Dioxin '97, Indianapolis, Indiana, USA

Influence of Different Treatment Methods for Sewage Sludge on the Levels of Chlorinated Dibenzodioxins and Dibenzofurans

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1. Introduction

We investigated the behaviour of a highly impacted sewage sludge according to different stabilization methods to find out which one has a favourable effect on the minimization of the PCDD/F levels in sewage sludge. Our own investigations (1) and those of other working groups showed that different methods for the stabilization of sewage sludge influence the PCDD/F levels in the sludge samples. Formation processes as well as degradation procedures of PCDD/F were described in the literature (3,4).

Besides the anaerobic stabilization mainly applied in Germany we therefore treated the sewage sludge under aerobic digestion by bubbling air into the liquid phase and by composting with wood chips.

2. Experimental

In our experiments we used a sewage sludge from an urban industrial region. Stored in open basins without ventilation and agitation it developed highly increasing PCDD/F levels. The PCDD/F concentration in the "younger" sludge (sludge sample A) was 231 ng/kg I-TEQ. In contrast, the PCDD/F concentration in the "older" sludge (sewage sludge sample B) from the same sewage purification plant was 453 ng/kg I-TEQ. In the evaluation of the results high PCDD/F concentrations are advantageous because fluctuations in the trace-analytical range of low PCDD/F levels always lead to less meaningful results.

Anaerobic Stabilization

The anaerobic stabilization of the sludge samples A and B was carried out in 3 L glass reactors. The temperature in the reactors was kept constant at 37 °C and the sludge stirred in intervals. After 8 and 20 weeks samples were taken from the reactors and the degree of mineralization as well as the PCDD/F levels were determined.

Aerobic stabilization

The aerobic stabilization was carried out only for sample A. We used the same reactors under the same conditions as for the anaerobic stabilization. Additionally we introduced air into the sludge at an air flow rate of 10 mL/min.

Composting

For the composting of the sludge sample A 2.5 kg of sludge were mixed with wood chips. The rotting occured in reactors which were supplied from the bottom with humified air without being stirred. The rotting of the sewage sludge was carried out in two test series at 60 °C and 75 °C. The PCDD/F concentrations were determined each after 3 and 12 months.

The analytical determination of the PCDD/F was performed according to the VDI-guideline 3499 (Germany).

3 Results

Anaerobic Stabilization

After 8 weeks an increase of the PCDD/F concentrations was observed and they increased continuously up to the 20^{ieth} week (Table 1).

The results of the tests performed simultaneously highly corresponded. The reason for the increase in the I-TEQ of the sludge sample A during the eight weeks was the rise of all PCDD/F isomers substituted in the 2,3,7,8 position but especially of the 1,2,3,4,7,8- and the 1,2,3,7,8,9-HxCDD compound (Figure 1).

Initial values		8 weeks 20 weeks ng I-TEQ/kg % ng I-TEQ/kg		%	
A	231,2	336,4	45,6	361,1	56,3
		323,5	40,0	351,9	52,3
В	453,5	519,4	14,7	649,1	43,3
}		606,9	34,0	684,4	51,0

Table 1: Time dependent concentration course in sludge A and B during anaerobic fermentation.

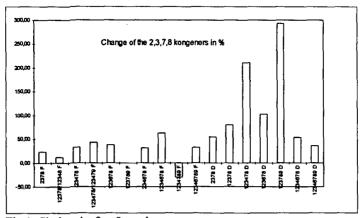


Fig.1: Sludge A after 8 weeks

Sludge sample B rather showed an indifferent pattern and the decrease of some congeners was significant (Figure 2).

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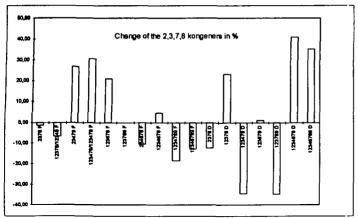
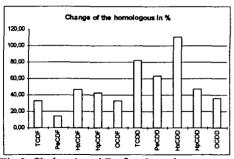


Fig.2: Sludge B after 8 weeks

Between the 8th and the 20^{ieth} week in all batches of the sludge samples A and B an above-average increase in the 1,2,3,4,7,8-HxCDF concentration of about 900 % was to be noted. Under consideration of the homologous groups the following result was obtained: Concerning the sludge sample A an increase in the PCDD/F levels was observed in all homologous groups after 8 weeks. In comparison, the sludge sample B showed increasing as well as decreasing concentrations of dioxins and furans in all homologous groups (Figure 3).



