PCDD/F in sewage sludges from two waste water treatment facilities in Rio de Janeiro State, Brazil

Márcia de Souza Pereira[1], Bertram Kuch[2]

[1]Departamento de Geoquímica – Instituto de Química, 5º andar, Universidade Federal Fluminense. Outeiro de S.J. Baptista S/N, Centro – Niterói, cep:24020-007, RJ, Brasil
[2]Institut für Siedlungswasserbau,Wassergüte- und Abfallwirtschaft, Abt. Hydrochemie Fakultät f. Bauingenieur- und Vermessungswesen - Universität Stuttgart, Bandtäle 2 D-70569 Stuttgart, Deutschland

Introduction

The increased rate of sewage sludge production in developing countries like Brazil is always a great matter of concern whenever the aspect of the final disposition is taken into account. At the moment, most of the municipalities in Brazil are trying to adopt as main alternatives to the final deposition of sewage sludge, classical end use methods like agricultural use, landfillig and biocomposting[1,2,3]. These methods should be taken with reserve considering that sewage sludge can carry chemical pollutants such as heavy metals and persistent organic pollutants (POP). In Brazil, up to now, there is no specific legislation regarding the maximum equivalent concentration levels of organochlorine compounds in especial polychlorinated dibenzo-p-dioxins and dibenzofurans (PCDD/PCDF) in sewage sludge/biocompost considered for agricultural use or final deposition in soils. Besides the great risk heavy metals pose to humans and environment, PCDD/PCDF are types of persistent environmental contaminants with enhanced toxicity and carcinogenic and bioaccumulating properties. To PCDD/F, the human exposure is primaly attributed to background contamination caused by diffuse contamination of these pollutants coming from different sources and subsequently biomagnification through the trophic chain. As alternative paths of the diffuse contamination with PCDD/F, the transport of these substances by air deposition, by residual waters from household, industrial processes as well as by laundry of products treated with contaminated chemicals [4,5] and the microbial activity on chlorophenols [6,7] are listed. Possible transference pathways of these compounds to humans would be both the uptake via contaminated crops and grazing livestock, coming from sludge-amended soils [11]. Concerning PCDD/F, a tolerable daily intake (TDI) of 1-4 pg I-TEQ/kg/day is recommended, according to the WHO/EURO standard guidelines, which would be exceeded if a persons diet came solely from land treated with sewage sludge containing high concentrations of PCDD/F [8].

This work shows the results of a first study about the heavy metal, PCDD/PCDF content of sewage sludge coming from both an urban and a semi-agricultural area in the State of Rio de Janeiro, Brazil in comparison to results found in the region of Baden-Württenberg, south Germany. The potential toxicity and probably sources related to these contaminants in Brazilian sewage sludge was also investigated.

Material and Methods

The sludge samples were collected from three different sewage sludge treatment plants: activated sludge L1 was collected from the wastewater treatment plant (WTP) Icaraí in Niteroí, a relatively great urban center in Rio de Janeiro State. Digested sludge L2 was collected from the WTP Maricá city, a semi-rural area about 50km from Rio de Janeiro. The digested sludge-sample L3 was collected from the WTP Balingen, a small industrial town in southern Germany. 1-2 kg of pressed digested sludge samples were collected by means of aluminum boxes and 5 l of the activated sludge were collected from the holding tank in a HDPE container. Once in the lab, the digested sludge-samples were mixed and divided into four 500 g sub-samples. The activated sludge sample was centrifuged in 6 x 250 mL tubes at 1200 rpm, the supernatant was discarded and all samples were lyophilized for 48 h and stored at 4 ºC until extraction. Sample characterization and PCDD/PCDF/PCB analyses were performed at the Institute for Organic Chemistry the University of Tübingen, Germany.

