

2006-2016: 10 years of continuous dioxins monitoring in Italy. Which assessment for which perspective?



Background

First cases

Seveso: July 10th, 1976: a plant producing 2,4,5-Trichlorophénol released a toxic smoke.

- 3 300 pets died
- 70 000 heads of cattle killed
- High quantity of fields and houses needed to be decontaminated



Dioxins

PCDDs/PCDFs

Polychlorinated dibenzo-p-dioxins

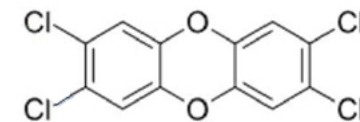
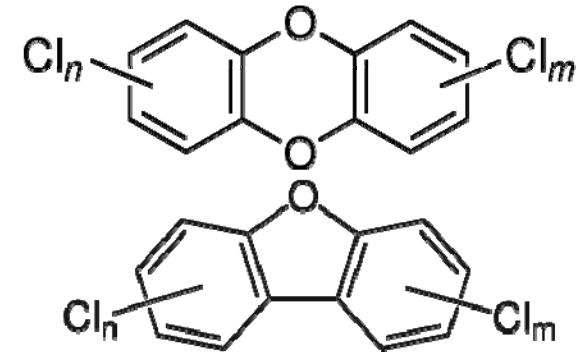
Polychlorinated dibenzofurans

Classification

There are 210 congeners.

17 are classified with for each of them a toxicity factor I-TEF.

2,3,7,8-tétrachlorodibenzo-p-dioxine (TCDD) is reference (coefficient equal to 1).



Physical properties

		TCDD	Others
Toxicity	I-TEF	1	0,001-0,5
Aspect		Crystal	Solid
Melting temperature	°C	305	196-332
Vapour pressure	mm Hg	$5,3 \times 10^{-9}$	$< 10^{-6}$
solubility	mg/ l of water at 25°C	$7,9 \times 10^{-6}$	$< 10^{-4}$

- At fumes temperatures in incinerators PCDD/PCDF are mainly solids
- They are quite insoluble
- Destruction over 850°C

Dioxins

Characteristics of PCDD/PCDF :

Odorless, high thermal stability, insolubility in water, high liposolubility, PCDD and PCDF are listed as POPs, which means Persistent Organic Pollutants.

They tend to concentrate in living organisms and increase their concentration, reaching also high toxicity levels.

Due to their high liposolubility, PCDD/PCDF concentrates in the human body through food (especially cooked).

Moreover, the 2,3,7,8-TCDD is a confirmed carcinogen while the other congeners are potential carcinogens.

Other effects are :

- Neurobehavioural
- Immunitary system alteration
- Disturbs on the nerve system
- Dermal alteration
- Epatic and kidneys disturbs
- Ormonal Alteration
- Effects on reproductive system
- Teratogenic
- Endometriosis

A pernicious pollution

As a resume Dioxins pollution is is very pernicious:

- **Non visible**
- **Low level of quantification**
- **Very dangerous**
- **Long term**
- **Question of environmental, human, and economical/legal safety.**

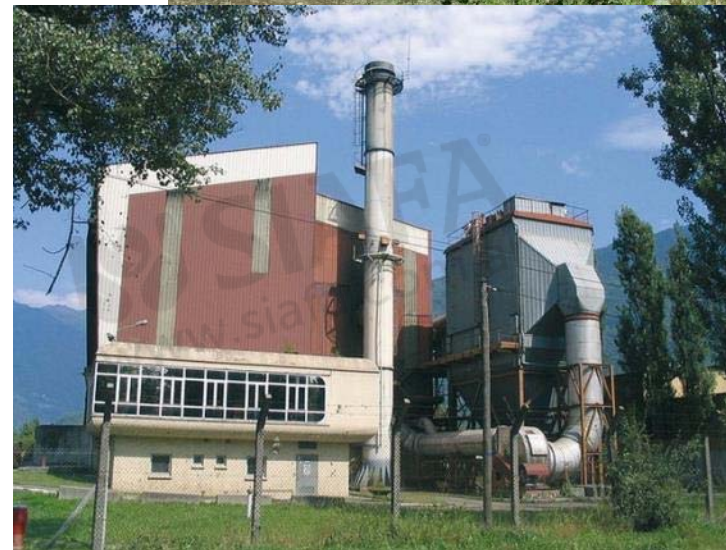
A pernicious pollution

Gilly-sur-Isère:



2001: dioxins were found in cows milk:

- 6 875 heads of cattle killed
- 2,23 millions of liters of milk and 24 tons of dairy products destroyed
- 8.500 tons of hay contaminated



Dioxins emissions control

Control of Dioxins

1994: DIRECTIVE 94/67/CE : emission limit of Dioxins 0,1 ng/Nm³ TEQ

1996: EN1948-1

Properties

- Very low quantities
- Gas and solid phases
- Toxicity is different from one congeners to another

As a consequence

- Sampling
- Long time (min 6 hours)
- High resolution analysis GC-MS-MS

Limits

- Low quantity of data (1-2/year)
- Partial understanding of emission



Long term sampling

France and Italy cases

Italy

decreto legislativo 133/2005 : fixes minimum control for dioxin
AIA (Autorizzazione Integrata Ambientale, Integrated Environmental Authorization)
is given by regional agencies and can request installation of dioxin semi-continuous samplers.

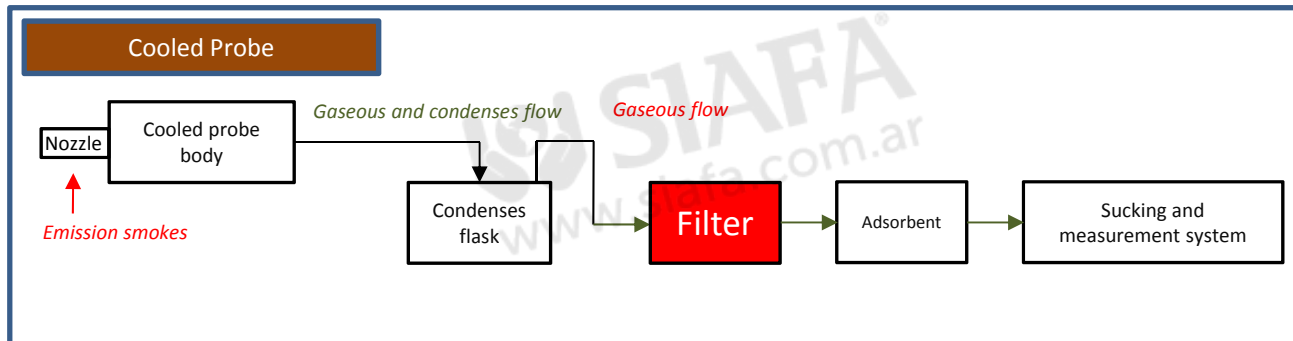
Ex.: Lombardia requests long term sampling of 15 days/month.

France

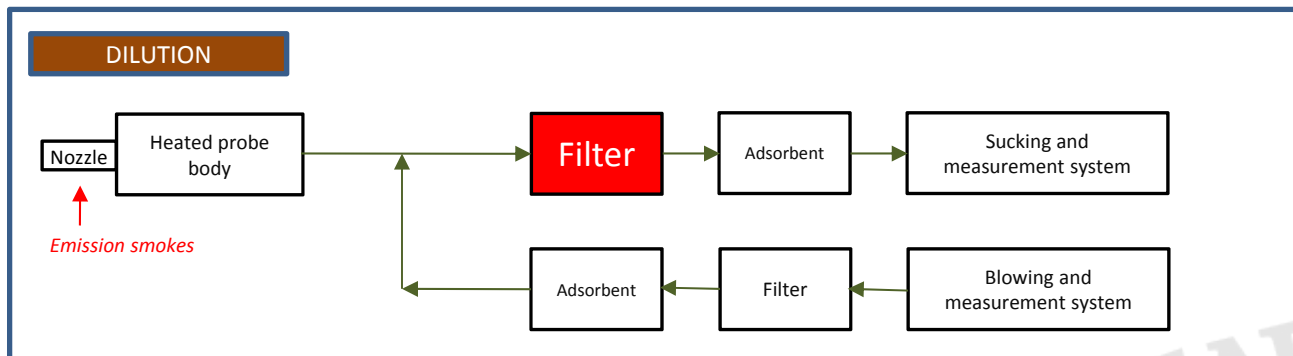
Arrêtés du 3 août 2010:

- All incinerators have to be equipped with Semi-continuous dioxin sampler at 1st July 2014
- Availability 85%
- Plants are responsible for the instrument installation and maintenance
- Sample management, analysis and calibration shall be done by accredited labs.

