# Correlation between quantization methods for POPs emission: Dioxin Monitoring System vs. manual sampling in the MSWI of Venice

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#### Introduction

The lagoon of Venice is formed by the Northern Adriatic Sea and it is the largest among Italian Lagoons, with a total surface of about 550 km<sup>2</sup>. On the mainland, facing Venice and the lagoon, is the area of Porto Marghera, which during the last century was converted into one of largest industrial areas of Europe. Here, a Municipal Solid Waste Incinerator (MSWI) is active in the vicinities of the Treatment Plant Area (TPA) of Fusina since late 1998. Such plant is located at 4 km far from the city of Venice and 2 km far from Mestre and Malcontenta

Actually, in the TPA area three different units coexist, the above-cited MSWI, a composting plant, and an RDF production plant, along with their management facilities.

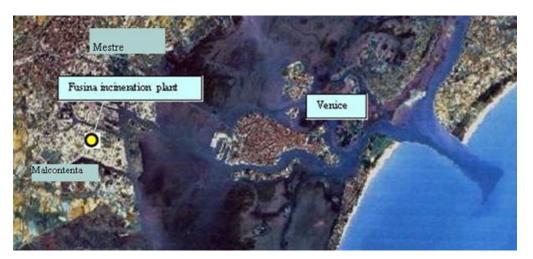


Figure n. 1: Location of the MSW Incineration Plant

The MSWI of Fusina is equipped with an energy-recovery system and is capable of incinerating 175 ton/day of Municipal Solid Waste.

In 2003, an automatic sampler was installed on the stack for continuous measurement of residual concentrations of POPs in atmospheric emissions. This results in a better monitoring as it can define the trend of the efficiency parameters during time, allowing to understand if the MSWI performance is valid and constant, both from a technical and an environmental point of view.

A sampling program and some preliminary analyses were conducted in collaboration with the I.N.C.A. Consortium (Inter-University National Consortium 'Chemistry for the Environment'), in order to properly test the performance of this innovative continuous sampling system. In the present study we compared the results of the continuous sampler with the values of the manual-sampling analyses performed in accordance to the Italian regulations for Municipal Waste Incineration (monthly controls, 8-hour sampling, and subsequent analysis of the emissions).

After one year of monitoring, such data comparison allowed to evaluate in a quite accurate way the quantity of micro-

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pollutants in the emissions of the MSWI of Fusina and to verify the nature of the emitted POP congeners.

#### **Materials and Methods**

The stack gas treater consists of a semi-dry reactor, with quick-lime feed and activated carbons powder injection, a bag filter, a scrubber and a 60 m high final stack.

Macro pollutants (CO, dust, NOX, SO<sub>2</sub>, TOC, HCL) values in gases are continuously measured while organic micro pollutants and heavy metals values are measured once a month, collecting 8 hours sample, according to methods and prescriptions of Province of Venice, Control Agency.

In 2003, a continuous sampler has been installed on the stack for PCDD, PCDF, PAH and PCB determination.

The DMS Dioxin Monitoring System consists of an aspirating system and a organic micro pollutants capture section (trap), placed right on the stack of incinerator.

There is also a control panel in order to control and keep constant the operative parameters in the trap chamber. This allows to sample isokinetic flow in the stack, keeping the aspiration rate equal to emission flow.

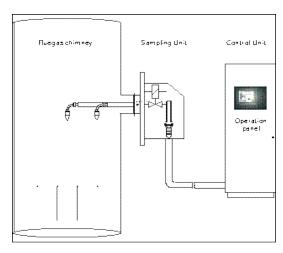


Figure n. 2 Continuous Sampling System

The new installed system minimizes human error during sampling in accordance to UNI EN 1948/99 Part 1 (76/2000/CE) and EPA Methods 23. The new system works in accordance to UNI EN 1948/99.

This system works continuously, throughout long sampling periods, and offers better guaranties to give faithful representation of the level of pollutants in gas emissions, and this allows to manage the consensus of neighbouring population.

Program to set up the continuous sampling system consists of three phases:

- 1 In first phase (quite 6 weeks) 4 weekly samples have been analyzed, with PCDD and PCDF determination
- 2 In second phase (5 months) 4 samples, collected in different times, have been analyzed to evaluate PCDD and PCDF concentration in particulate and steam phase. Markers for PCB and PAH have been also added to evaluate validity of sampling for this pollutants.
- 3 In third phase 3 monthly samples have been planned, to set up the sampler for consecutive and regular use in monthly sampling

In the future, also values of PAH and PCB concentration in gases will be studied to verify the nature of the emitted POP congeners.

