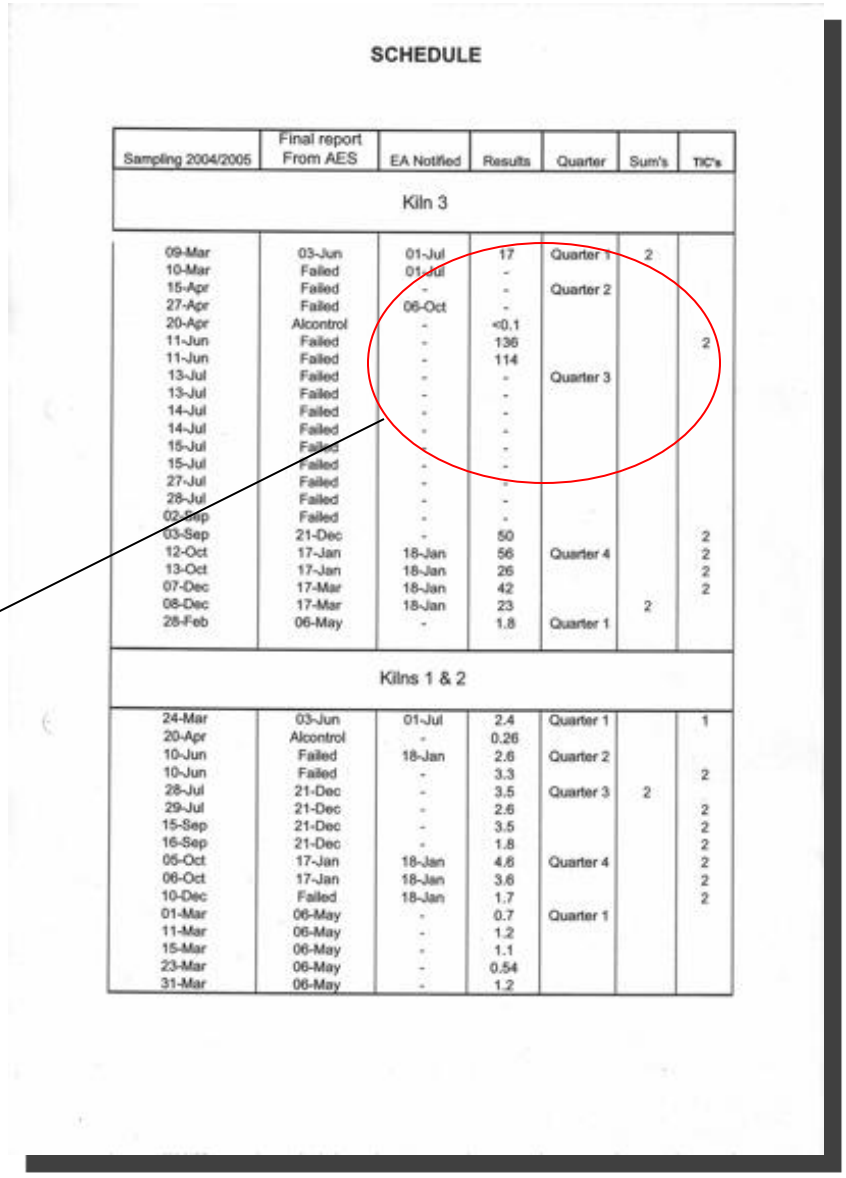
“Staff found a cement kiln door hanging off its hinges and tried to force it shut. Despite knowing the door was not secure, Cemex restarted the kiln, which was experiencing operating difficulties.

A Cemex spokeswoman said Cemex had achieved "exceptional levels of performance" since taking over the site.”

