IS BIOEXSICCATION RELEASING DIOXINS?

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Introduction

Bioexsiccation is a relatively new process to treat urban solid wastes. We studied the possible release of dioxins from this process, measuring dioxin concentration in the emissions from a bioexsiccation plant. As a comparison, we measured atmospheric levels nearby the plant. The biofilter treating gaseous emissions was also evaluated to assess its efficiency. Dioxin concentrations in the biofilter effluent were lower than both those before the biofilter and the nearby atmosphere.

In the last years the management and treatment of solid urban wastes produced some improved processes, in a general attempt to cope with the problem of the huge amount of wastes produced by the modern society. Bio-exsiccation of waste aims at affording a much more biologically inert and manageable material compared to the original waste. In this process the urban solid waste is kept under an air stream for about two weeks. The waste undergoes biological transformation, due to fermentation, which produces an increase of the temperature up to 60-70°C. At the end of the process the weight waste is typically reduced by one third, due to the loss of water and to the degradation of putrescible compounds.

Since this is a relatively new industrial process, we studied the possible release of dioxins in the atmospheric emissions of the bioexsiccation plant.

Experimental part

Bio-exsiccation plant

We studied a typical bioexsiccator, located in Montanaso Lombardo (Lodi), Italy. Figure 1 shows the plant scheme with indication of the sampling points. In particular, as a background we sampled atmospheric air at about 200 m from the plant, which is in agricultural area, with a near thermoelectric power plant. To monitor the plant we collected samples before and after biofilter. In both cases we used pool samples. The waste is introduced in the plant, and atmospheric air is sucked through the waste for about two weeks. Meanwhile new waste (200 ton/day) is introduced in the plant in other areas. Temperature is continuously monitored in the different areas of the plant, to evaluate the process evolution.

Before its release in the atmosphere air is filtered by a biofilter, made of a 100-cm layer of wood chips coming from the overscreen fraction of composted green waste. The filtration system is composed by three sectors with a surface of :
E1-1= 305 m², E1-2=255 m² E1-3=255 m².

Sampling campaigns

We did two sampling campaigns in different meteorological condition. The first campaign was done in November, in rainy days. Aeriform samples were collected for four days, in order to reach a high volume collected. Another sampling campaign was done in March, in sunny days. This allowed us to evaluate filter performances in different humidity conditions.

Sampling procedure

Before sampling, we spiked the sampling apparatus with a mixture of 16 $^{13}C_{12}$-labelled 2,3,7,8-PCDD/F substituted congeners to compensate the losses of the analytes during both the sampling and the entire analytical procedure.
We collected aeriform samples with a modificated high volume sampler with sampling volumes as reported in table 1.

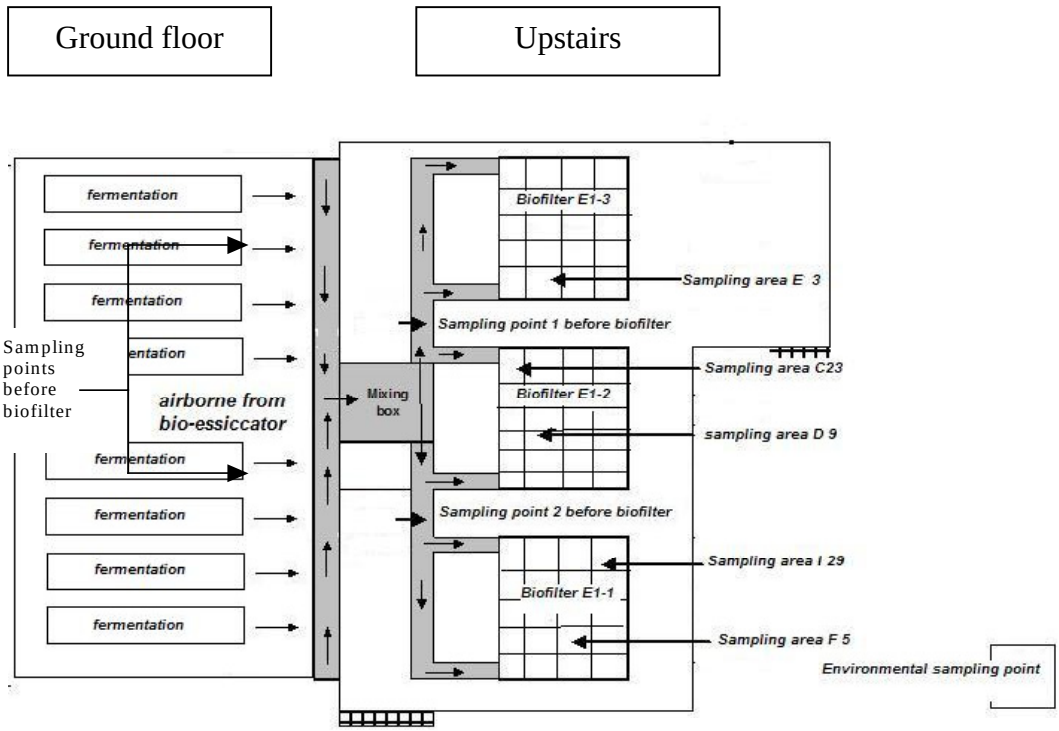

Figure 1: Plant scheme of the bioexsiccator

Table 1: Sampled volumes in campaign at the bioexsiccator (m^3 at 25°C and 1013 hPa)