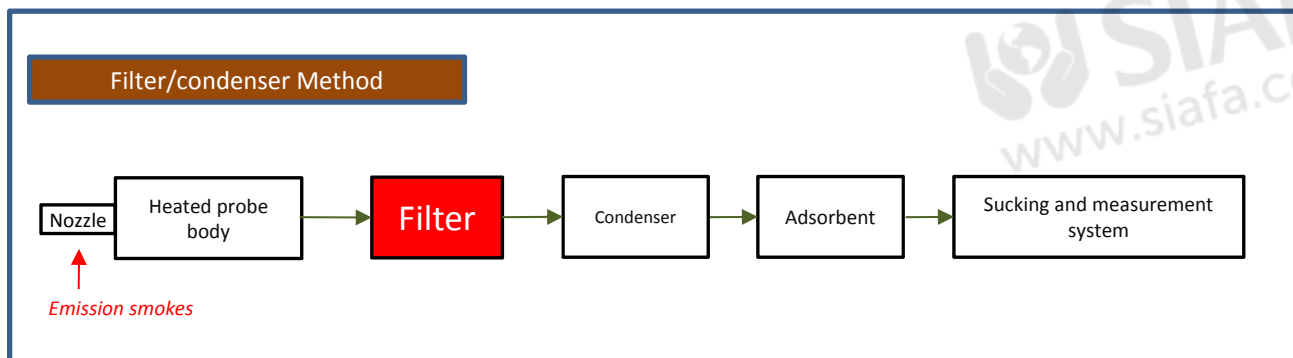
Technology choice



Condensates need to be analyzed
(in CEN/TS1948-5 condensates are not analyzed)

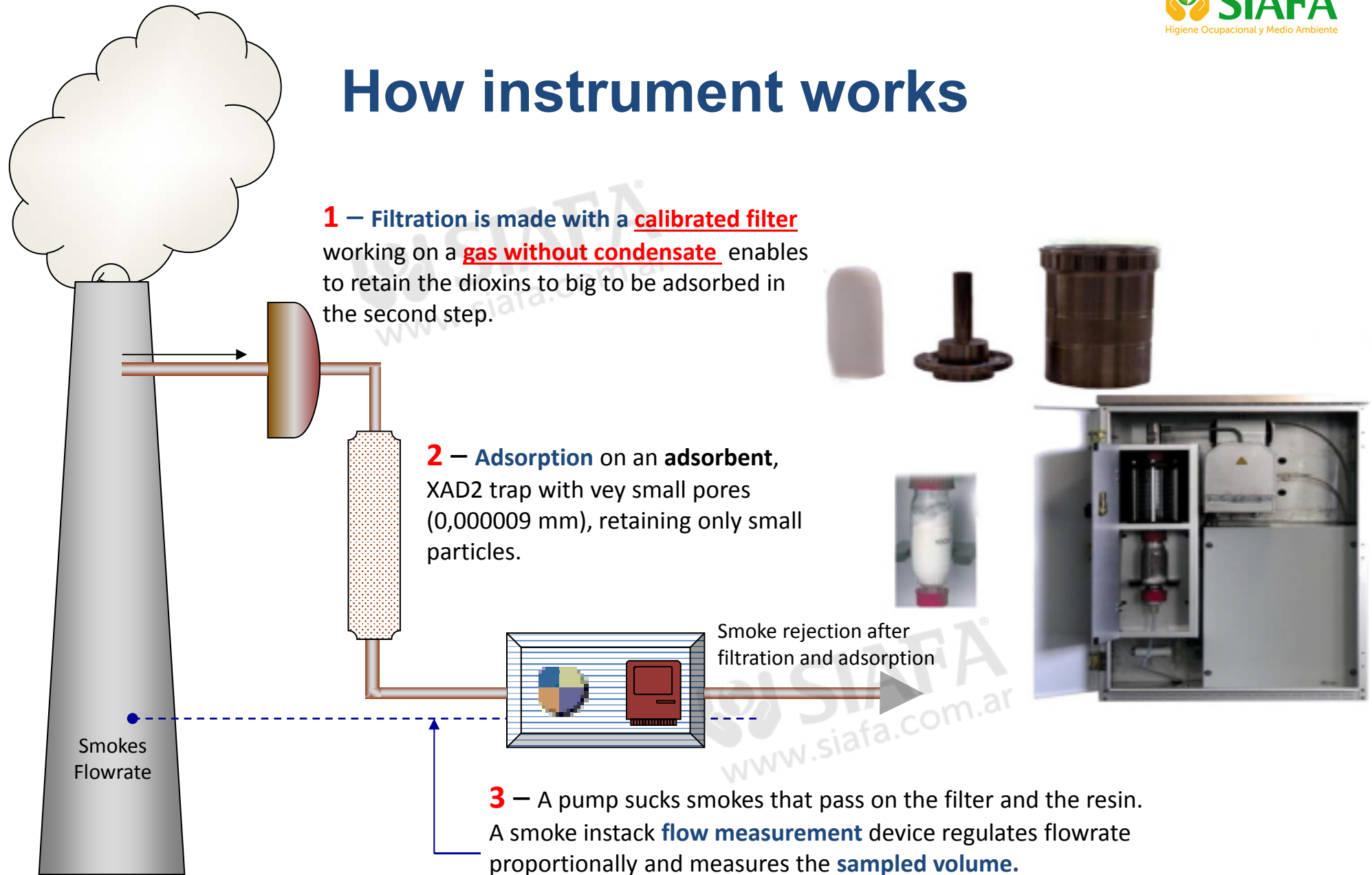


Not enough Precision in volume measurement



Most accurate method. Compatible with EN1948-1 and EPA23

How instrument works



CEN/TS1948-5

CEN/TS 1948-5 Stationary source emissions Determination of the mass concentration of PCDDs/PCDFs and dioxin-like PCBs

Part 5: Long-term sampling of PCDDs/PCDFs and PCBs

- Description of the several sampling methods
- Sampling point determination
- Instrumentation requirement
- Instrument certification
- Instrument installation validation
- Check-up and maintenance
- QA/QC management