ENDS 381, 2006

Dioxin emissions at Padeswood North Wales

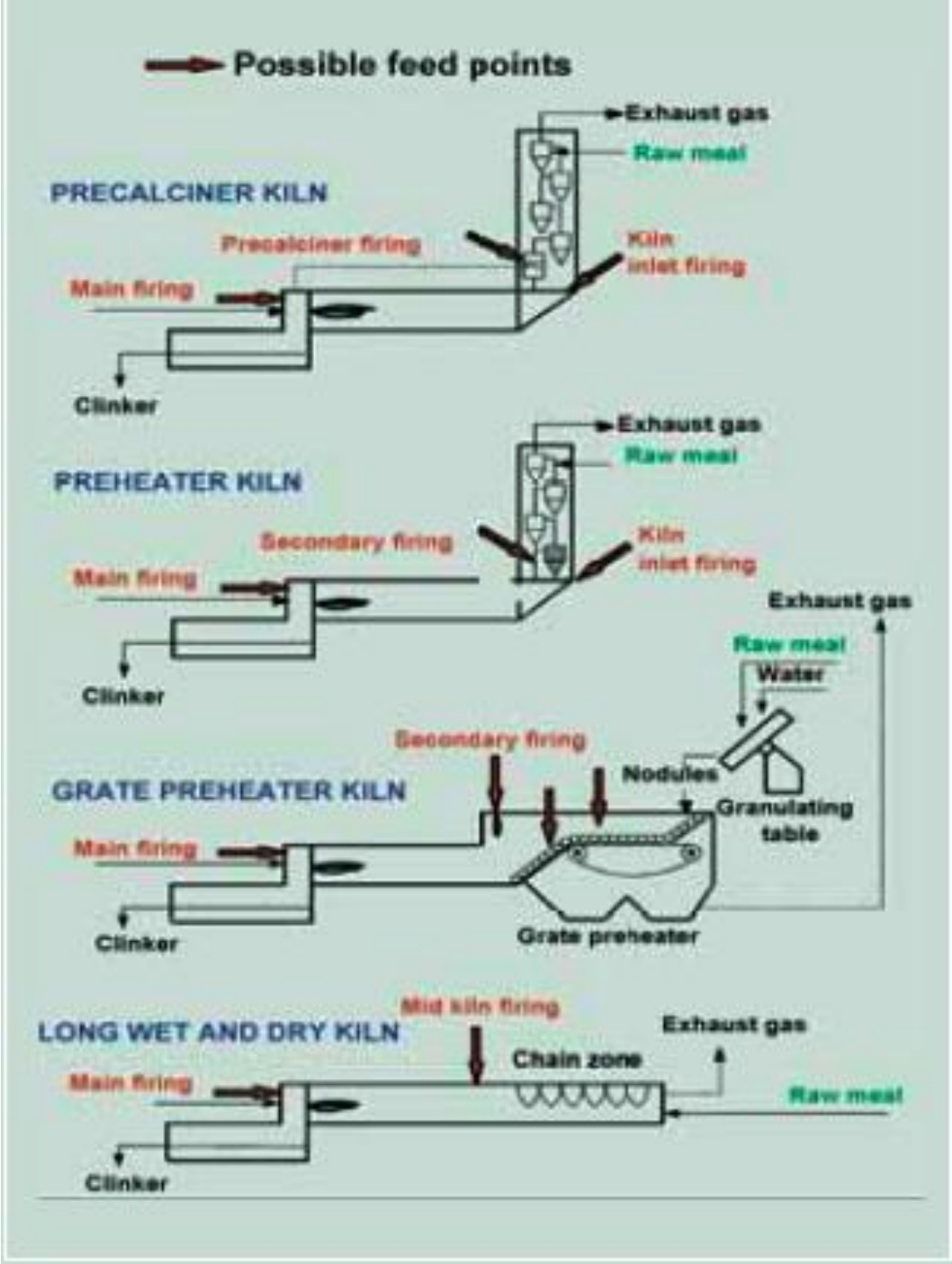
136 ng TEQ/m^3



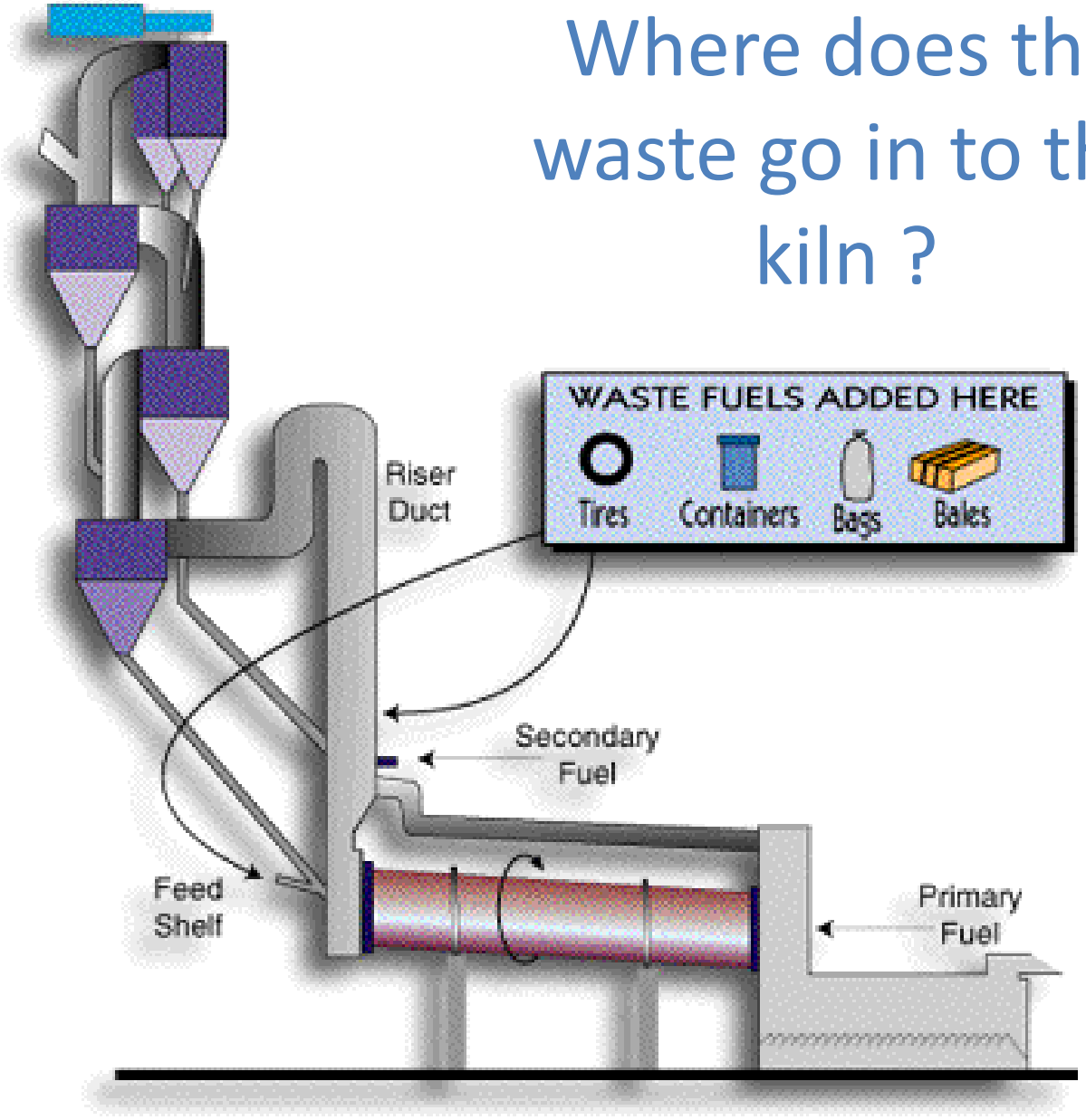
SCHEDULE

Sampling 2004/2005	Final report From AES	EA Notified	Results	Quarter	Sum's	TIC's
Kiln 3						
09-Mar	03-Jun	01-Jul	17	Quarter 1	2	
10-Mar	Failed	01-Jul	-			
15-Apr	Failed	-	-	Quarter 2		
27-Apr	Failed	06-Oct	-			
20-Apr	Alcontrol	-	<0.1			
11-Jun	Failed	-	136			2
11-Jun	Failed	-	114			
13-Jul	Failed	-	-	Quarter 3		
13-Jul	Failed	-	-			
14-Jul	Failed	-	-			
14-Jul	Failed	-	-			
15-Jul	Failed	-	-			
15-Jul	Failed	-	-			
27-Jul	Failed	-	-			
28-Jul	Failed	-	-			
02-Sep	Failed	-	-			
03-Sep	21-Dec	-	50			2
12-Oct	17-Jan	18-Jan	56	Quarter 4		2
13-Oct	17-Jan	18-Jan	26			2
07-Dec	17-Mar	18-Jan	42			2
08-Dec	17-Mar	18-Jan	23		2	
28-Feb	06-May	-	1.8	Quarter 1		
Kilns 1 & 2						
24-Mar	03-Jun	01-Jul	2.4	Quarter 1		1
20-Apr	Alcontrol	-	0.26			
10-Jun	Failed	18-Jan	2.6	Quarter 2		
10-Jun	Failed	-	3.3			2
28-Jul	21-Dec	-	3.5	Quarter 3	2	
29-Jul	21-Dec	-	2.6			2
15-Sep	21-Dec	-	3.5			2
16-Sep	21-Dec	-	1.8			2
05-Oct	17-Jan	18-Jan	4.6	Quarter 4		2
06-Oct	17-Jan	18-Jan	3.6			2
10-Dec	Failed	18-Jan	1.7			2
01-Mar	06-May	-	0.7	Quarter 1		
11-Mar	06-May	-	1.2			
15-Mar	06-May	-	1.1			
23-Mar	06-May	-	0.54			
31-Mar	06-May	-	1.2			

Waste Feeds


Possible feed points
PRECALCINER KILN
Exhaust gas
Raw meal
Precalciner firing
Kiln inlet firing
Main firing
Clinker
PREHEATER KILN
Exhaust gas
Raw meal
Secondary firing
Kiln inlet firing
Main firing
Clinker
Exhaust gas
Raw meal
Water
Secondary firing
GRATE PREHEATER KILN
Nodules
Granulating table
Main firing
Clinker
Grate preheater
LONG WET AND DRY KILN
Mid kiln firing
Exhaust gas
Chain zone
Main firing
Raw meal
Clinker

Where does the waste go in to the kiln ?



