# PCDD/PCDF presence in the waste water to depuration plant of Fusina - Venice

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## Introduction

In July 1999 the Environmental Department issued a decree, well-known as 'Ronchi -Costa' referring to authors' names, that imposed limits more and more restrictive for micropollutants concentrations, as PCDD/PCDF in waste water discharging in Venice Lagoon (Table 1).

**Prior to the application of this decree, VESTA S.p.A., that manages the Fusina WWTP situated near Venice Lagoon, planned a systematic monitoring on all flows entering the plant, on produced sludge and on water discharging in lagoon.**

The aims of monitoring were: the determination of micropollutants source and nature; the individualization of tendency of the concentrations in final discharge and in sludge and to state possible correlations between entering and leaving quantities of pollutants.

Table. 1 – Values of micropollutants concentration for discharging in Venice Lagoon

| SUBSTANCE | CONCENTRATION LIMIT |
|---|---|
| **PAH** | **1 µg/l** |
| **Dioxin** | **0,5 pg/l (TE)** |
| **Cyanides** | **5 µg/l** |
| **Arsenic** | **1 µg/l** |
| **Lead** | **10 µg/l** |

| SUBSTANCE | CONCENTRATION LIMIT |
|---|---|
| **Cadmium** | **1 µg/l** |
| **Mercury** | **0,5 µg/l** |
| **PCB** | **absent** |
| **OC Pesticides** | **absent** |
| **Tributyltin** | **absent** |

**Methods and Materials**

**General data**: the Fusina-Venice biological treatment plant is located near the Venice lagoon; (Figure 1); it has a treatment capacity for approx. 330000 inhabitants and it discharges into the lagoon about 40000000 mc of purified water every year. The plant treats the following flows, according to the indicated percentages:

- Waste waters from domestic sewerage system [90,4%];
- Waste waters from industrial sewerage system [9,5%];
- Liquid sludge from septic tanks, conveyed by tank-trucks or tank-barges from dry-land or Venice historical centre [0,1%]

Previous studies[1] showed that in Venice lagoon PCDD/PCDF have essentially two origins:

-the first one is connected to chlorine's chemistry production, with relative abundance of PCDF congeners compared to PCDD;

-the second one is typical of human dejections and of combustion processes (incineration of municipal wastes, domestic heating, vehicular traffic) with relative abundance of PCDD congeners compared to PCDF. Particularly the OCDF/OCDD ratio is able to indicate civil or industrial origin of micropollutant entering the plant.

**Figure 1 –Waste Water Treatment Plant Location**

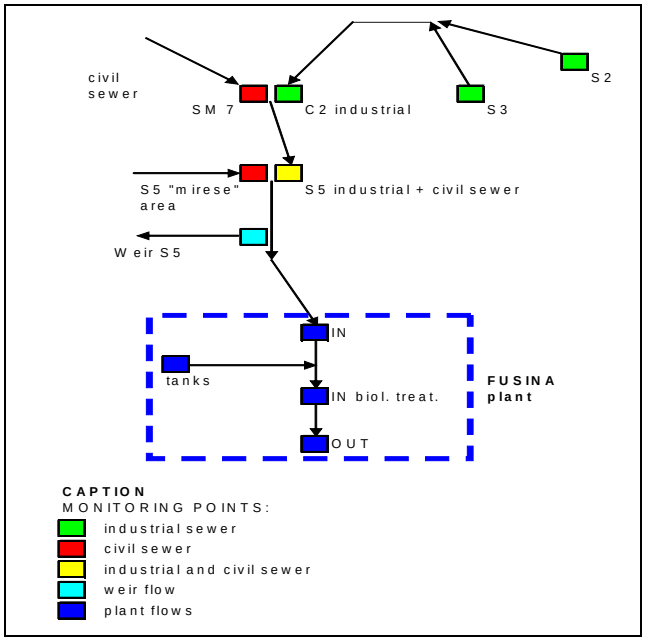
**Monitoring Plan**: the monitoring plan has been elaborated with the agreement of ARPAV (Enviromental Protection Regional Agency – Veneto) and of "Provincia di Venezia", Control Agencies, with the following principal aims:
- locating eventual dioxin flows;
- studying dioxin origin by congeners distribution and relative abundance;
- verifying eventual correlations between entering and leaving micropollutants also through mass balance;
- programming possible actions to limit micropollutants entering the plant.