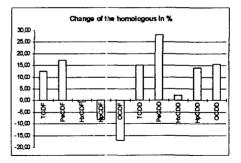
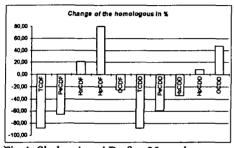


Fig.3: Sludge A and B after 8 weeks

After 20 weeks the decrease of the PCDD/F concentrations in all homologues were predominant for the sludge sample A and especially for the sludge sample B, except the OCDD and the HpCDF in the sludge sample A (Figure 4).



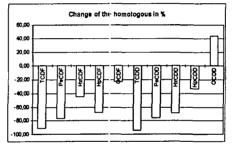


Fig.4: Sludge A and B after 20 weeks

Arobic Stabilization

After 8 weeks a decrease in the I-TEQ of about 30 % from 243 ng to 163 ng was detected. The main reason for this decrease was the OCDD decrease of 75 ng I-TEQ (37 %). The increases and the decreases for the other 2,3,7,8-congeners were in the marginal range. In general, the decrease of the PCDDF levels up to 30 % could be established for all homologues (Figure 5).

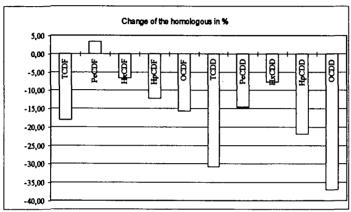


Fig.5: Sludge A after 3 weeks aerobic fermentation

Composting

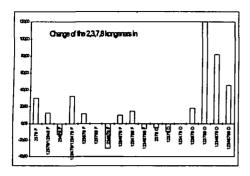
A significant increase in the PCDD/F concentrations could be determined in all composting tests. Composting at 75 °C the concentrations increased even up to 246 % and 360 % after 12 months. A comparison of the PCDD and the PCDF levels in the homologous groups and the 2,3,7,8-congeners also showed a homogeneous result in all tests (Table 2).

Rotting temperature	3 month increase in %	12 month increase i %
60 °C	48,5	54,6
	80,1	86,7
75 °C	150,5	246,4
	158,2	360,9

Table 2: Time dependent concentration course in sludge A during composting

Up to the third month, at both composting temperatures the increases of the I-TEQ resulted nearly to equal parts from the concentration increase in the 1,2,3,4,6,7,8-HpCDD and the OCDD. In contrast, composting at 75 °C a significant increase of the 1,2,3,4,7,8-HxCDD could be observed. However, it lead to an only insignificant increase of the I-TEQ (Fig 6).

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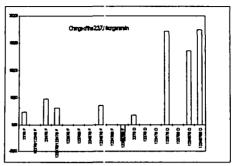
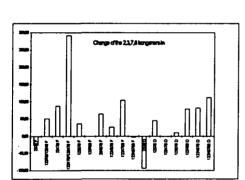


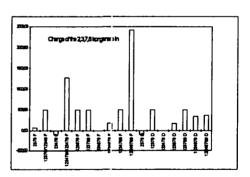
Fig.6: Sludge A after 3 month composting at 60 °C and 75 °C

After a 12 months composting at 60 °C an additional slight increase in the I-TEQ occurred (Figure 7). It was caused by an increase in the 1,2,3,4,7,8-HxCDD, 1,2,3,4,6,7,8-HpCDD and the OCDD.

Considering the homologues a degradation of the TCDD/F-HxDDF as well as the HpCDF was indicated. It was nearly complete for the TCDD/F, and it amounted to about 50 % for the HxCDD-congeners.

After a 12 months composting at 75 °C an additionally strong increase in the I-TEQ to 246 ng/kg and 360 ng/kg was detected (Fig. 7). Like in all other test series the 1,2,3,4,7,8-HxCDD, 1,2,3,4,6,7,8-HpCDD and the OCDD lead to the I-TEQ increase.





Change of the 2,3,7,8 congeners in %

Fig.7: Sludge A after 12 month composting at 60 °C and 75 °C

In contrast to the other composting tests it was not possible to find a decrease of the concentration sums of the homologues at 75 °C. On the contrary between the 3rd and the 12th month the formation of 7 congeneric 2,3,7,8-substituted dioxins and furans was established.

SOURCES

4. Conclusion

The investigations of three sewage sludge stabilization methods in the anaerobic fermentation in the liquid phase only lead to a decrease of the PCDD/F and the I-TEQ values. In contrast to the other methods OCDD was degraded.

In the anaerobic fermentation as well as in composting the increase of the I-TEQ values was mainly due to the rise of 1,2,3,4,6,7,8-HpCDD and OCDD. The highest increase rates of the PCDD/F compounds were found in the composting experiments. Although this method is based on an aerobic biological process higher temperatures (60-75 °C) seem to strongly favour the formation of PCDD/F. However, a catalytic formation caused by the sewage sludge containing copper concentrations also cannot be excluded.

References

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- (3) Krauß, T.; Krauß, P.; Hagenmeier, H.; Chemosphere, 1994, Vol. 28, No. 1, p. 155