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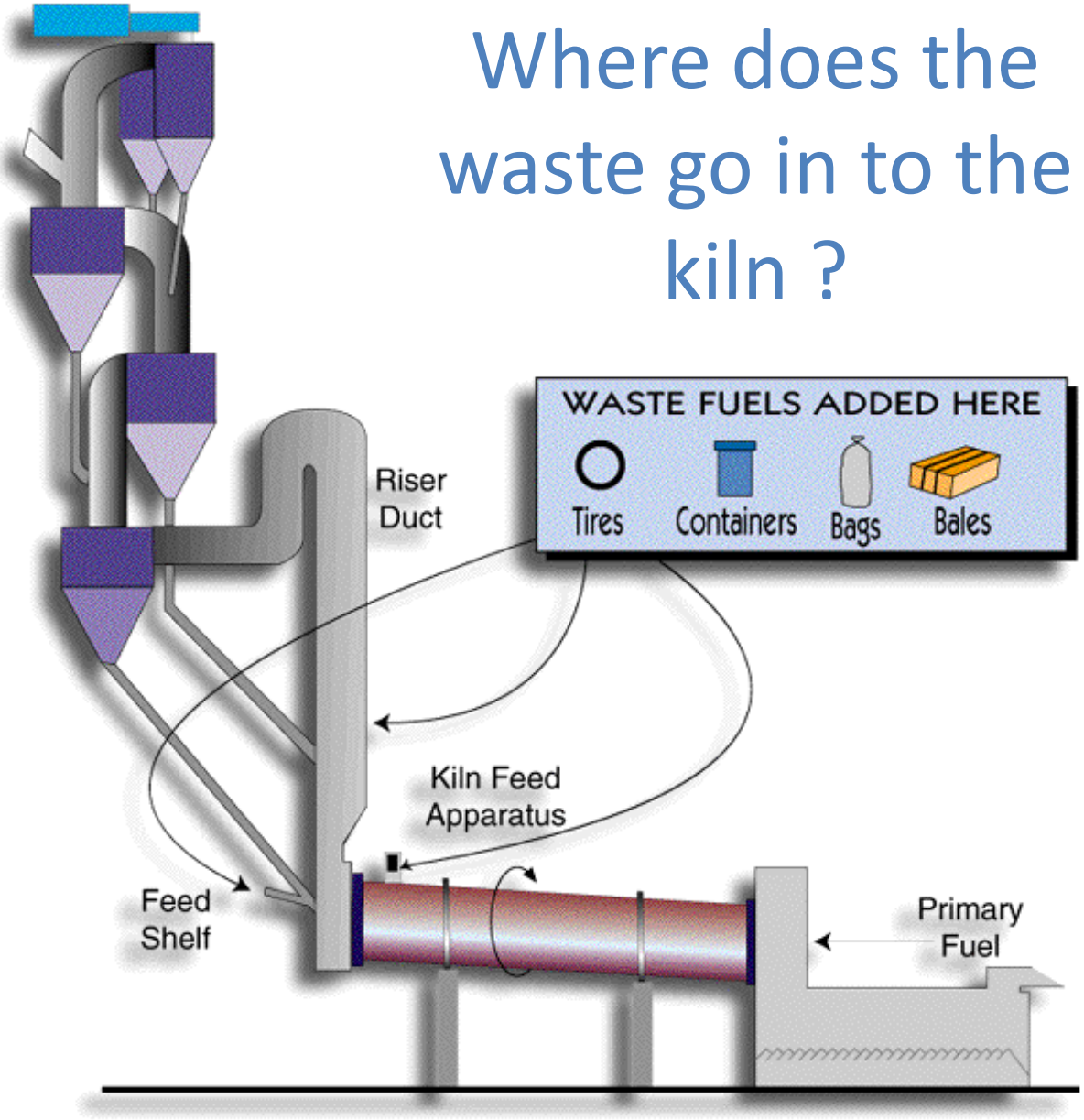