Control and analysis plan involved the sewerage system in the different civil and industrial lines, the conferring of extra-sewer wastes through tank-trucks/barges and the leaving flows from the plant (discharge in lagoon and pressed sludges) according to scheme in figure n°2.
Analytic plan has been structured according to:
- a 24 h medium composite sample with monthly analytical frequency on points indicated on figure.2;

- a significant sample with weekly frequency on the tank-trucks/barges on the coming wastes from septic tanks/black wells.

On every sample the analysis of ten dangerous substances indicated by 'Ronchi-Costa' decree have been executed by accredited external laboratories, also other organic and inorganic characteristic parameters have been analyzed.

**Figure 2 –Flows scheme**




**RESULTS AND DISCUSSIONS**

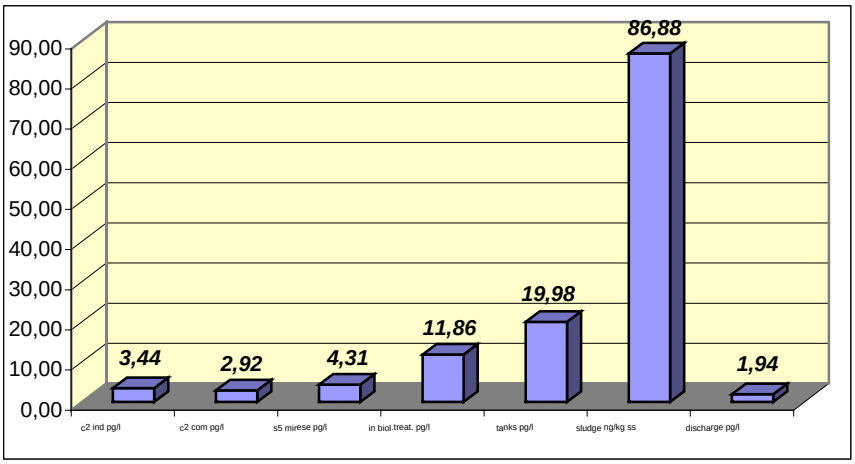
The realization of the monitoring plan and of the different analytical campaigns allowed to collect a significant number of analysis (high resolution) for every sampling point , all executed during the year 2003:

1- Sewer pumping stations (civil and industrial): n°59 chemical tests.
2- Tank-trucks/barges (domestic sewages from septic tanks): n°78 chemical tests
3- Biological treatment entrance: n°20 chemical tests
4- Biological producted sludges: n°11 chemical tests
5- Effluent water: n°24 chemical tests.

The average values of concentration have been determinated for every congener. The result can be synthesized as follow:

- the average concentration of micropollutants (PCDD/PCDF), expressed as TEQ, does not show particularly different values between industrial and municipal flows, as results from figure n° 3.

**Figure 3-Dioxins (TEQ) concentration comparison**

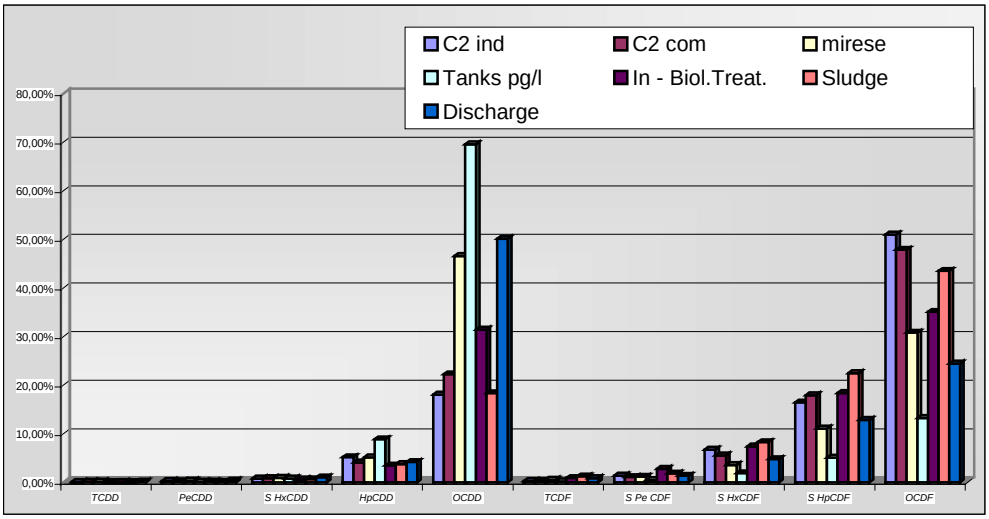



It's important to notice that PCDD and PCDF's analysis show an extreme variability in every sampled points; this variability is probably connected to the difficult methodology of sample's purification and to immediate discharges in sewerage. For example the calculated average concentration on influent water is not congruent to the sum of the partial flows concentration.

