CHLOROPHENOLS AND PCCD/Fs DURING SEWAGE SLUDGE COMPOSTING

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Introduction

Sludge composting consists of the microbial conversion of the material in the presence of suitable amounts of air and moisture into a product with the general appearance and other characteristics of a fertile soil [1]. The sludge is conditioned for composting by the use of a bulking material (e.g. straw, sawdust, leaves, woodchips…) to make it permeable to air. As the aerobic microorganisms biologically oxidize the organic material of the sludge, they release heat and the temperature increases. The material reaches a stable state resistant to odor production. Heat produces the decomposition of many human pathogens. However, it is a source of macro and micronutrient to plant growth when applying with soil. Composting procedures use very little external energy.
According to this definition of composting, organic compounds should be reduced, but at a previous research [2] it was observed an increase in the total amount of PCDD/Fs after 40 days at the end of the composting process. This research was carried out with samples from a sewage sludge composting plant. The main contribution to the I-TEQ was due to 1,2,3,4,6,7,8-HpCDD and OCDD.
Some authors [3] found an OCDD and HpCDD formation during semi-anaerobic digestion of sewage sludge at low temperature (20ºC) while many other authors have suggested an enzymatic formation of PCDD/Fs from some chlorinated organic compounds such as chlorophenols [4,5].
The aim of the present study is to analyze the content in PCDD/Fs, chlorophenols and chlorobenzenes in samples from a composting plant.

Materials and methods

The samples of biosolid used in this work were collected at a composting plant in Alicante (Spain) which is located in the same enclosure as the wastewater treatment plant (WWTP). The plant processes sludge generated in its WWTP, as well as those from the nearby WWTP. The system used in the plant for sewage sludge composting consist of a combination of parallel tunnels, each one of which can process one type or a mixture of different initial material. Each tunnel in this facility is 3 m wide, 2 m high and 75 m long. The aeration is based on three air turbines. The operation conditions of the process plant are shown in table 1.

Table 1. Operating conditions of the composting plant.

Residence time	5 weeks
Turnings-over per week	3
Advance per turning-over	4 m
Aeration 1st part	15 min. + 15 min. resting
2nd part	15 min. + 30 min. resting (day and night)
Temperature profile	50 – 70 º C (1st part) 35- 25 º C (2nd part)
Compost moisture	≤ 50 %
Organic matter	50 – 60 %

The material composted in this facility is a mixture (1:1 w/w) of sewage sludge and bulking materials (sawdust and straw in a proportion of 1:3 w/w). Five samples of biosolid, which were taken every 15 m along the composting tunnel, were sampled. Samples of sawdust and straw were also analyzed, due to the fact that they use them as bulking material. To each sample, moisture content and ash content were determined. The chemical composition of the samples was determined as follows: the content of C, H, N, S was determined with a CHNS-O EA 1108 apparatus from Carlo Erba (Rodano, Italy) whereas the semiquantitative analysis for elements with an atomic weight higher than that of Mg was carried out with an automatic sequential X-Ray spectrometer model PW 2400 (Philips Magix Pro).

An amount of 5-7 g of each sample was Soxhlet extracted with 80 ml of 1:1 (v/v) mixture of acetone-hexane for the simultaneous analysis of, chlorophenols and chlorobenzenes. Afterwards a cleanup procedure (EPA method 3640) was followed by gel permeation chromatography using a DeltaChrom™ Sample Clean-Up system SCS 200 with a PAH Prep Column (21.2 x 300 mm) from Watrex. The solvent used was dichloromethane with a flow rate of 2.5 ml· min^{-1}.
The final analysis of the extract was done by gas chromatography/mass spectrometry in an Agilent instrument 5973N apparatus with a gas chromatograph Agilent 6890 N. A chromatographic column HP5-ms (30 m x 0.25 mm i.d) was used. Different analysis methods were used in order to identify each group of compounds: chlorophenols and chlorobenzenes.
On the other hand, an amount of approximately 20 g of each wet sample was spiked with the internal standard solution and then was extracted using accelerated solvent extraction with a Dionex 100 apparatus, in 100 ml extraction cells. The solvent used was toluene. Extraction was followed by a clean-up procedure according to the 1613 EPA Method, consisting of an acid-basic treatment and a clean-up procedure using a FMS Power Prep™ System (FMS Inc., Boston, MA, US) using a silica, alumina and a carbon column. Finally, the recovery standard was added. The analysis of the extract was done by HRGC/HRMS on a Micromass Autospec-Ultim NT high resolution mass spectrometer in SIM mode coupled to a HP6890 HRGC. A DB5-MS chromatographic column (60 m x 0.25 mm) with programmed temperature vaporizer (PTV) inlet was used. The identification and quantification of each compound was performed by the isotope dilution method and the analysis was based on the US EPA method for PCDD/Fs determination[7]
A blank was also conducted following the same procedure as for the samples to identify possible interferences.
Solvents used in this study were analytical grade and purchased from Merck (Germany). Standards were all purchased from Wellington Laboratories (Ontario, Canada).

Results and discussion

The concentration of chlorophenols is shown in table 2. The concentration of chlorobenzenes was very small and under 2 μg/g (dry basis) for all the samples.

Table 2. Concentration of chlorophenols in all the biosolid samples, straw and sawdust μg/g (dry basis).