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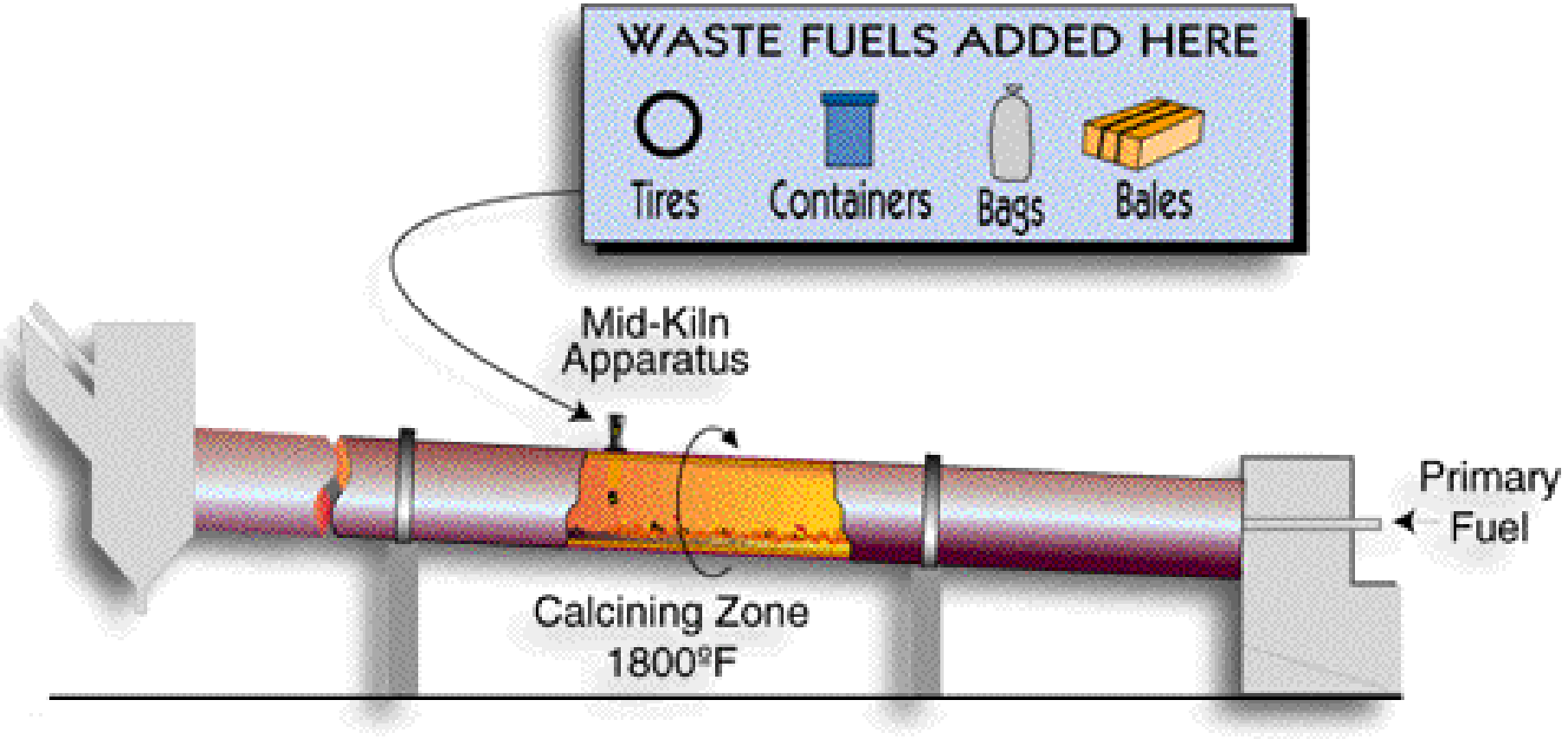
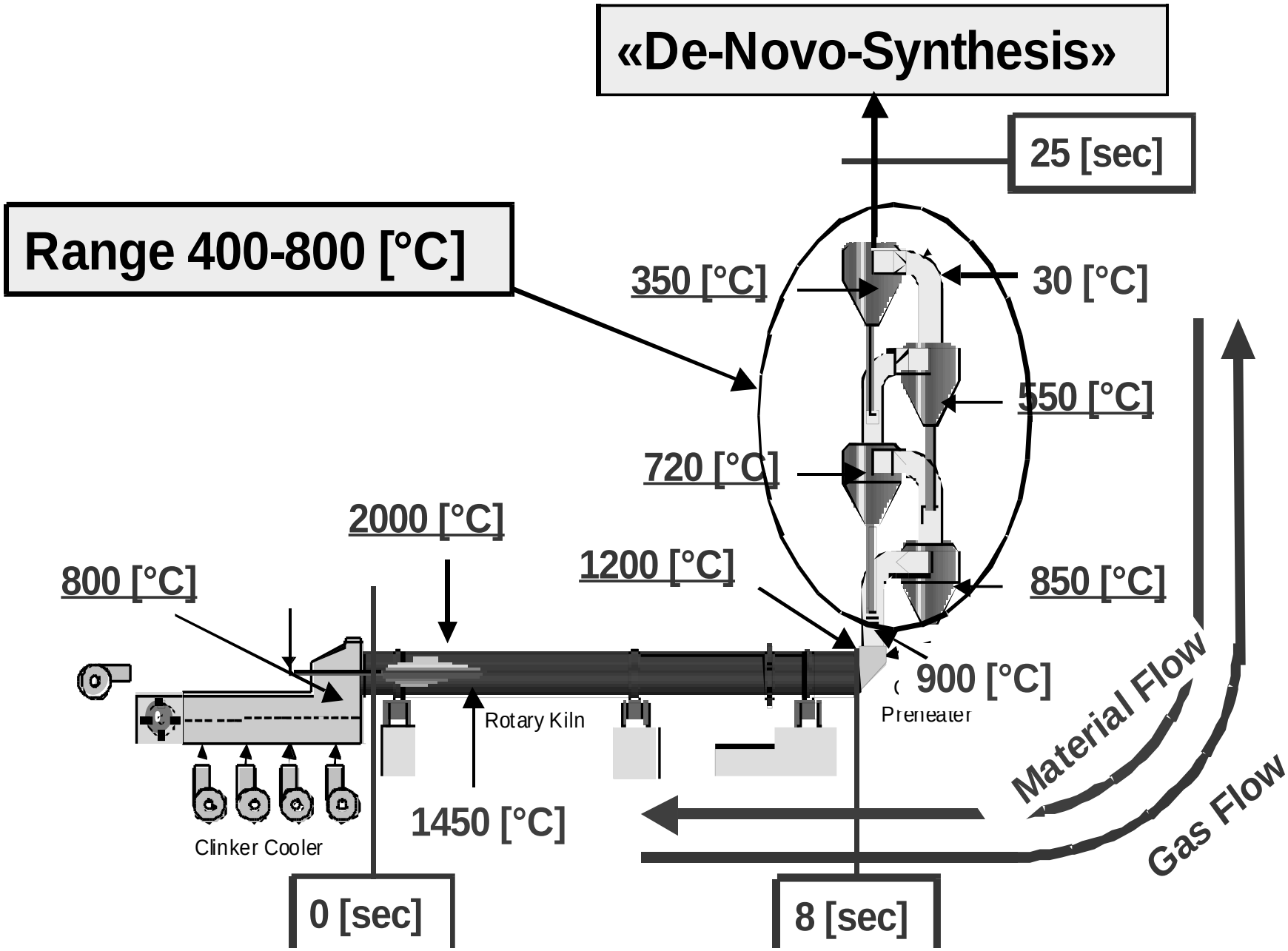
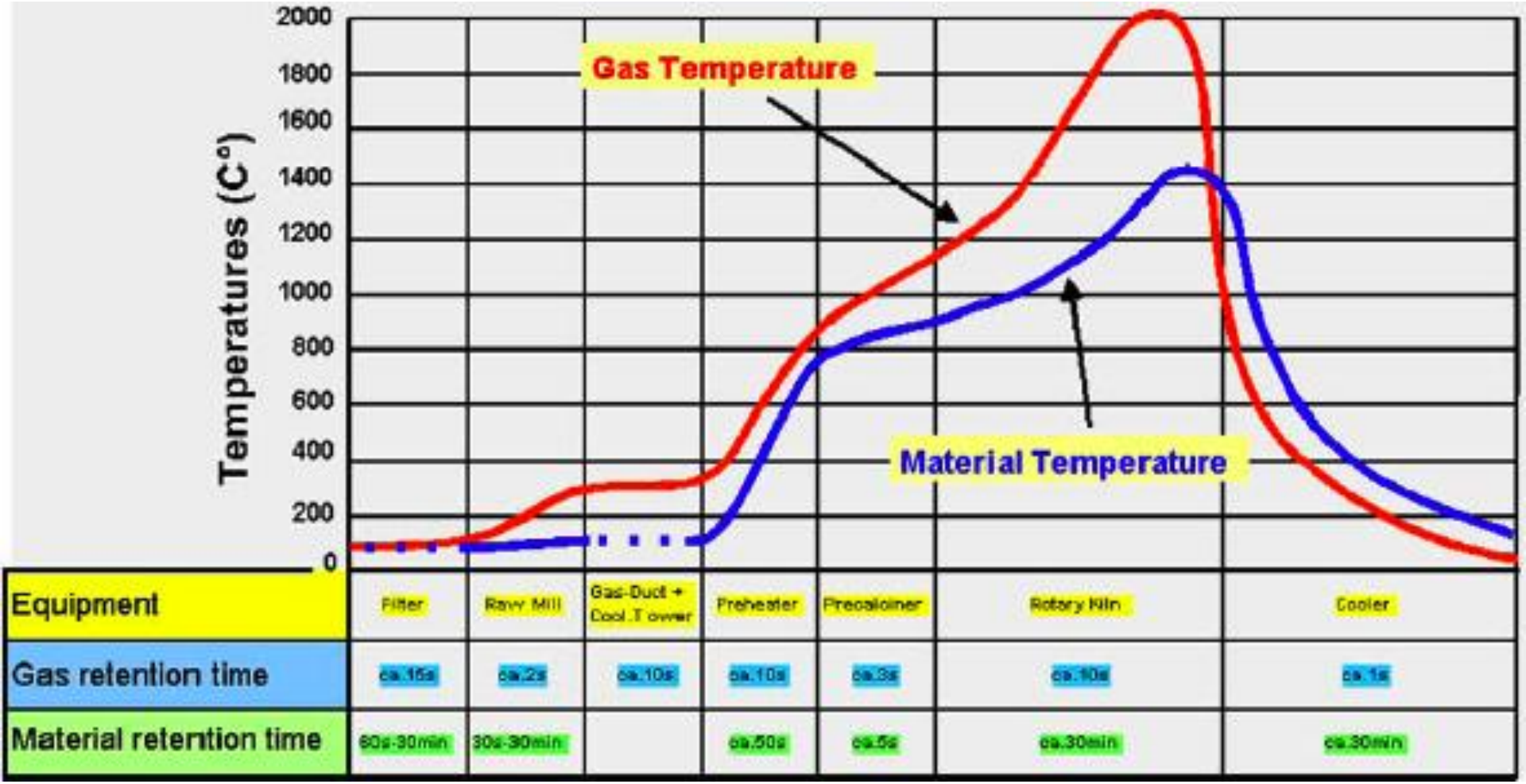