The results of three samplings are reported in table 1.

Table n. 1 Analysis of Results

Continuous sampling system - Samples collected																
	Preliminary Samples															
Sample ID.	1			2		3	4		5		7			8		
Sampling cycle	1 <sup>st</sup> Phase, Weekly Samp							les 2 <sup>nd</sup> Phase,								
	1		2		3	4	4 21 d		16	16 d		14 d 21				
PCDD- PCDF (pg/Nm <sup>3</sup> -l- TE)	0.085		15.099		11.106	10.4	42	10.406	3 27.	496	8.914	4 7	.920			
	3 <sup>rd</sup> Phase , Monthly samples							Parallel sample								
Sample ID.	1			2	2 3		Continuous Sampling		5 -	Traditional methods						
PCDD- PCDF (pg/Nm <sup>3</sup> -l- TE)	4.840			6.9	70	2.129		6.51			4.17					
·		Average														
Average of:	Preliminary samples						Monthly samples						Total			
PCDD- PCDF (pg/Nm <sup>3</sup> -l- TE)	13.055 *						4.646						9.326 *			
									d sam							
	Dic	Jan	Febr	Mar	Apr	May	June	Jul	Aug	Sep	Oct	Nov	Dic	AV.		
PCDD- PCDF (pg/Nm <sup>3</sup> -l- TE) 11%O2	1.5	1.6	3.66	0.1	2.15	5 1.3	8.9		3.54	< 2	3.47	4.17	3.36	2.98		

<sup>\*</sup> average do not includes weekly sample n. 1

### **Results and Discussion**

Results obtained in 2004 with continuous sampling of emissions of MSW Incinerator of Fusina- Venice have been compared to historical data obtained with the manual sampling.

Considering Table 1 we are able to introduce following considerations:

- 1. First phase samples values (weekly samples) and second phase samples values (2-3 weeks samples) are comparable, except first sample;
- 2. Third phase samples values (monthly samples) are on average inferior to those of the first and second phases samples;

- 3. Micro-pollutants concentration (PCCD and PCDF as I-TEQ) observed in samples from the continuous monitoring system are on the average superior to the concentration observed with traditional 8 hours samples with monthly frequency (9.326 pg/ Nm<sup>3</sup> vs. 2.98 pg/ Nm<sup>3</sup>);
- 4. PCCD PCDF concentration (as I-TEQ) obtained with continuous sampler results never overcome limits imposed to MSWI by European Norm (100 pg/ Nm<sup>3</sup>), this demonstrates the good efficiency of the emissions treatment section.

In Figure 3 and 4 are reported histograms of principals congeners of PCDD and PCDF, obtained with continuous sampling analyses.

Analysis of histograms shows the prominent presence of EPTA CDD/F and OCTA CDD/F in each individual sample, and this is further evidence that EPTA-CDD/F and OCTA-CDD/F are markers of MSW Incineration.

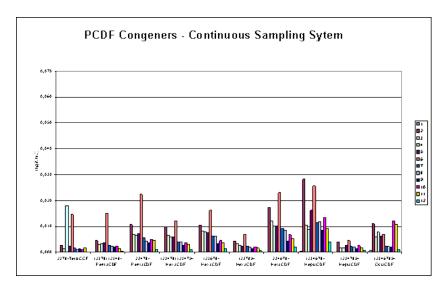


Figure n. 3: PCDF Congeners Distribution

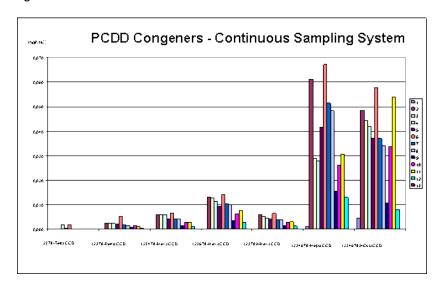


Figure n. 4: PCDD Congeners Distribution

## References

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- 2. Guerzoni S.,. Raccanelli S., (2003) The sickLagoon \_ Dioxin and other persistent organic pollutants (POPs) in the Lagoon of Venice