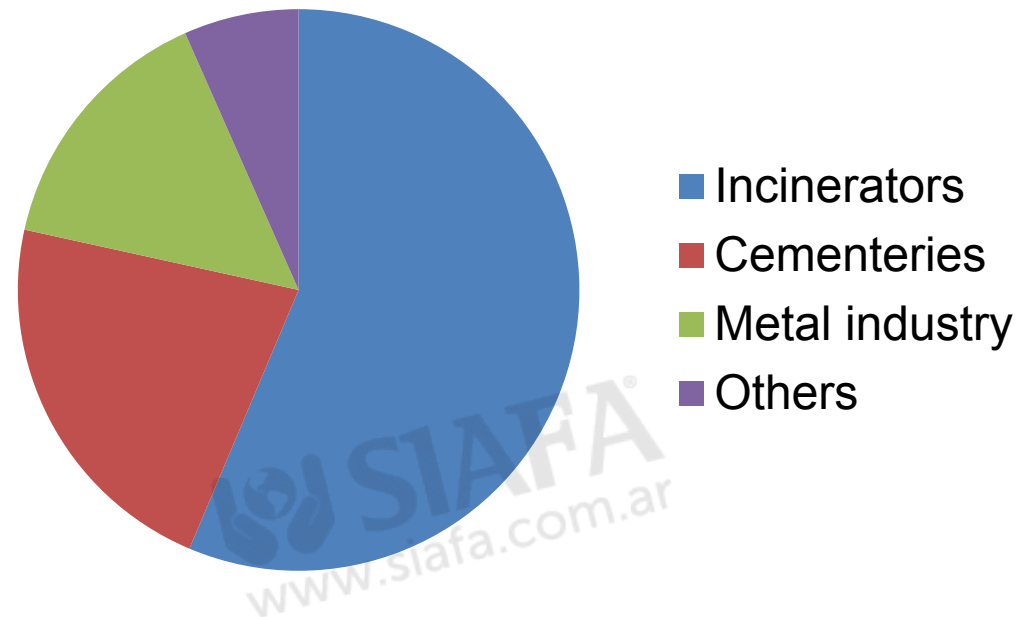
Publication: 1st April, 2015



Italian Market

Italy

- between 150 and 200 instruments
- Main market: incinerators
- Renewal market

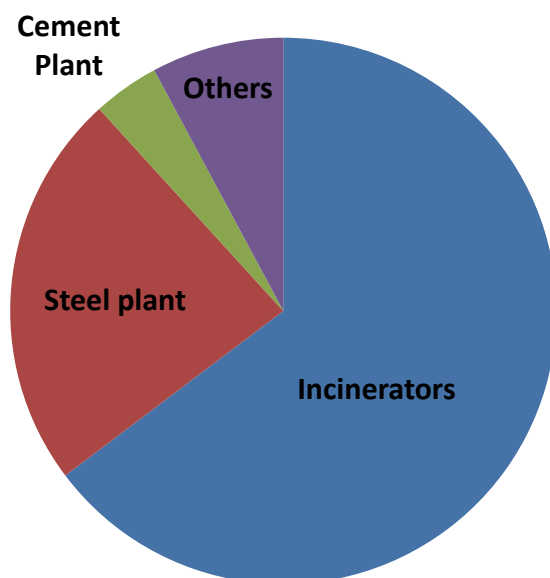


Italian Market experience

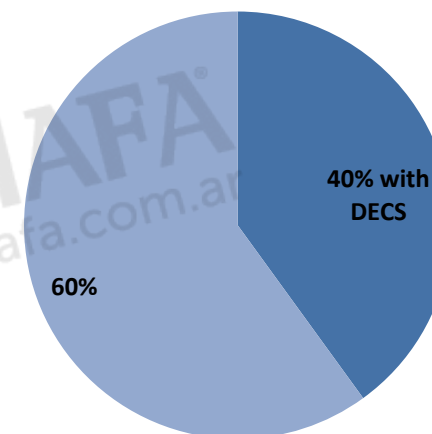
DECS in Italy: 60 instruments installed



DECS installed in Italy



Incinerator Market

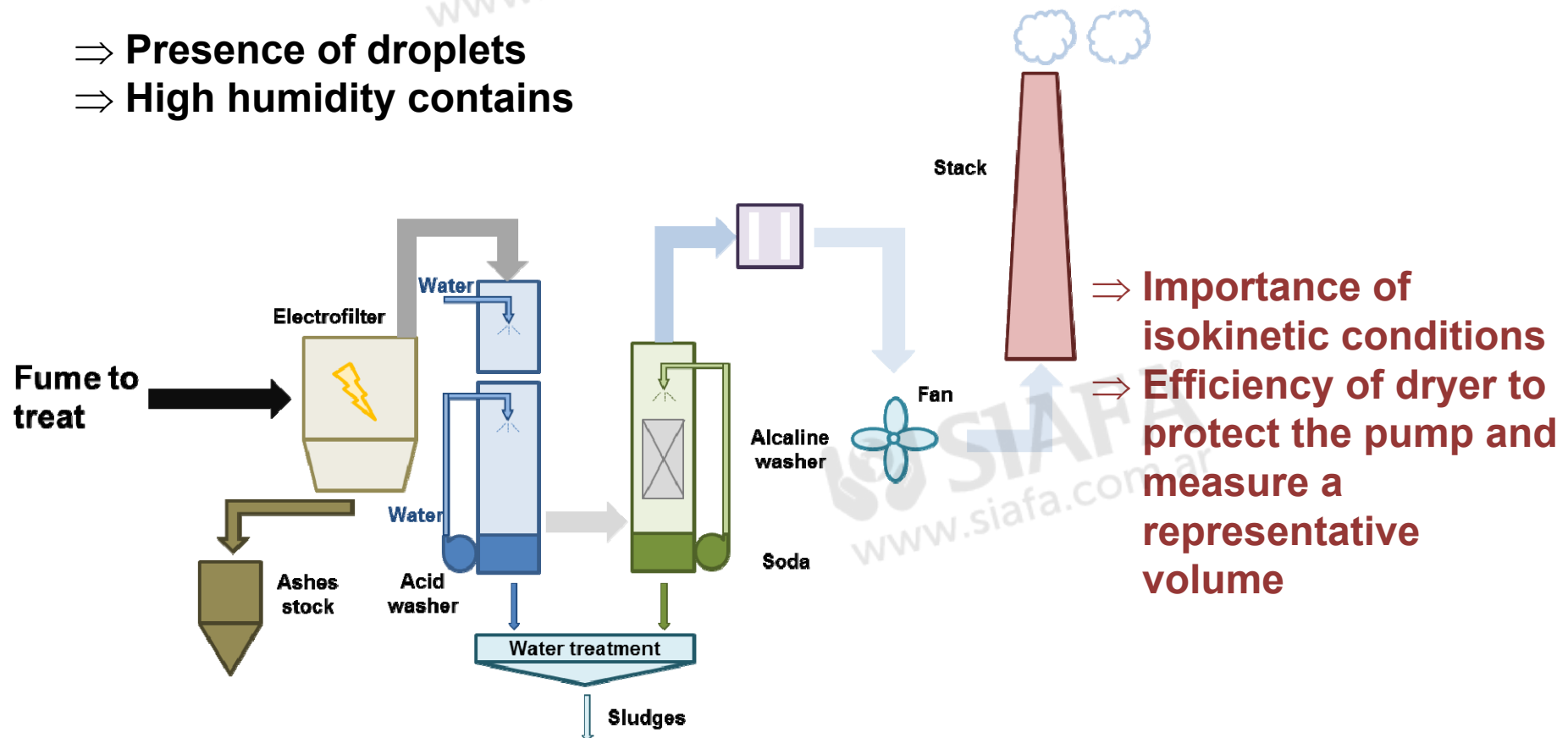


Incinerators: Return on Experience

Wet process

- Temperature between 50 and 70°C
- Absolut humidity: 15-30%

⇒ **Presence of droplets**
⇒ **High humidity contains**

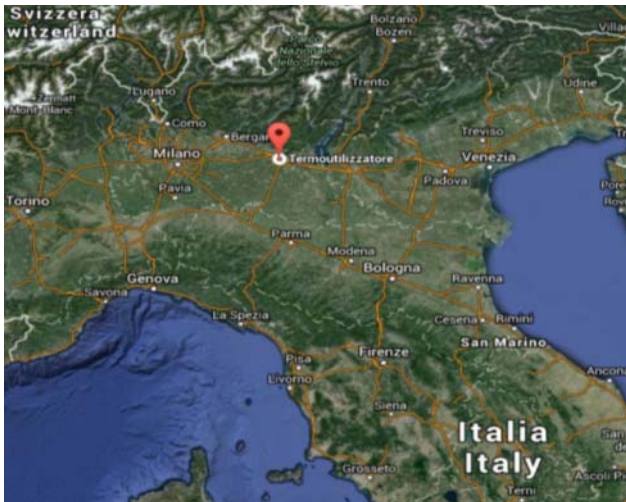


Incineration industry:

A2A Brescia incinerator_Case study



Courtesy of A2A Ambiente



Type of plant: Incineration with energy recovery (heat and electricity)
Place: Brescia (North Italy)
Management: A2A Ambiente (A2A SPA group)
Combustion units: 3
Emission: 3 lines

Fumes treatment process: Dry process

2006: "Industry Award" by Wtert (Waste of Energy Research and Technology Council), Columbia University of New York

2011: Cewep, Confederation of European Waste-to-energy, assigned to the plant the best Energy efficiency index (EEI) according to European directive

Treatment:

Household wastes and biomass: 750 000T

Energy recovery and CO₂eq saved:

600 GWh of electricity

800 GWh of heat

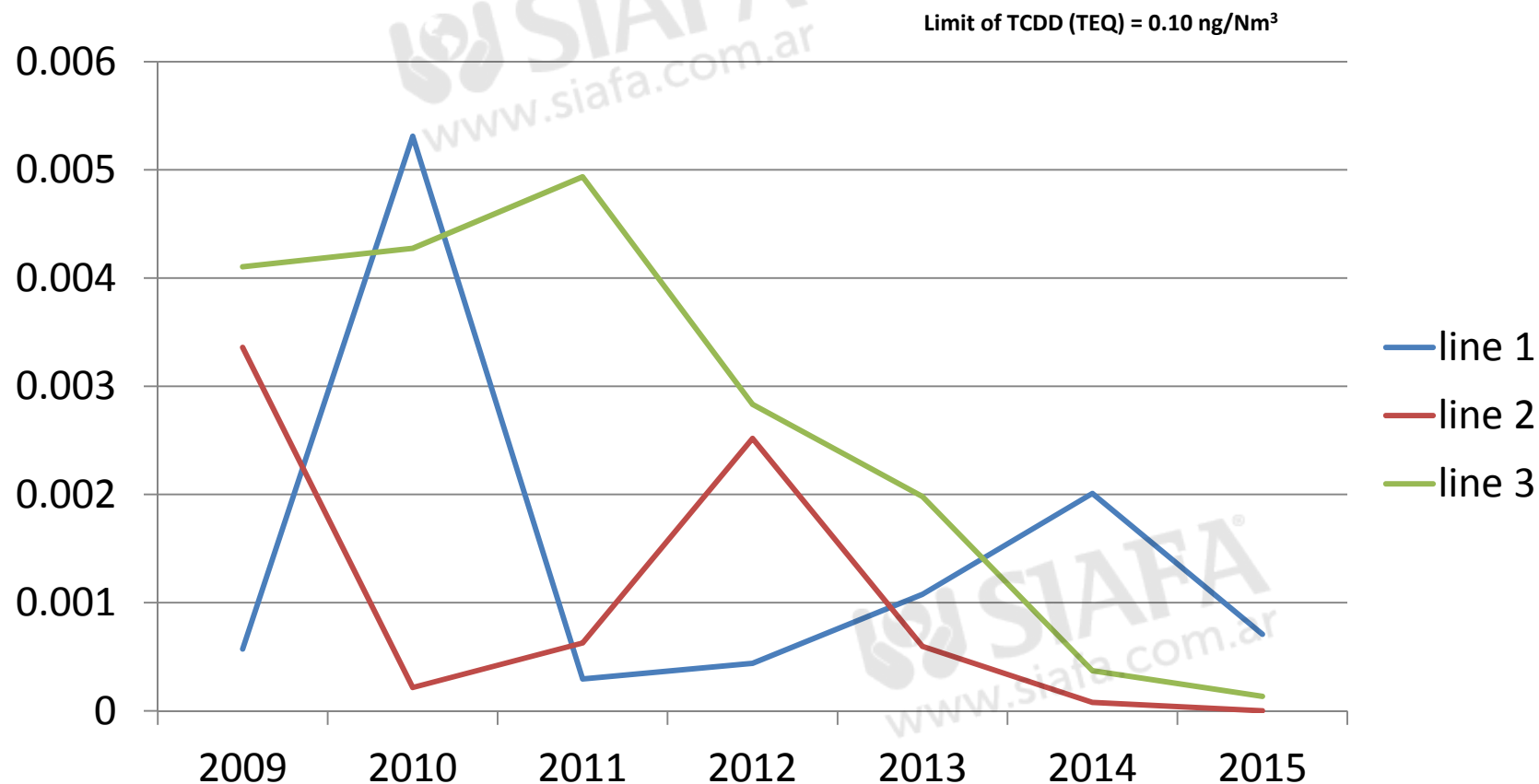
400 000 Tons of CO₂

Regulatory Compliance: AIA (Autorizzazione Integrata Ambientale, Integrated Environmental Authorization) request installation of dioxin semi-continuous samplers

Installation: - 2 full DECS were installed in 2006 and 2008 (CU+SU) to control PCDD/PCDF emissions in line 1 and 3
 - Other 3 DECS were installed in 2015 to gradually replace the old ones

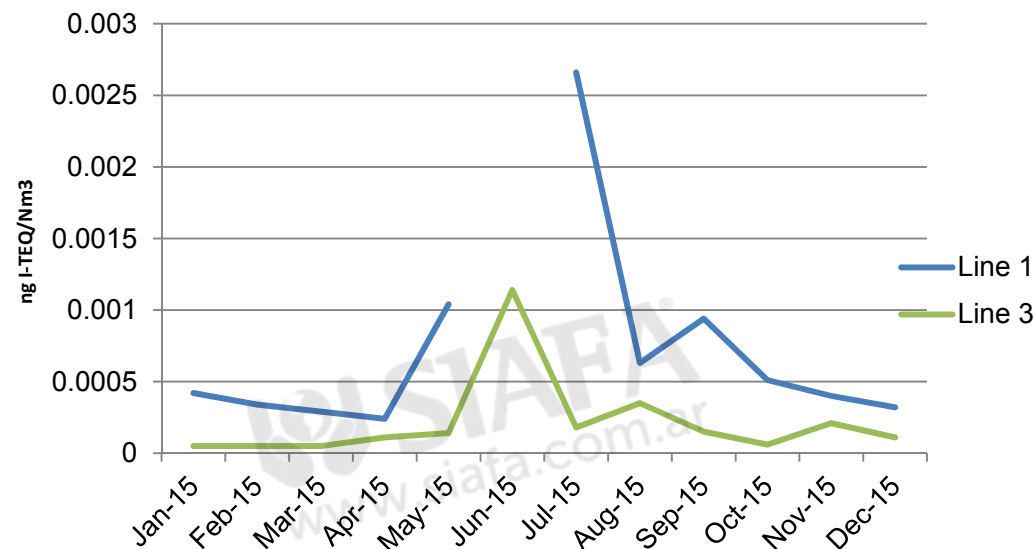
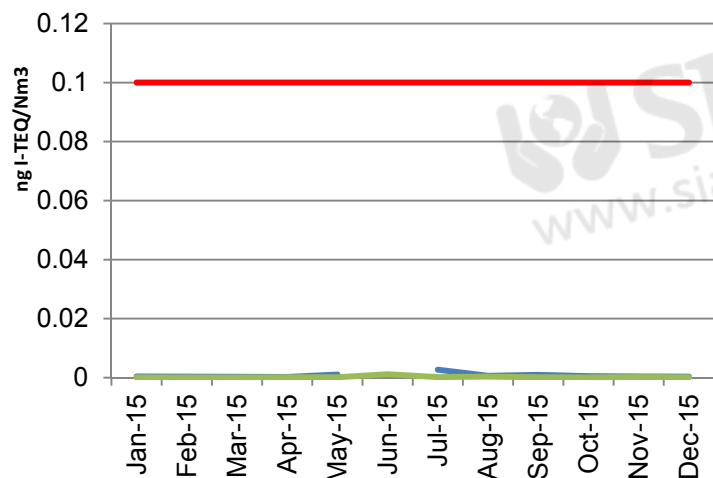
Incineration industry: A2A Brescia incinerator_Case study

Results of DECS analysis over years



Great improvement of dioxins emissions

Incineration industry: A2A Brescia incinerator_Case study



Emissions stable far under the limits

Incineration industry:

Calce incinerator



Type of plant: Incineration with energy recovery
Place: Calce, close to Perpignan, France
Owner: TIRU - EDF group

ovens

Number : 3
Total capacity: 29T/hour

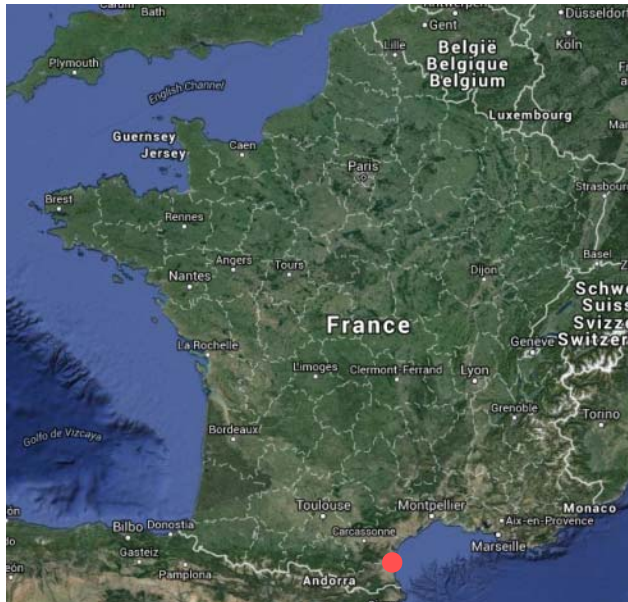
boilers

Number : 3
Total flowrate: 90T/hour

Treatment:

Household wastes: 240 000T
water treatment sludges: 20 000T
Hospital wastes: 17 000T

3 DECS were installed 2013 to control PCDD/PCDFs emissions

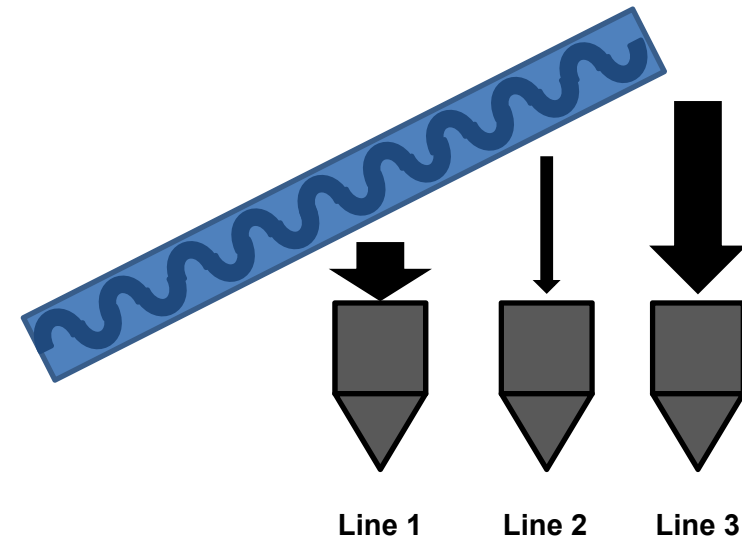


Incineration industry:

Calce incinerator Case study

Sampling results

	Dioxin emissions (I-TEQ/Nm ³)		
	Line 1	Line 2	Line 3
Oct. 2013	< 0.05	0.14	< 0.05
Nov. 2013	< 0.05	0.15	< 0.05



Explanations

It was found that the common screw supplying lignite coke to the 3 washers was malfunctioning and:

- Over charged washers of lines 1 and 3
- Under charged washer of line 2

Neither plant analyzers nor lignite coke consumption were able to alarm on this malfunctioning.

=> Installation was modified to solve this issue

Incineration industry:

Calce incinerator Case study

It also appears that dioxin samplers are very sensible to Bag filters aging. As soon as the bag filter reaches its limits dioxins emission increase.

- ⇒ More frequent bag filters changing
- ⇒ Better control of pollutants emissions (fine dusts, heavy metals...)

Dioxin semi continuous monitoring avoid overpassing emission limits of micropollutants.

“Dioxin samplers give us new information to manage our fumes treatment installations, and help us to work in a better way”

Daniel Connan
Energy Recovery Unit Director



Steel industry: Return on Experience

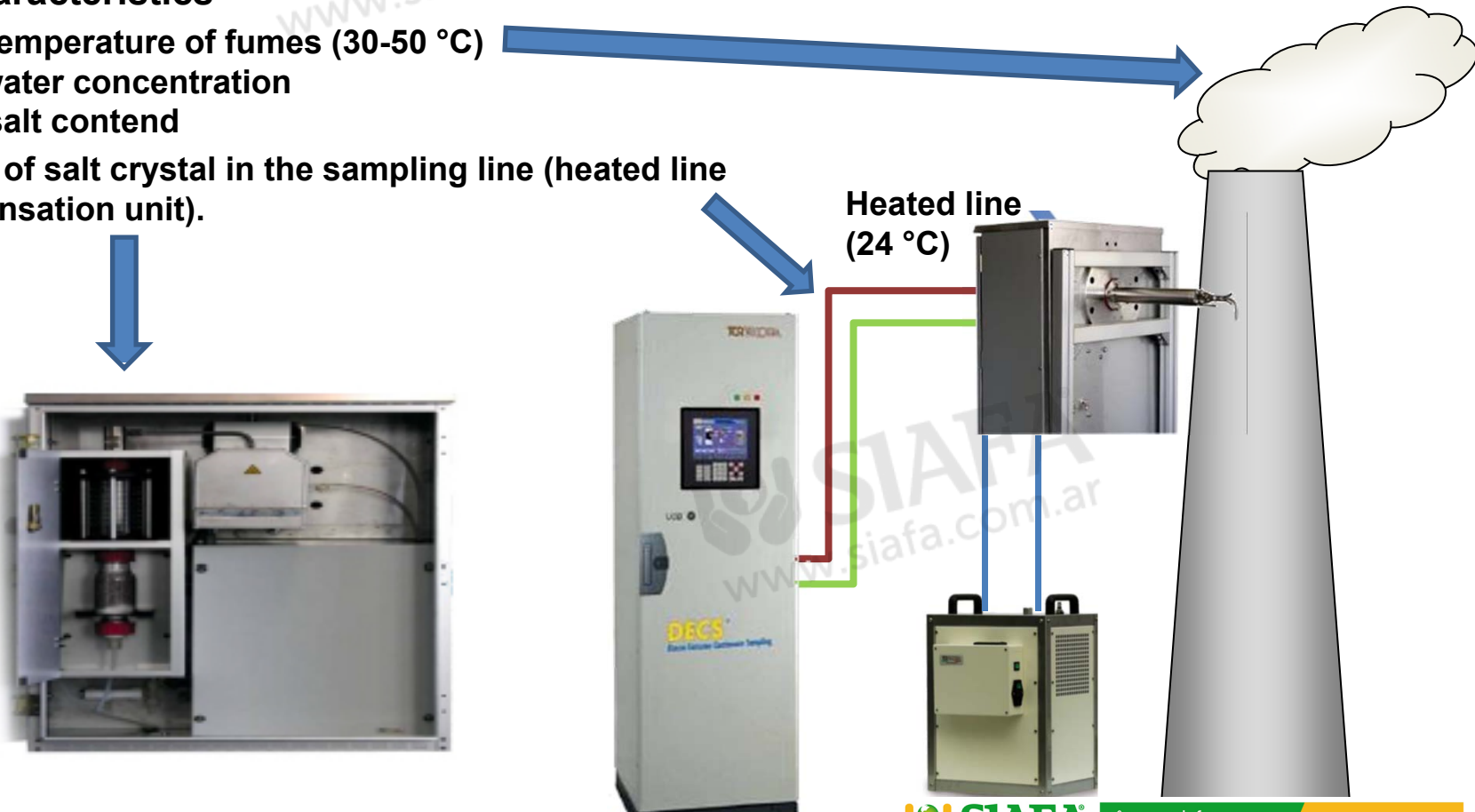
National Regulatory Compliance: Semi-continuous sampling not mandatory

Regional Regulatory Compliance: Regional agencies may require Dioxin semi-continuous samplers

Fumes characteristics

- 1) Low Temperature of fumes (30-50 °C)
- 2) Low water concentration
- 3) High salt content

Formation of salt crystal in the sampling line (heated line and condensation unit).



Steel industry: Return on Experience

Simple solutions

1) More powerful heater

2) washing of the line with water

3) Definitive approach

Change of probe nozzle (smaller diameter)
in order to slow down the pump



Lower flow to keep isokinetic condition



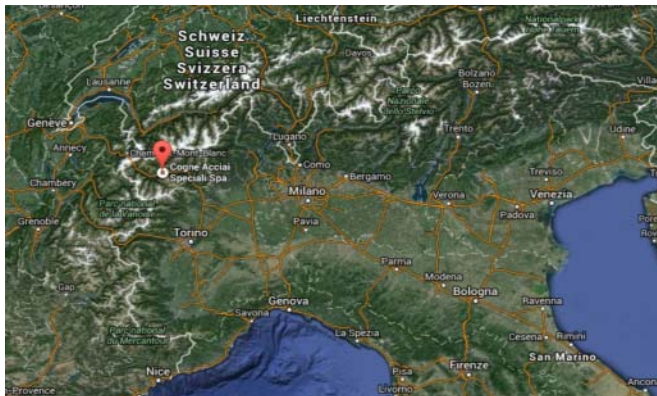
Condensation enhanced, dissolution of salt crystal



Steel industry:

Cogne Acciai Speciali_Case study

Type of plant: Steel Plant
Place: Aosta (North of Italy)
Owner: Cogne Acciai Speciali S.p.A.