Temperatures and retention time in a preheater cement kiln

Residence times in cement kilns



Cembureau 1999

Vietnam Trial Burns

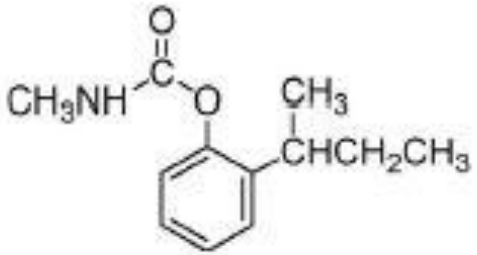


Fig. 1 – Chemical structure of Fenobucarb.

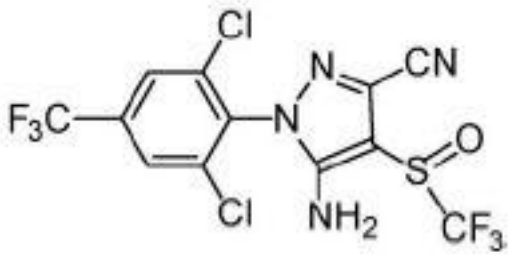


Fig. 2 – Chemical structure of Fipronil.

journa

Environmentally so
in developing count

Kåre Helge Karstensen [a,*], *Ng*
an [e], *Doan T*
i [i], *Doan Hu*

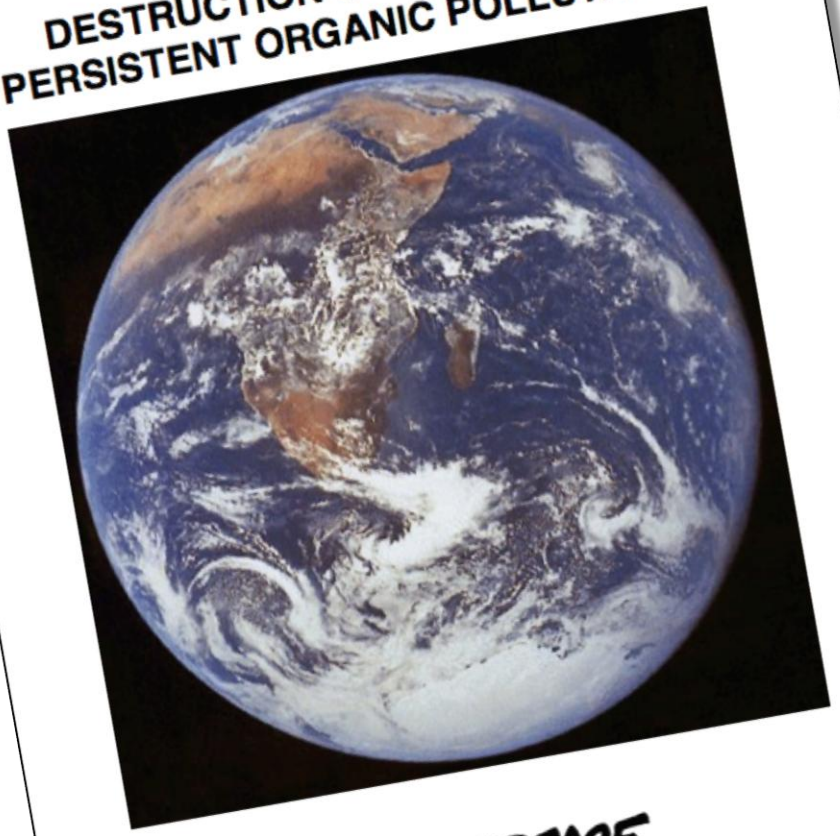
ıtific and Industrial Research (SINTEF), P.O. Box 124, N-0314 Oslo, Norway
ources and Environment, Department of EIA and Appraisal, 83 Nguyen Chi Thanh, Hanoi, Viet Nam
Protection Agency, 67 Nguyen Du, Hanoi, Viet Nam
nce, Research Centre for Environmental Technology and Sustainable Development,
Viet Nam
nmental Protection Agency, 23 Tran Phu, Ward 4, Ho Chi Minh City, Viet Nam
lesources and Environment, 244 Dien Bien Phu Street, Ho Chi Minh City, Viet Nam
lesources and Environment, 260 Quoc Lo, Bien Hoa City, Dong Nai, Viet Nam
Resources and Environment, Huynh Van Nghe, Thu Dao Mot, Binh Duong, Viet Nam
lesources and Environment, 130 Ly Thuong Kiet, Vung Tau, Viet Nam
lesources and Environment, 1226 Nguyen Trung, Rach Gia Bo, Kien Giang, Viet Nam