20-50 g of each sample were submitted to an extraction and clean-up procedure prior to analysis. The extraction and clean-up methods are described at Hagenmaier (1987). Possible lab contamination and quality control was performed by means 2 blanks during the procedure. Identification and quantification of each PCDD/PCDF congener was carried out using the isotope dilution method. Samples were spiked with each $^{13}C_{12}$ 2,3,7,8-substituted PCDD/F and PCB Congeners (Standard mix 99%puriss. Promochem GmbH) and extracted with toluen during 24 h. PCDD/F absolute concentrations used were TCDD/F-HxCDD/F=25 ng.mL^{-1}, HpCDD/F=50 ng.mL^{-1}, OCDD=80 ng.mL^{-1}.and OCDF= 50 ng.mL^{-1}. The recovery of the Standards after extraction and clean-up procedures were situated between 70-85%. For Identification and quantification of PCDD/F a HRGC/HRMS system (Mega Series 5160 Carlo Erba® coupled to a VGA Autospec Ultima) and both a Quartz capillary column DB-Dioxin (J & W Scientific®) and a polar CP-Sil 88 column (Chrompack®) were used for separation and isomer specific analysis.

Results and Discussion

Table 1 shows the concentration of each homologue group of PCDD/F (ΣTCDD/F-OCDD/F)for each sludge sample as well as the PCDD/F median values for Baden-Württenberg region, and the toxicity equivalent concentration calculated according to NATO/CCMS and WHO.

The sludge samples in general show a low contamination in respect to PCDD/F (ΣTCDD/F-OCDD/F) with values ranging from 1312,0 (L2) to 3965,0 pg g^{-1} (L1). Such values are within the range found for the sewage sludges from Baden-Württenberg.The toxicity equivalent concentrations were situated between 2,7 - 98,9 pg-ITEQ g^{-1} and 1,8-128,1 pg-ITEQ g^{-1}. According to NATO/CCMS and WHO, respectively. The lowest I-TEQ value is attributed to sludge-sample LDD1, which originates from a rural region. It can be observed that the Brazilian sludge L1 shows doubled I-TEQ value when compared to the values found for the region of Baden-Württenberg. However, the values found are within the range observed by other authors in this field [9,10,11].

Table 2. PCDD/F concentrations in the sewage sludge samples and corresponding equivalent concentrations (I-TEQ) according to NATO/CCMS and WHO.

Homologue Group (pg.g-^{1})	L1	L2	L3	Mean values Baden-Württemberg
∑TCDD	15,0	<0,5	154,0	12,3
∑PeCDD	<0,5	<0,5	62,0	38,7
∑HxCDD	111,0	<0,5	120,0	78,6
∑HpCDD	743,0	151,0	230,0	405,7
OCDD	2866,0	955,0	1568,0	2156,7
∑TCDD-OCDD	**3735,0**	**1106,0**	**2134,0**	**2691,8**
∑TCDF	8,0	19,0	8,6	74,4
∑PeCDF	2,0	<0,5	12,1	55,5
∑HxCDF	7,0	<0,5	30,0	63,4
∑HpCDF	68,0	71,0	102,0	170,6
OCDF	145,0	116,0	466,0	**383,1**
∑TCDF-OCDF	**230,0**	**206,0**	**619,0**	**747,0**
2,3,7,8- substituted isomers				
2,3,7,8 TCDD	0,8	n.n.	58,7	<0,2
1,2,3,7,8- PeCDD	n.n.	n.n.	31,0	1,0
1,2,3,4,7,8- HxCDD	n.n.	n.n.	n.n.	0,3
1,2,3,6,7,8-HxCDD	n.n.	0,9	n.n.	8,7
1,2,3,7,8,9- HxCDD	0,7	1,0	n.n.	3,4
1,2,3,4,6,7,8- HpCDD	5,0	n.n.	1,7	203,9
2,3,7,8-TCDF	0,6	n.n.	0,5	5,7
1,2,3,7,8-PeCDF	0,1	n.n.	0,2	3,2
2,3,4,7,8- PeCDF	n.n.	n.n.	2,4	4,6
1,2,3,4,7,8-HxCDF	19,1	n.n.	0,7	4,9
1,2,3,6,7,8-HxCDF	n.n.	n.n.	0,6	4,8
1,2,3,7,8,9-HxCDF	n.n.	0,4	0,1	4,2
2,3,4,6,7,8-HxCDF	n.n.	n.n.	n.n.	7,4
1,2,3,4,6,7,8-HpCDF	n.n.	0,12	0,9	105,4
1,2,3,4,6,7,8,9-HpCDF	0,1	n.n.	0,1	<1,64
I-TEQ (NATO-CCMS)	**29,4**	**2,7**	**98,9**	**12,8**
WHO-TEQ	**26,8**	**1,8**	**128,1**	**11,0**