Production: Ingots, blooms, billets, round and flat forged, round by extrusion of seamless tubes and profiles

Equipments:

steel production: EAF UHP, AOD converter, RH degassing, continuous casting (3-4 streets), blooming mill for Ingots, blooms, billets, round and flat forged, round by extrusion of seamless tubes and profiles

Forging area: 2 pull-down oleodynamic presses: 5000 tons and 2000 tons; and GFM SXP 40 hammer machine;

Rolling mills: integrated mill for bars and wire rods and furnaces for heat treatment;

Finishing dept.: processing cycle for producing pickled wire rod, stainless steel bars, rods, and blocks for tools and tool bars for valves of internal combustion engines;

Machines area: CNC machine tools suitable for the productions of pieces up to about 24 m in length;

Powder production unit: air induction furnace, atomization tower in inert gas, ultrasonic vibrating separation machine.

Steel industry:

Cogne Acciai Speciali_Case study

Installation

1 DECS (CU+SU) on 2014 due to regulatory reason (AIA)

Place

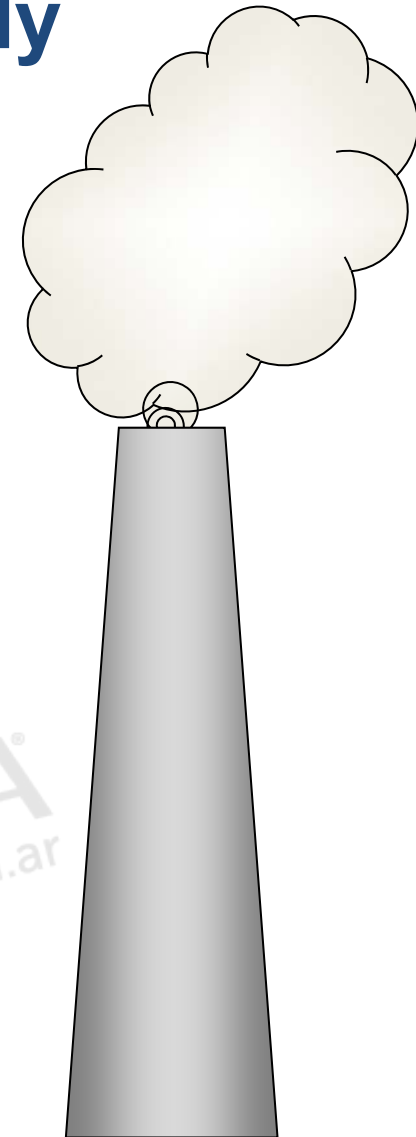
UHP smelter

Objective of project

Long term monitoring of PCDD/PCDF emission coming from UHP smelter. Need of more reliable data (annual mass flux) compared to regulatory manual sampling (according to EN 1948-1)

Stack features

Label:	E1
Height	15 m
Sampling point	10 m
Diameter	2.4 m
Nominal flow	235 000 Nm ³ /h



Steel industry:

Cogne Acciai Speciali_Case study

First phase: Validation test

- Point of Emission E1 (stack of UHP smelter)
- Parallel manual and semi-continuous sampling on the same sampling plane in the stack, same volume sampled and time of sampling

Second phase: Installation of PCDD/PCDF abatement system

In preparation for new BAT (PCDD/F from 0,5 down to 0,1 ng I-TEQ /Nm³) of steel industry (in force from 2016, but applied from 01/03/2015).

Third phase: Sampling campaign

From July 2014: 1 week sampling (2 weeks per month)

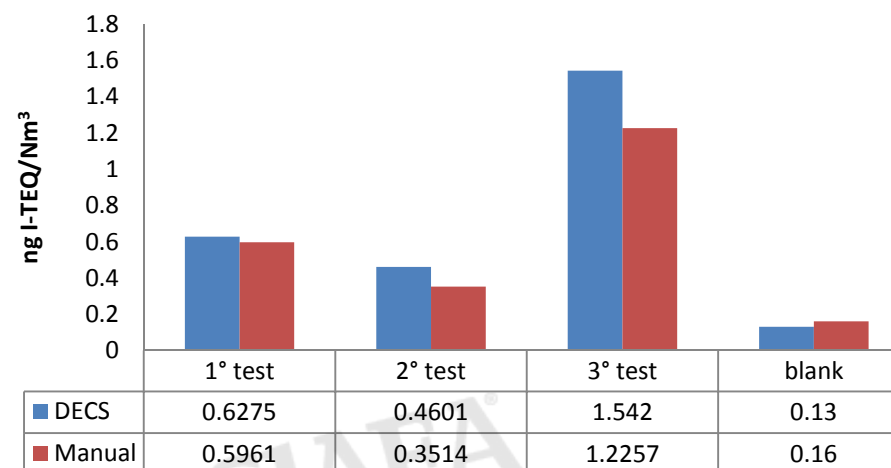
2015: monitoring of 20 weeks (no sampling during winter and summer plant stop)

Steel industry: Cogne Speciali Terni_Case study

First phase (Validation)

sampling	Duration
1° test	From 20/05/2014 (12:48) to 21/05/2014 (8:37)
2° test	From 21/05/2014 (10:26) to 21/05/2014 (23:18)
3° test	From 22/05/2014 (00:31) to 22/05/2014 (11:17)
blank	20/05/2014, time 10:30

Validation Test



	SRM ng/Nm3	ASM (DECS) ng/Nm3	Scarto %
1° PROVA	0,5961	0,6275	5,3
2° PROVA	0,3514	0,4601	30,9
3° PROVA	1,2257	1,5423	25,8
MEDIA	0,7244	0,8766	21,0

→ 21 %

<35%

Steel industry: Cogne Speciali Terni_Case study

First phase (Validation)

Prima prova

Rapporto di prova	UM	14LA13784	14LA14202	Scarto %
2,3,7,8 TCDD	pg	454,77	348,81	17,0
1,2,3,7,8 PCDD	pg	1485,145	1503,07	1,2
1,2,3,4,7,8 HxCDD	pg	86,975	71,595	6,5
1,2,3,7,8,9 HxCDD	pg	100,131	138,118	13,8
1,2,3,6,7,8 HxCDD	pg	152,013	153,577	7,1
1,2,3,4,6,7,8 HpCDD	pg	20,7333	25,918	20,0
OCDD	pg	0,51493	0,77737	33,8
media		768,03	717,55	6,8

Seconda prova

Rapporto di prova	UM	14LA13765	14LA14203	Scarto %
2,3,7,8 TCDD	pg	280,81	247,54	13,4
1,2,3,7,8 PCDD	pg	598,02	550,31	8,7
1,2,3,4,7,8 HxCDD	pg	26,106	22,766	14,7
1,2,3,7,8,9 HxCDD	pg	39,853	31,986	24,8
1,2,3,6,7,8 HxCDD	pg	59,549	48,222	23,5
1,2,3,4,6,7,8 HpCDD	pg	8,2365	7,956	3,5
OCDD	pg	0,19968	0,27715	28,0
2,3,7,8 TCDF	pg	503,106	408,417	23,2
2,3,4,7,8 PCDF	pg	2261,73	1838,8	23,1
1,2,3,7,8 PCDF	pg	227,107	201,207	12,9
1,2,3,4,7,8 HxCDF	pg	331,135	271,164	22,1
1,2,3,6,7,8 HxCDF	pg		65,424	25,7
OCDF	pg		257,191	18,2
media			179,936	20,2