		Sampling site		
Sampling period		environmental	after biofilter	before biofilter
First campaign	9:30 - 16:30 (1st day)	229	479	111
	8:00 - 18:30 (2nd day)	388	994	155
	9:30 -18:30 (3rd day)	284	427	187
Second campaign	8:30 - 17:30 (1st day)	244	748	444
	9:00 - 17:00 (2nd day)	187	769	556
	9:00 - 16:00 (3rd day)	347	489	301

Sampling apparatus

The aerifom was first filtered on glass wool, second the analytes were adsorbed on polyurethane foam and finally was condensed to remove excess humidity.
We collected aeriform samples inside the plant, before the biofilter, and at the emission of the bio-filter. Before the biofilter the sample was collected at point 1 and 2 inside the collected aeriform stream. In this way the sample is an average of the emissions from the different plant areas.
To obtain a representative sample of the emissions from the biofilter we collected emissions from all the three biofilters, according to a standardised procedure [1]. First, we ideally split each biofilter in 250÷300 squares of 1x1 m, and then we measured air flux in each square meter, by a hood with the same section. The air flux through the filter ranged between 0,6 and 1,7 m/sec. For dioxin measurements, we collected in each sector aeriform samples in both the square meters that had minimum and maximum velocities. All samples were then combined before analysis to obtain an average value.
Furthermore we collected samples of atmospheric air about 200 m from the plant, simultaneously to the emission samplings.

Materials and Methods

Native Dioxin standards (EPA 8290 STN) and Labelled Internal standards (NK-LCS-M and NK-LCS-N) were purchased from Wellington Laboratories, Ontario-Canada. Solvents (*n*-hexane, toluene, dichloromethane, tetra chloromethane and sulphuric acid 98%,) were pesticide grade from Carlo Erba Reagenti (Rodano, Milan, Italy).
Polyurethane foam (PUF) 10 cm x 10 cm was obtained from Klaus Ziemer GmbH (Langerwene, Germany).Extrelut NT, silica gel 60 (70-230 mesh) and neutral alumina oxide (70-230 mesh) phases were obtained from Merck (Damstadt, Germany).

Chemical analysis

Samples were extracted and purified as reported elsewhere [2]. Briefly, the glass wool filter with the PUF were extracted in a soxhlet apparatus with toluene for 24 h. Twice the initial glass probe from filter to PUF container was rinsed with toluene and the organic phase obtained were to put togheter with the respective aeriform sample. Extracted samples were purified by Extrelut column coated with sulphuric acid 98%, silica gel column and finally with alumina neutra column. Instrumental analysis was carried out with a MAT 95XP (Thermofinnigan) high-resolution mass-spectrometry (HRGC-HRMS). A SGE (Australia) capillary column BPX-5, 50m x 0.25mm, film thickness 0.25µm and splitless injection were used. Temperature programme: 160 for 1 min, 2.5°C/min until 300, maintained for 10 min. Constant flow: 1 ml/min. Injector temperature: 280°C. GC-MS interface: 280°C. The MS was employed in selected ion monitoring and the resolution power was 10.000.

Results and Discussion

In order to evaluate the possible release of dioxins from the bioexsiccator we measured samples collected in the effluents from the biofilter. These concentrations were compared with those before the biofilters and with the atmospheric nearby levels. TCDD equivalent concentrations are reported in Table 2. In both campaigns atmospheric levels are higher than those both before and after the biofilters. The atmospheric levels are lower than those in Milan and in Seveso [2], two areas in the same region, Lombardy; indeed the area were the bioexsiccator is located is agricultural. These values are in agreement with others agricultural area [3].

In the first campaign biofilters removed about 82% and 74% of the dioxins present in atmospheric air and plant aeriform, respectively. In the second campaign bio-filters removed about 64% and 20% of the dioxins present in atmospheric air and plant aeriform , respectively. This can be explained considering that at the effluent temperature (20-40°C) by far most of the dioxins are not in the gas phase, but are adsorbed in particulate, which is trapped by the biofilter. It is likely that a similar process occurs to the dioxins present in the atmospheric air, passing through the waste. Indeed, the waste layer in the plant is about 6-meter thick.

The influence of the meteorological conditions, and humidity in particular, seem to play role. We were interested in humidity because humidity can play a role in the efficiency. In fact, we have found a variation in the biofilter efficiency.

A previous study evaluated dioxins release in the effluent of bioexsicator after burning the effluents [4]. Dioxins were found in the emissions at higher levels than those we measured, but the situation was very different for the presence of the combustion process.

There could be a role of waste degradation in a possible dioxin presence in waste and consequently in emissions. Several studies evaluated dioxin formation and degradation in waste related materials [5,6,7]. Composting is a process, which typically lasts much longer than bio-exsiccation. We have not measured dioxin levels in waste, since the target of our research was dioxin atmospheric release. Figure 2 shows the dioxins patterns detected in different sampling point and in atmospheric sample during both campaigns. The pattern changes going through the TCDF and OCDD increase and the other chlorinated classes decrease waste. Both campaign have the same behaviour.