Detection limit: $5x10^{-1}$pg g^{-1}. n.n.=absolut concentration <0,5 pg g^{-}

The PCDD/F equivalent concentrations found in the Brazilian samples are below but already near to the upper limit concentration for land disposal according to the German federal legislation regarding agricultural use/final deposition. The maximun PCDD/F levels for sludge/biocompost prior to disposition in soils on dry basis is 100 pg-ITEQ g^{-1}.

Figure 1 shows a comparison between the profile of homologues found in the sludge samples. The homologue profile in the sludge samples shows a characteristic predominance of the highly chlorinated congeners HxCDD/F-OCDD/F. Their contribution accounts to more than 90% (L1=99,4%; L2=98,6%; L3=91,4%) of the total PCDD/F in each sample. Such a pattern, in principle, discards thermal processes as main sources of contamination of these sludges. The sludge

sample profiles resemble the typical PCDD/F contamination profile stemming from "PCP-like contamination"[9].

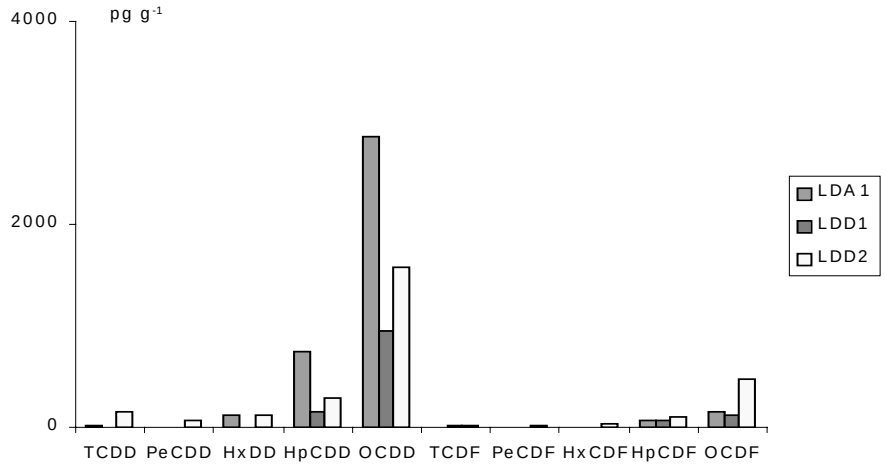

Figure 1. homologue profile of the sludge samples.

Despite these main characteristics, the German sludge-sample (L3) shows low values of TCDD/F-PeCDD/F congeners in an typical "Burning profile" while in the Brazilian sludge samples (L1 and L2) these homologues are almost absent. Such difference could be explained through differences in the energetical matrix and the severe weather conditions in Europe that enforces the domestical use of combustible stuffs mainly during the winter. As a result of these mainly differences, only a small amount of the low-chlorinated homologues can be noticed in the activated sludge L1 (0,4%), which is probably due to the atmospheric deposition from the traffic in the surroundings of the sewage treatment plant. In the digested sludge L2 this contamination is absent, probably because of the localization of the sewage treatment plant, which can be considered a remote area with neither punctual sources nor high traffic volume. As the samples of this study show an overall low PCDD/F contamination and according to the observed patterns, it was concluded that, rather than PCDD/F contamination coming from a punctual source, diffuse sources like residual waters and atmospheric deposition are contributing to the contamination pool.