Terza prova

Rapporto di prova	UM	14LA13766	14LA14204	Scarto %
2,3,7,8 TCDD	pg	526,93	407,86	29,2
1,2,3,7,8 PCDD	pg	2146,81	2022,26	6,2
1,2,3,4,7,8 HxCDD	pg	94,474	85,677	10,3
1,2,3,7,8,9 HxCDD	pg	131,952	124,298	6,2
1,2,3,6,7,8 HxCDD	pg	229,653	217,306	5,8
1,2,3,4,6,7,8 HpCDD	pg	25,7831	26,9839	4,5
OCDD	pg	0,61023	0,67548	9,7
2,3,7,8 TCDF	pg	869,88	736,674	18,1
2,3,4,7,8 PCDF	pg	8414,565	5222,545	22,8
1,2,3,7,8 PCDF	pg	505,011	419,148	20,5
1,2,3,4,7,8 HxCDF	pg	895,74	843,724	6,2
1,2,3,7,8,9 HxCDF	pg	246,712	212,555	16,1
1,2,3,6,7,8 HxCDF	pg	865,004	793,828	9,0
2,3,4,6,7,8 HxCDF	pg	681,318	647,73	5,2
1,2,3,4,6,7,8 HpCDF	pg	80,3399	83,2151	3,5
1,2,3,4,7,8,9 HpCDF	pg	10,4825	10,3702	1,1
OCDF	pg	0,88295	0,98912	10,7
media			10,9	

Congeners of PCDD/PCDF: 1°, 2°, 3° Test

Difference among congeners of PCDD/PCDF (I-TEQ)
referred to I-TEF method of NATO (<35%)

Average

→ 15.7%

→ 18.1%

→ 10.9%

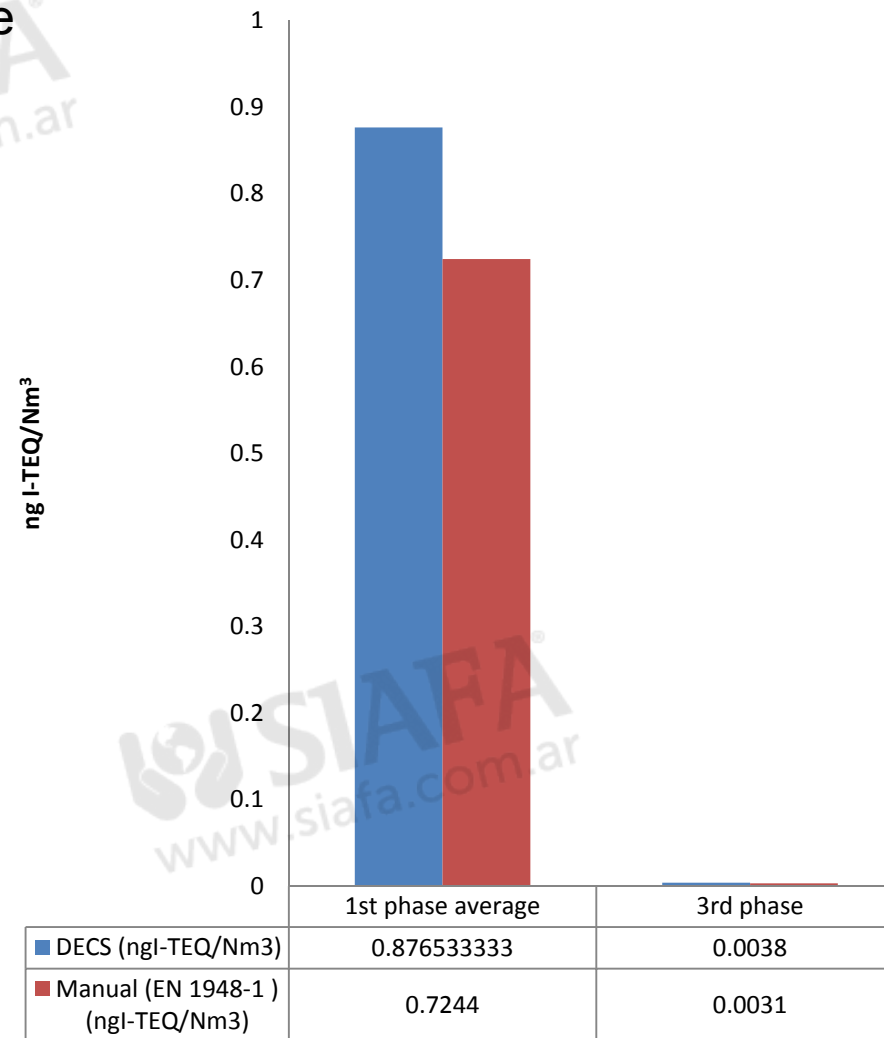
<35%

Steel industry: Cogne Speciali Terni_Case study

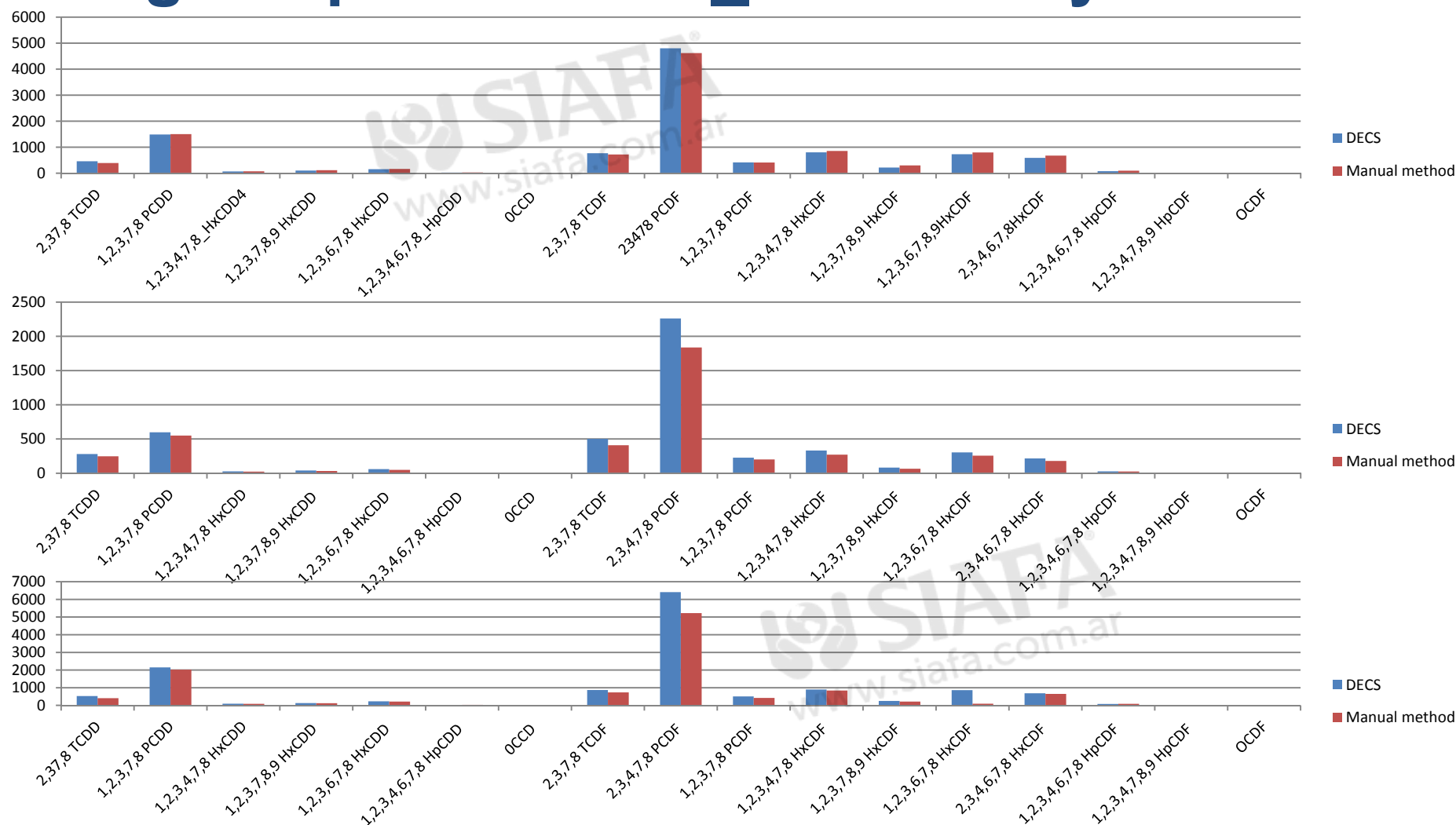
Third phase

Results

Type of sampling	Duration	ng/Nm3 I-TEQ
DECS	2015 (20 weeks)	0.0038
Manual (EN 1948-1)	2015 (20 weeks)	0.0031



Steel industry: Cogne Speciali Terni_Case study



Ratio between congeners is a fingerprint of a plant.