Chlorophenols(mg/g)	**Straw**	**Sawdust**	**M1**	**M2**	**M3**	**M4**	**M5**
MONO-	2.17	1.65	0.08	0.12	0.09	0.07	0.11
DI-	0.03	0.06	3.96	2.28	1.14	1.49	1.83
TRI-	0.00	0.02	3.90	3.67	2.98	1.94	1.38
TETRA-	1.19	0.12	1.78	3.65	5.42	3.68	0.36
PENTA-	0.00	0.00	2.12	0.00	0.09	0.13	0.00
TOTAL	**1.25**	**2.77**	**7.50**	**9.46**	**9.93**	**7.28**	**3.40**

The results for all the PCDD/Fs congeners are shown in table 3. Take note that M1 refers to the initial mixture, M2 refers to the sample after 15 m, M3 is the sample at 30 m, M4 at 45 m and M5 corresponds to the final mixture. For the calculations of the i-TEQ, the i-TEF (1998) was used.
On the other hand, taking into account the ash content, the concentration effect (initial mass of ash content / final mass of ash content) was measured, where initial mass corresponds to the M1 sample and final to the corresponding sample. The corresponding results are also shown in table 3. Note that the concentration effect is small, close to the unity and consequently the composting was not carried out properly.

Table 3. Concentrations of PCDD/Fs for all the samples in ng I-TEQ/kg (dry basis) and concentration effect (take note that *res.* means residue or ash content).

	ng I-TEQ/kg (dry basis)						
concentration effect (kg initial res./kg final res.)	-	-	1	1.01	1.12	1.14	1.35
Name	**Sawdust**	**Straw**	**M1**	**M2**	**M3**	**M4**	**M5**
2378-TCDF	0.3	<0.1	0.2	0.4	0.2	0.2	0.2
12378-PeCDF	0.1	<0.1	0.5	1.0	0.04	0.1	0.02
23478-PeCDF	2.0	<0.1	1.3	10.8	0.7	1.6	0.8
123478-HxCDF	0.6	<0.1	0.7	2.3	0.3	0.4	0.2
123678-HxCDF	0.5	<0.1	0.6	2.2	0.2	0.3	0.3
234678-HxCDF	0.6	<0.1	1.4	2.4	0.2	0.5	0.3
123789-HxCDF	0.1	<0.1	0.3	1.5	0.1	0.2	0.2
1234678-HpCDF	1.3	<0.1	0.9	0.9	0.4	0.5	0.3
1234789-HpCDF	0.1	<0.1	0.04	0.4	0.0	0.0	0.02
OCDF	0.6	<0.1	0.1	0.4	0.1	0.2	0.1
Sum PCDF	**6.3**	**<0.1**	**6.1**	**22.3**	**2.2**	**4.1**	**2.4**
2378-TCDD	0.0	<0.1	1.1	4.3	0.1	0.7	-
12378-PeCDD	0.3	<0.1	7.6	10.6	0.5	2.3	1.1
123478-HxCDD	0.2	<0.1	0.8	1.8	0.1	0.4	0.3
123678-HxCDD	0.6	<0.1	8.5	3.1	0.4	2.5	1.1
123789-HxCDD	0.3	<0.1	0.2	1.6	0.1	-	0.1
1234678-HpCDD	4.6	<0.1	2.4	7.7	1.4	2.0	1.2
OCDD	4.7	<0.1	1.7	18.1	2.0	1.8	1.1
Sum PCDD	**10.7**	**<0.1**	**22.4**	**47.2**	**4.6**	**9.7**	**4.9**
Sum PCDD/Fs	***16.9***	***<0.1***	***28.5***	***69.5***	***6.8***	***13.8***	***7.4***

Note that the concentration values of PCDD/F in the straw sample were lower than 0.1 ng I-TEQ/kg (dry basis). It was observed a slightly amount of 1,2,3,4,6,7,8-HpCDD and OCDD in sample M2 among others, showing the higher I-TEQ concentration value compare to the others.
For all the samples PeCDD/F, OCDD, HxCDD and HpCDD showed the higher i-TEQ, being the OCDD the highest one.
As commented previously, the compost process was not carried out properly and the dioxins and furans analysis corroborate this conclusion. The concentrations of chlorophenols are in the range of 3-10 μg/g (dry basis), chlorobenzenes concentrations are less than 2 μg/g (dry basis) and dioxins and furans concentrations are in the range of 7-70 ng I-TEQ/kg (dry basis).

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References

(1) G.B. Wilson, J.F Parr, E. Epstein, P.B. Marsh, R.L. Chaney, D. Colacicco, W.D. Burge, L.J. Sikora, C.F. Tester, S. Hornick. (1980); EPA – 600/8-80-022.
(2) M.F. Gómez-Rico, (2008); Doctoral Thesis. Univerity of Alicante.
(3) C. Klimm, K. W. Schramm, B. Henkelmann, Dr. Martens and A. Kettup. (1998); *Chemosphere* 37 (9-12): 2003-2001.

(4) L.G. Öber, C. Rappe, (1992); *Chemosphere* 25 (1-2): 49-52.
(5) L.G. Öberg, B. Glas, S.E. Swanson, C. Rappe, K.G. Paul., (1990); *Arch. Environ. Contam. Toxicol.* (19): 930-938.
(6) M. Tuomela, M. Vikman, A. Hatakka, M. Itävaara, (2000); *Bioresource Technology* (72): 169-183.
(7) EPA. *Method 1613: tetra-through octa-chlorinated dioxins and furans by isotopic dilution HRGC/HRMS*. Washington, 1994:89 p. Available from: <http://www.epa.gov/region03/1613.pdf>. Accessed: May 2, 2007
(8) J. Wittsieoe, Y. Kullmann, P. Schrey, F. Selenka, M. Wilhelm, (2000); *Chemosphere* 40(9-11): 963-968.
(9) J.C. Quintero, G. Feijoo, J.M. Lema, (2006); *VITAE* 13(2):61-67.