Figure 2; show the isomer-specific analysis of the homologous groups ranging from TCDD/F to HpCDD/F in the sludge-samples L1, L2 and L3, and the perceptual contribution of each isomer for their homologue group. For all samples, it must be noted that the PeCDD/F groups are almost absent and there's only a little contribution of the HxCDF group. Furthermore once present, these groups are dominated almost only by the 2,3,7,8-substituted congeners. In the case of the Brazilian samples L1 and L2, this absence can be explained by both the little input of thermal sources such as traffic via atmospheric deposition observed in these samples, associated with a

preferential enrichment of the high-chlorinated groups in the organic material. For the German sludge the transport phenomena during sludge generation would be the main responsible for this discrepancy. The TCDD homologue group in the Brazilian sludge sample L1, is dominated by the co-eluted pair 1,2,4,6/9-, 1,2,3,4-TCDD (L1= 44,3%), which is the main indicator congener under the TCDD group for PCP/PCP-Na contamination [12]. Further significant peaks are 1,2,8,9-TCDD (11,4%), 2,3,7,8-TCDD (10,0%), 1,2,3,9-TCDD (10,0%), 1,2,6,9-TCDD (7,1%), 1,3,6,8-TCDD (5,7%), 1,3,7,8-TCDD (5,7%) and 1,2,7,8-TCDD (5,7%). Such equitable distribution within the TCDD group keep some resemblance to a typical "2,3-termal" profile commonly found in low temperature combustion processes (300-600ºC) [13]. This evidence is enforced by the isomer distribution found in theTCDF group, where the predominance of the 2,3,7,8-TCDF (70%) followed by 1,2,7,8-TCDF (14%) and 3,4,6,7-TCDF (12,0%) can be noted. This distribution found confirms the contribution in some extension of depositional sources in this sample. The HxCDD group is dominated by the isomer 1,2,3,6,7,9-HxCDD (55,2%), that was also reported by Hagenmaier[9] as main indicator for PCP-Na contamination. Further peaks in this group are the isomers 1,2,4,6,7,9-HxCDD (35,8%) and 1,2,3,4,6,8-HxCDD (9%), By the HxCDF group, only the isomer 1,2,3,4,7,8-HxCDF could be detected, while the HpCDF group is dominated by 1,2,3,4,6,8,9-HpCDF (79,3%), which confirms the main origin of the contamination from chlorophenols such as PCP and its derivatives [5].

The HpCDD/F and OCDD/F groups prevail in the sludge sample LDD1. The isomer-specific analysis of the HpCDF group shows a balanced distribution between the isomers 1,2,3,4,6,7,8-HpCDF (52%) and 1,2,3,4,6,8,9-HpCDF (48%), both indicators of a PCP-like precursor contamination as well as the predominance of the isomer 1,2,3,7,8,9-HxCDD (91,4%) in the HxCDD group[14]. Further isomers present in this sample are 1,4,6,8-TCDF (63%), 2,3,7,8-TCDF (37%), and 1,2,3,6,7,8-HxCDD (8,6%). Rappe[10] has listed the latter two isomers as indicators of a "sewage sludge" pattern. This isomeric-specific distribution in combination with the homologue profile and low concentrations observed in this sample seems to indicate that rather than a contamination stemming from chlorophenols like PCP, there's a great chance that only transport and adsorptions phenomena during sludge generation, are contributing to the contamination pool found.