The relative abundance of every congener present in the examined flows was calculated.

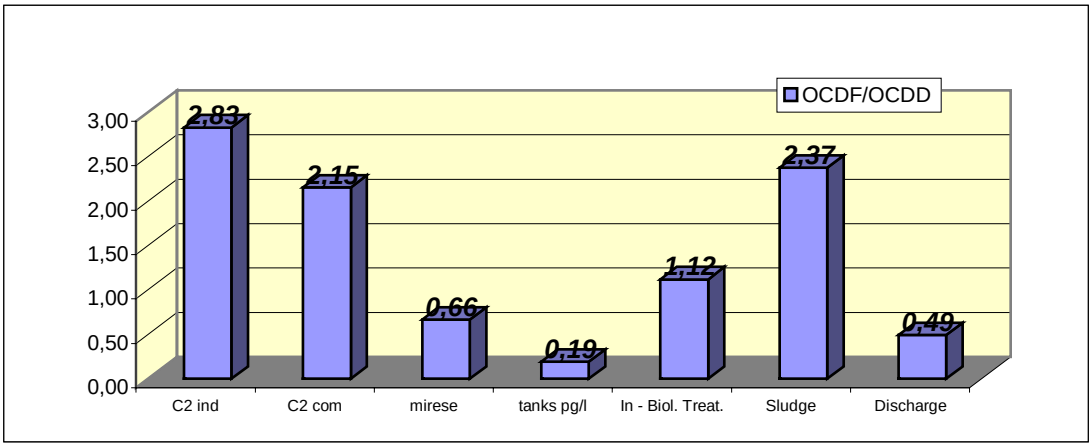
As evident from the figure 4, the OCDD and OCDF relative abundance resulted greater than the other.

**Figure 4-Congenerics relative abundance comparison**




The ratio's comparison OCDF/OCDD (figure 5) does not permit to identify with reasonable certainty the origin and the nature of dioxins in different flows. In fact the OCDF/OCDD ratio found out for municipal and industrial sewer system are quite the same, they present values included between 2,15 and 2,83 revealing an unexpected origin mixed civil and industrial; tank-trucks and barges are quite surely of municipal origin, presenting a OCDF/OCDD ratio value equivalent to 0,19.

**Figure 5-OCDF/OCDD relation**




Referring to PCDD/PCDF concentration average data, expressed as TEQ of the following flows:
- influent to biological treatment
- produced sludge
- effluent water in lagoon

it was possible to calculate the follow indicative mass balance, (see table 2)

**Table 2- Dioxins material balance**

| Flow | Annual Quantità [mc/y] | Dioxin Concentration [pg/l] | Dioxin's Quantity [g/y] |
|---|---|---|---|
| influent | 40 x $10^6$ | 11,9 | 0,472 |
| effluent | 40 x $10^6$ | 1,94 | 0,077 |
| Biological sludges | 17.650 [ton/y] | 86,9 [ng/kg ss] | 0,386* |

*17650 (t/y)x86,9(ng/kgss)x0,25(ss)=0,386(g/y)

The quantity of dioxin discharged in the lagoon with the actual process is so equivalent to about 0,08 g/year, with a range included between 0,04 and 0.18 g/y

The plant shows a dioxin reduction equivalent of about 82%, dioxins are essentially retained in the sludges. After all, on the basis of the related results and associated considerations, it's possible to draw the following conclusions:
- important dioxin supplies were not encountered in industrial waters, so particular actions for their containment are not foreseen; the majority seems to be due to municipal waters.
However it will be maintained a monitoring of the sewer system and of the tank-trucks/barges as preventive measure.
- the biological sludges produced by Fusina plant are disposed in authorized landfill.
- the plant effluent, that today presents a micropollutants concentration superior than limit of Ronchi-Costa decree (0.5 pg/l) is the object of an important initiative, known as Progetto Integrato Fusina (PIF),which will start in 2005.
This Project provides that effluent will be treated in a specific area by phytodepuration process.
After that the effluent, further purified, will be recovered as cooling water in industrial processes and discharged out of lagoon, at sea, through a special submarine piping.

**References**

1. Guerzoni S., Raccanelli S. , (2003) - La Laguna ferita