Table 3 – Gaseous compounds (mg/N m^3)

	Baseline	Test burn	ELV Vietnam
HCl	2.1	2.4	90
HF	<0.21	<0.23	4.5
NH_3	<1.0	<0.44	45
CO	99	131	225
O_2 (%)	5.24	5.21	–
SO_2	1.8	2.0	225
NO_2	21	40	–
NO	760	1220	–
NO_x expressed as NO_2	1180	1910	1000

Karstensen, K. H., N. K. Kinh, et al. (2006). "Environmentally sound destruction of obsolete pesticides in developing countries using cement kilns." Environmental Science & Policy **9(6): 577-586**.

TECHNICAL CRITERIA FOR THE DESTRUCTION OF STOCKPILED PERSISTENT ORGANIC POLLUTANTS



GREENPEACE

7 October 1998

ISBN 90-73361-47-8

Criteria (1)

Closed Systems

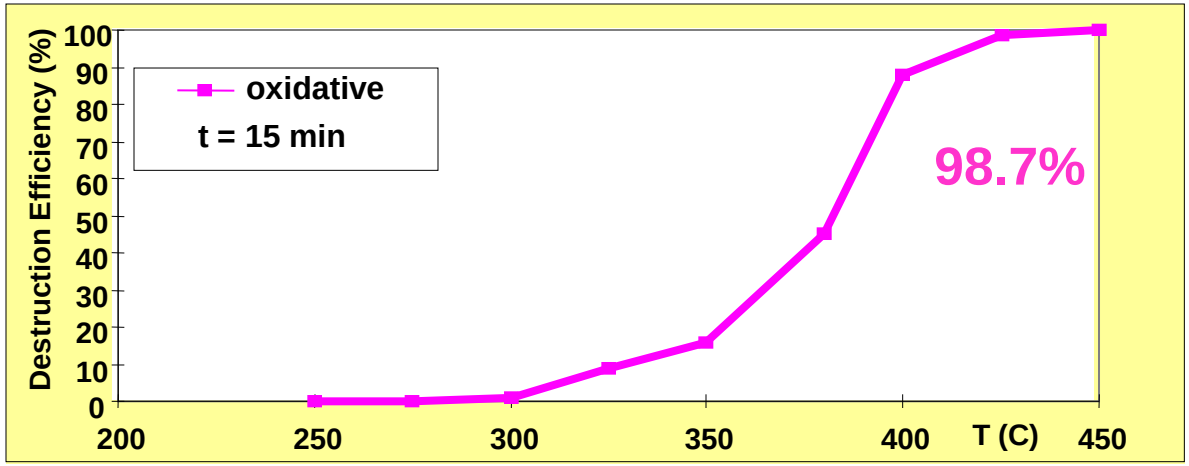
Complete containment of all residues

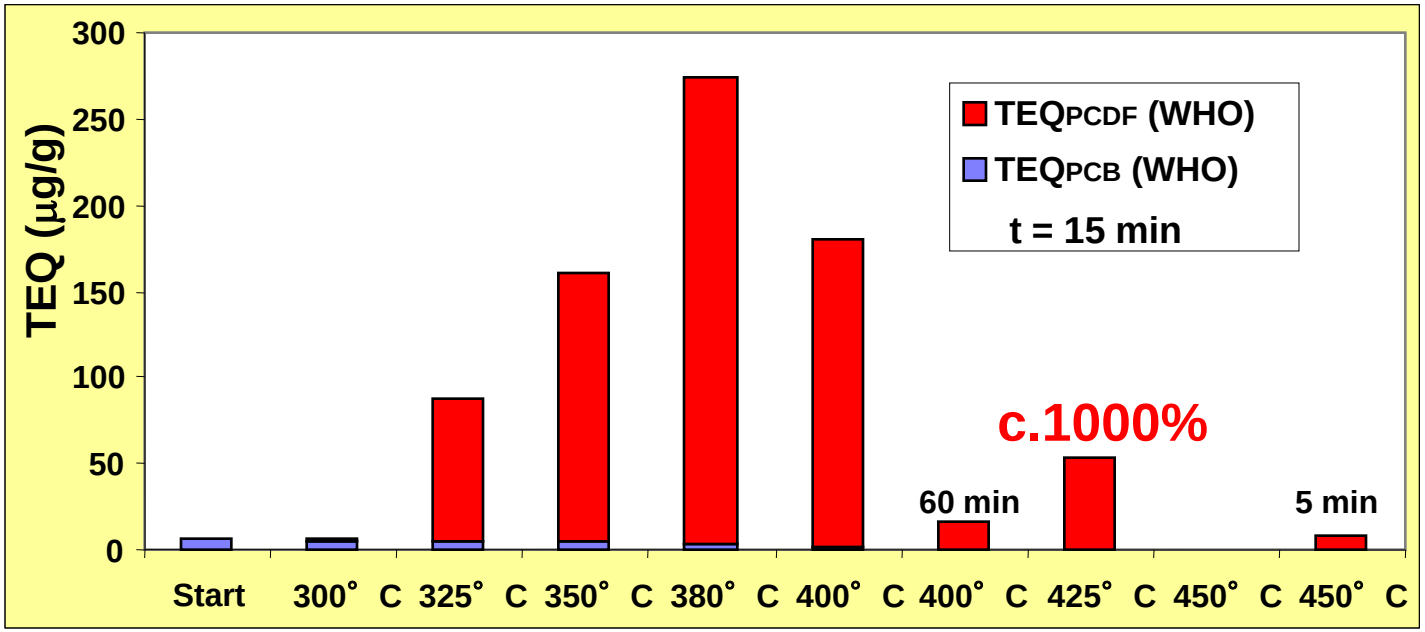
Criteria (2)

Destruction Efficiencies (DEs)

Effectively 100% for chemicals of concern

Evaluation of Toxicity based on TEQ





Criteria (3)