The German sludge sample LDD2, contains in the TCDD group only the following isomers: 2,3,7,8-TCDD (38,2%), 1,3,7,9-TCDD (35%) and 1,2,4,6/9- 1,2,3,4-TCDD (27%), what can be viewed as a "2,6-termal" profile commonly found, among other processes, during high temperature combustion processes[13]. HxCDD group shows a decreasing distribution for the isomers 1,2,4,6,7,9/1,2,4,6,8,9/1,2,3,4,6,8-HxCDD (44,8%), 1,2,3,4,6,8-HxCDD (34,5%) and 1,2,3,4,6,7-HxCDD (20,7%). A quite equitable distribution between the isomers 1,2,3,4,6,7,9- HpCDD (42,8%) and 1,2,3,4,6,7,8-HpCDD (57,2%) was detected in the HpCDD group. In the TCDF group the isomers 3,4,6,7-TCDF (50,0%) and 2,3,7,8-TCDF (31,3%) predominate, while in the PeCDF group only the 1,2,3,7,8-PeCDF isomer could be detected. The HpCDF group shows the predominance of the isomer 1,2,3,4,6,7,8-HpCDF (88%), which is commonly classified as a thermal source indicator[12], over the 1,2,3,4,6,7,9-HpCDF (11%). Such congener distribution within the homologues seems to indicate that this sludge rather than a "PCP-like" contamination has a contamination pool stemming mainly from depositional sources. The observed high concentration of the HpCDD/F-OCDD/F groups in this sample could be explained through transport and adsorptions phenomena that promote the enrichment of high chlorinated homologues during sludge generation.

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References

1 Andreoli, C. V., Fernandes, F., Domaszak, S. C. (1997). Reciclagem agrícola do lodo de esgoto - Estudo preliminar para definição de critérios para uso agronômico e de parâmetros para normatização ambiental e sanitária. SANEPAR Curitiba.

2 GOVERNO ESTADUAL. 1999. Plano de despoluição da Baía de Guanabara. http//www.baiadeguanabara@org.gov.br.

3 TSUTIYA, M. T. (1999).20º Congresso Brasileiro de Engenharia Sanitária e Ambiental, , Rio de Janeiro. Associação Brasileira de Engenharia Sanitária - ABES. p. 744-752.

4 Öberg, L. G., Wàgman, N. , Koch, M. , Rappe, C. (1994). Organohalogen Compd 20, 245-250.

5 Horstmann, M., McLachlan, M.S. (1994). Organohalogen Compd, 20, 251-254.

6 Krauß, T. Krauß, P. Hagenmaier, H. (1994). Chemosphere, 28, 155-158

7 Rappe, C., Oberg, L., Andersson, R. (1999). Organohalogen Compd. 43. 249-253.

8 Wild, S., Harrad, S., Jones, K., (1994). Environ. Pollut. 83, 357-369

RAPPE, C., Andersson, R., Karlaganis, G., Bonjour, R. (1994). Organohalogen Compd. 20, 79-84.

9 Hagenmaier, H. (1987). Abschlussbericht zum Forschungs- und Untersuchungsvorhaben "Belastung der Umwelt mit Dioxinen". Umweltministerium Baden-Württemberg Tübingen.

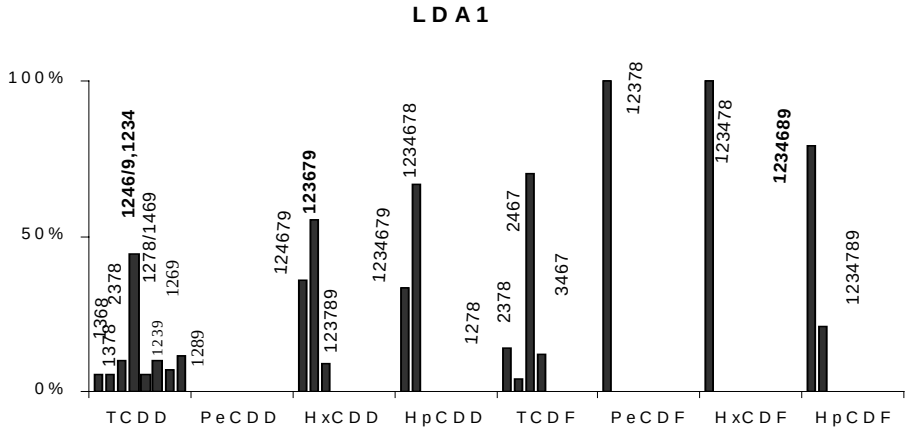
10 RAPPE, C. Kjeller, L-O., Andersson, R. (1989). chemosphere 19, 13-20.