Steel industry:

Cogne Acciai Speciali_Case study

Positive results:

Validation of semi-continuous sampling method (DECS) Vs regulatory manual sampling (according to EN 1948-1)

Validation of abatement system

Avoids overpassing emission limits of PCDD/PCDF (0.10 ng/Nm³ TCDD (TEQ)), indicated in the new 2016 BAT (Best Available Technique)*

*Directive 2008/1/EC of the European Parliament and of the Council of 15 January 2008 and Directive 2010/75/EU of the European Parliament and of the Council of 24 November 2010 on industrial emissions (integrated pollution prevention and control)

Steel industry:

Acciai Speciali Terni - Case study



Courtesy of Acciai Speciali Terni

Type of plant: Steel Plant
Place Terni (Centre Italy)
Owner: Acciai Speciali Terni S.p.A.

Description

Acciai Speciali Terni is one of the world's leading manufacturers of stainless steel flat products

Application fields

Food preservation, household electrical appliances, constructions, kitchenware, energy production and distribution as well as the base, mechanical and steelmaking industries

Plant

The production cycle includes:

- two electric-arc furnaces (Furnace 4, Furnace 5)
- steel refining plants (AOD, VOD e ASEA/SKLB)
- slab continuous casters
- a hot-rolling mill
- cold-rolling mills
- shearing, packing and finishing equipment...



Steel industry:

Acciai Speciali Terni_Case study

Voluntary installation to comply to BAT.

Installation: 2 full DECS (CU+SU) + 1 SU were installed in 2012 to control PCDD/PCDF emissions

Objective: optimize addition of activated carbon in the abatement system

Abatement system

- 1) Hot Quench Tower
- 2) Activated charcoal abatement system (for micropollutant)
- 3) Bag filter



2) Activated charcoal abatement system (continuous addition)

- Stockage of activated charcoal
- Addition, injection and weighting line for activated charcoal
- Automation and control system

Steel industry:

Acciai Speciali Terni_Case study

Tests performed between 01/12/2015 and 15/01/2016 on furnace 5.

Aim was to select the best charcoal for dioxin trapping.

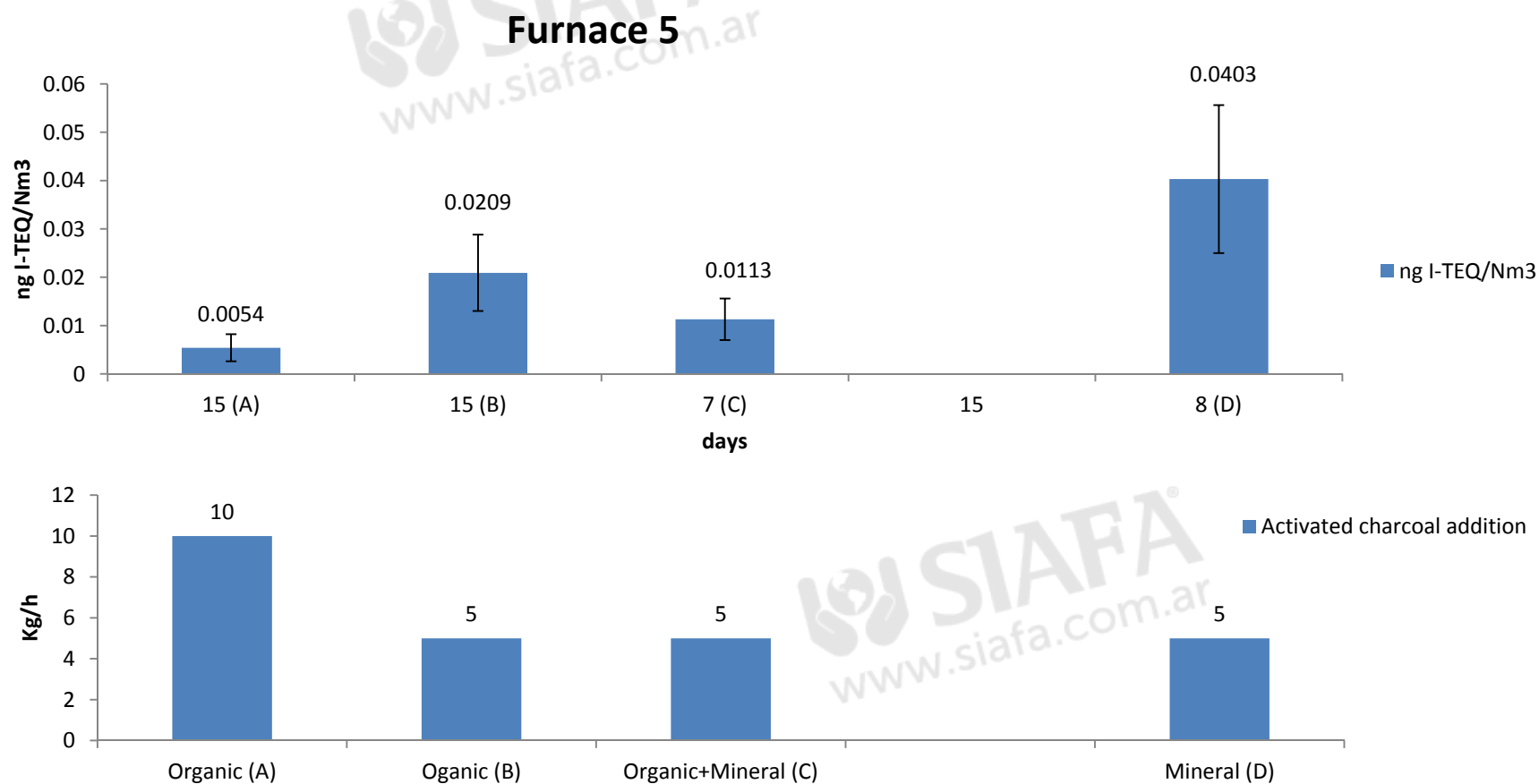
Charcoal tested:

- An organic charcoal
- A mineral charcoal

Start date	Stop date	Number of days	Type of charcoal	Dose of charcoal	Dioxin analysis [ngITEQ/Nmc]	Uncertainty [ngITEQ/Nmc]
16/11/2015	01/12/2015	15	Organic	10 Kg/h	0,0054	0,0028
01/12/2015	15/12/2015	15	Organic	5 Kg/h	0,0209	0,0079
15/12/2015	22/12/2015	7	Organic + minerale	5 Kg/h	0,0113	0,0043
07/01/2016	15/01/2016	8	minerale	5 Kg/h	0,0403	0,0153

Steel industry: Acciai Speciali Terni_Case study

Tests performed between 01/12/2015 and 15/01/2016 on furnace 5



Steel industry:

Acciai Speciali Terni_Case study

Positive results

Dioxin semi continuous sampling system enables optimization of activated carbon addition in the dedicated abatement plant

This avoids overpassing emission limits of PCDD/PCDF (0.10 ng/Nm³ TCDD (TEQ)), indicated in the new 2016 BAT (Best Available Technique)*

*Directive 2008/1/EC of the European Parliament and of the Council of 15 January 2008 and Directive 2010/75/EU of the European Parliament and of the Council of 24 November 2010 on industrial emissions (integrated pollution prevention and control)

Conclusion

1) Dioxin Semi-countinuous sampling is not anymore a niche application:

- More than 500 lines installed
- Standardized method (CEN/TS1948-5)
- Existing national market at renewal stage

2) Dioxin Semi-countinuous sampling has proven its interest for:

- Compliancy with regulations
- Fumes treatment processes control and design
- Limit micropollutants emissions
- Build trust relationship with courtneyard
- Reduce legal risks due to eventual damage risks to environment and humans

3) Future:

- Generalization of Dioxin Semi-countinuous sampling in Europe
- Generalization of the method in industrialized countries (China...)
- Dioxin sampling can be used as a model for other micropollutants (heavy metals, POPs...)