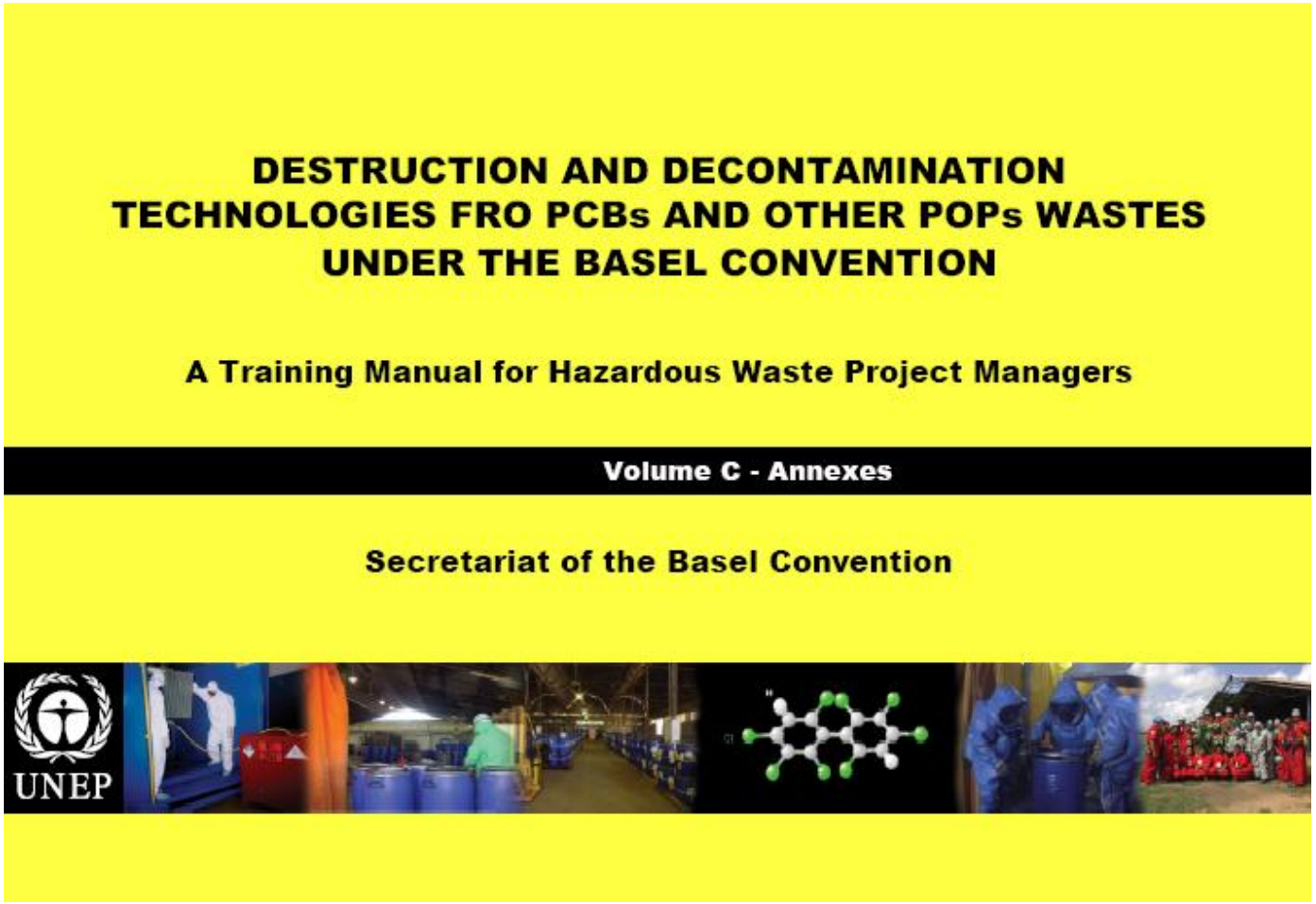
Releases

No uncontrolled releases

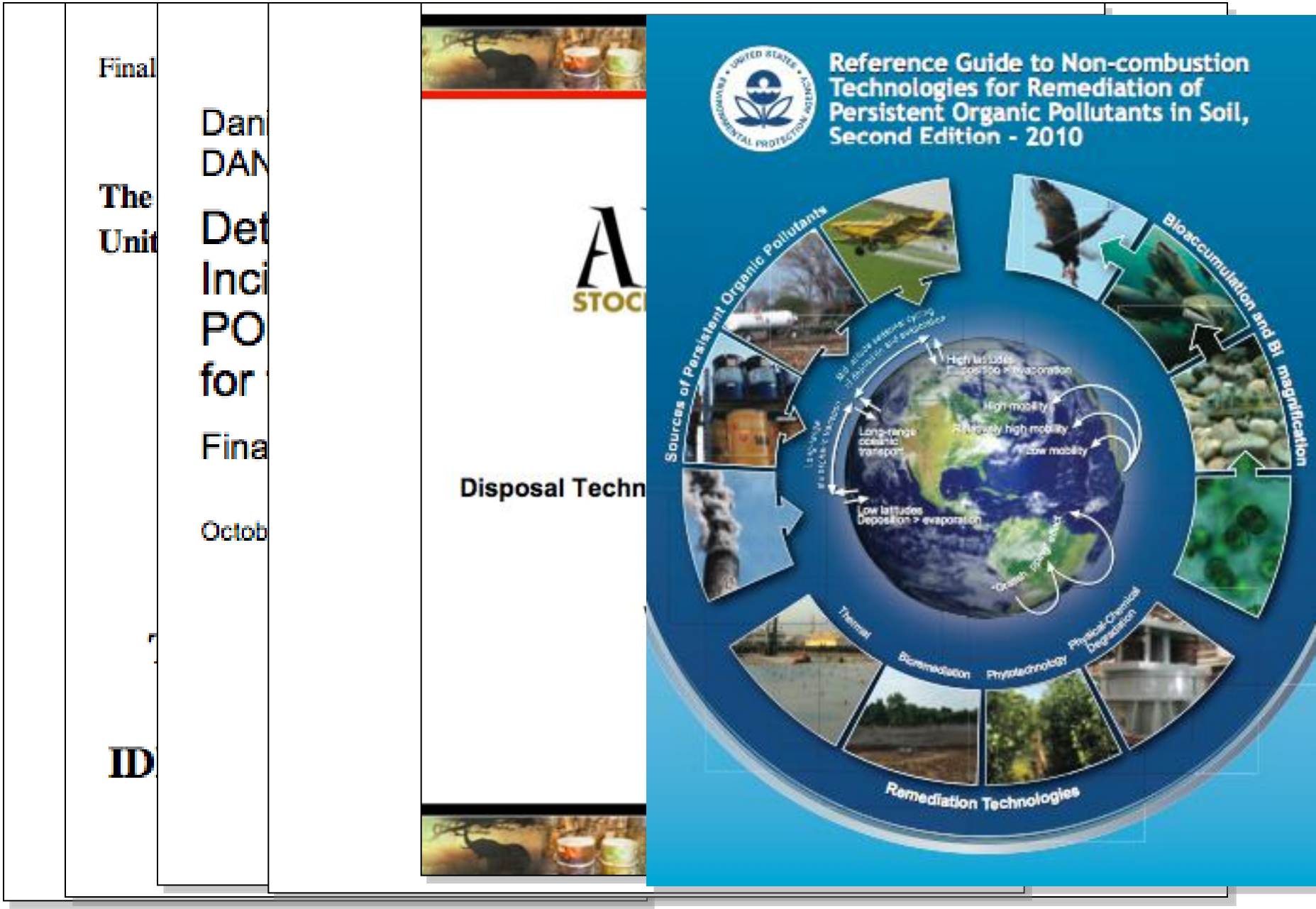
Non Combustion Alternatives:

1. Base-catalysed decomposition (BCD)
2. Bioremediation/Fenton reaction
3. Catalytic hydrogenation
4. DARAMEND® bioremediation
5. Enzyme degradation
6. Fe (III) photocatalyst degradation
7. Gas-phase chemical reduction (GPCR)
8. GeoMelt™ process
9. In situ bioremediation of soils
10. Mechanochemical dehalogenation (MCD)
11. Mediated electrochemical oxidation (AEA Silver II)
12. Mediated electrochemical oxidation (CerOx™)
13. MnOx/TiO2 – Al2O3 catalyst degradation
14. Molten metal
15. Molten salt oxidation
16. Molten slag process
17. Ozonation/electrical discharge destruction
18. Photochemically enhanced microbial degradation
19. Phytoremediation
20. Plasma arc (PLASCON™)
21. Pyrolysis
22. Self-propagating high-temperature dehalogenation (SPHTD)
23. Sodium reduction
24. Solvated electron technology
25. Supercritical water oxidation (SCWO)
26. TiO2 – based V2O5/WO3 catalysis
27. White rot fungi bioremediation

BC Training Manual: http://www.basel.int/meetings/sbc/workdoc/techdocs.htm



Technology Reviews



Non-Combustion Review History

- **1986**: USEPA (1986) evaluated ten combustion-based and eight non-combustion technologies.
- **1991**: Greenpeace catalogued 28 technologies, including biological, chemical, photochemical, electrochemical, neutralisation, chemical reprocess, and thermal processes potentially applicable to stockpiles of obsolete chemical weapons;
- **1992**: U.S. Office of Technology Assessment reviewed eight thermal technologies, eight chemical dechlorination technologies and bioremediation.
- 1998: Greenpeace publishes Technical Criteria for the Destruction of Stockpiled Persistent Organic Pollutants.
- **2002**: NATO/CCMS Pilot Study . John Vijgen evaluated eleven non-combustion technologies.
- **2003**: GAIA –the Global Alliance for Incinerator Alternatives – described 9 non-combustion technologies for POPs stockpiles in their broad critique of incineration.
- **2004**: STAP/GEF released their detailed review and classification of some 27 technologies
- **2005:** USEPA review published - Evaluated 17 technologies
- **2006:** Final Draft BAT BEP guidelines for Stockholm Convention completed
- **2007:** ICS – UNIDO review completed considering 15 technologies
- **2008**: WTO ASP project reviews alternatives for ASP- 7 non com technologies +ISTD, cement kilns and HTI
- **2010:** USEPA review updated

Maturity criteria

Established	Emerging	Transition	Promising
BCD	Ball Milling	CerOx	HydroDec
GPCR	MSO	GeoMelt	Silver II
PLASCON	PWC	PACT	SPHTD
SR	SET		
	SCWO		

Status	**Commercial status**	**Scale**	**Applicability proof**	**Data**
Established	established	large	applied	available
Emerging	emerging	large/medium	applied/demonstrated	recent/limited
Transition	established/emerging	large/medium	theoretical/trial	scarce/no
Promising	none/neo-commercialized	lab/pilot	trial	available

Technology	Commercial scale	Countries where licensed and/or used for commercial treatment
Gas Phase Chemical Reduction	full	Australia, Canada, USA, Japan
Sodium reduction	full	France, Germany, UK, Netherlands, South Africa, Australia, USA, Saudi Arabia, Japan, New Zealand
Base Catalysed Dechlorination	full	Australia, USA, Mexico, Spain, New Zealand, Japan, Czech Republic
Solvated electron	full	USA
Electrochemical	limited	USA, UK
Copper Mediated Destruction	pilot/limited	Poland, Czech Republic
Super-critical water oxidation	limited	USA, Japan
Ball milling	full	Japan

Challenges

- **Over-capacity of high temperature incineration capacity in Europe.**
- **Interdependence of criteria (e.g. DE, DRE, depend on waste type/strength, waste strength and throughput depends on configurations, consumables and prices depend on everything, etc.)**
- **Short experience or early development phase of most technologies (no large plants, or the existing plants differ from each other)**
- **Missing/Poor information on many existing projects**
- **Lack of feedback from technology vendors**

UNITED NATIONS DEVELOPMENT PROGRAMME
GLOBAL ENVIRONMENT FACILITY

GOVERNMENT OF SLOVAKIA
PROJECT DOCUMENT

(21 November 2005)

Project Number: GLO/03/G3X/A/1G/72 **PIMS** : 2115

Project Title: Global Programme to Demonstrate the Viability and Removal of Barriers that Impede Adoption and Successful Implementation of Available, Non-Combustion Technologies for Destroying Persistent Organic Pollutants (POPs)

Short Title: Non-combustion Demonstration project in Slovakia

Starting Date: March 2006

Completion Date: December 2011

Summary of Financing (US$)		
UNDP (in-kind)	US$	95,000
Others: GEF		
GEF (incl. AOS)	**US$**	**10,004,040**
Parallel Funding: Phase I		

GEF Slovakia Project

BCD Plant - Spolana

Kwinana GPCR plant Australia

PLASCON

Current Situation

- C. 75-90% of all pesticides are destroyed by dedicated incinerators mainly in Europe
- Major interest by international cement industry
- Alternative technologies: smaller part of market and work in specialised niches

NGO Principles

- Precaution
- Social acceptability
- Transparency - Right to Know
- Hazard avoidance - Zero Discharge
- Internalising environmental costs


AT LAST, WE'VE CRACKED IT— WE FINALLY ATTAINED ZERO EMISSIONS...
MITCH