11 Stevens, J. Green, N.J.L. Jones, K. C. (2001). Chemosphere 44, 1455-1462.

12 Koch, M. K., W. Rotard, W. (2001). Chemosphere, 43, 737-741

13 Ballschmiter, K. Bacher, R. 1996. Vorkommen der PXDD und PXDF - Quellen und Substanzmuster der PXDD und PXDF. In: Ballschmitter, K. Bacher, R. (Eds.) Dioxine - Chemie, Analytik, Vorkommen, Umweltverhalten und Toxikologie der halogenierten Dibenzo-p-dioxine und Dibenzofurane. Weinheim-VCH, Weinheim, Germany. p. 247-249.

14 Hagenmaier, H. 1988. Untersuchungen der Gehalte an polychlorierten Dibenzodioxinen, polychlorierten Dibenzofuranen und ausgewählten Chlorkohlenwasserstoffen in Klärschlämmen. Umweltbundesamt Tübingen.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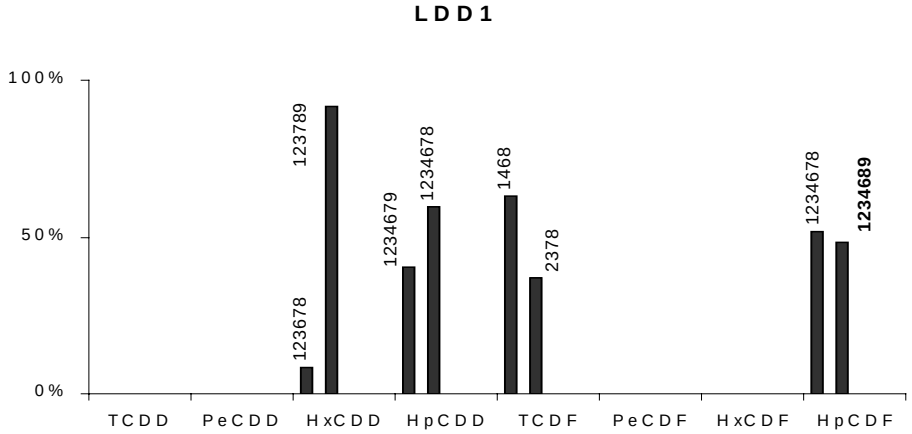
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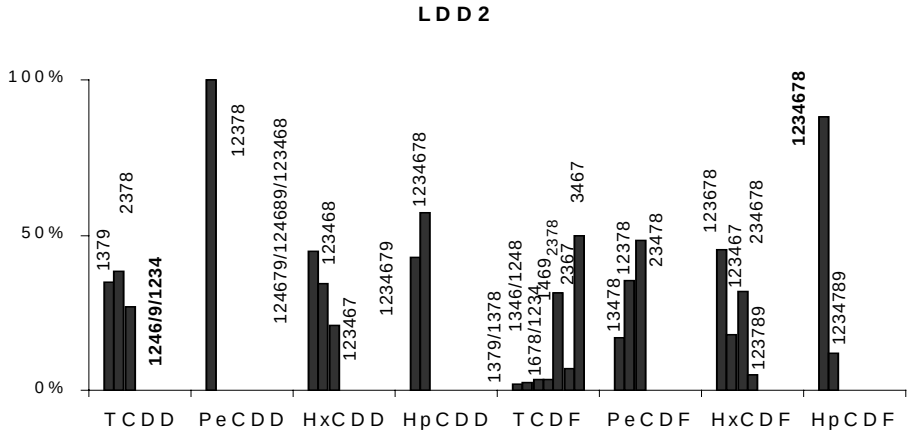
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