Conclusions

We reported dioxin measured in aeriform emission from a bioexsiccation plant. No significant emission was found. The levels were lower than those in the nearby atmospheric air, an agricultural area. We measured levels before and after the bio-filter, which appeared to achieve a certain abatement of the dioxins present in the plant effluents.

Table 2: TCDD equivalent concentrations in different sampling points

First campaign			
	Atmospheric Air	**Before Bio-filter**	**After Bio-Filter**
Data	20-25/11/02	20-25/11/02	20-25/11/02
Concentration in:	pg/m^3	pg/m^3	pg/m^3
I-TCDD Equivalent	0,173	0,124	0,034
Human-TCDD Equivalent	0,181	0,129	0,033
Second campaign			
Data	4-6/3/2003	4-6/3/2003	4-6/3/2003
Concentration in:	pg/m^3	pg/m^3	pg/m^3
I-TCDD Equivalent	0,092	0,042	0,034
Human-TCDD Equivalent	0,094	0,044	0,036

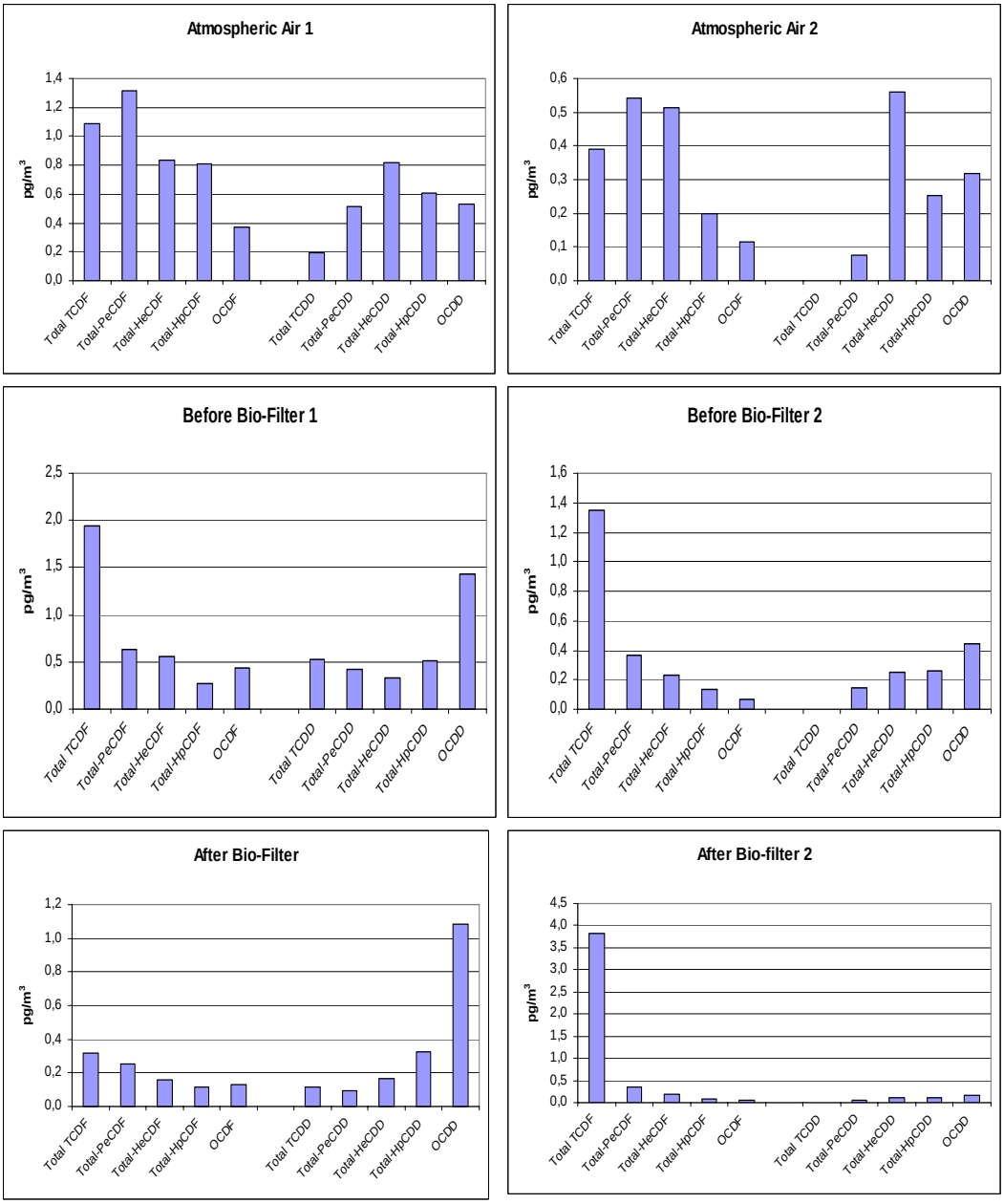

Figure 2: PCDD/F patterns in different sampling points

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