

Dioxin distribution in a Tertiary sedimentary clay profile (Germany)

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Introduction

Since 1999 dioxin of possibly natural origin has repeatedly been found in kaolinitic clays of different countries ^{1-5, 7-10}. Until today it is not generally agreed how the dioxin was generated. The aim of this study is to determine the relationship between the dioxin content and the mineralogical composition of clays as well as the distribution of dioxin in different grain size fractions and its behaviour within a profile of Tertiary kaolinitic clays from Germany. The study may provide a hypothesis of dioxin formation, based on the genesis of the clays.

Kaolinitic clays may be of fluvial, limnic or brackish origin and often occur in contact with peat or lignite. The composition of these clays is generally dominated by the mineral kaolinite, with lower amounts of illite, montmorillonite, quartz and organic carbon (lignite or peat). The congener data of former studies ¹⁻¹⁰ show that PCDDs are absolutely dominant, whereas PCDFs were at low or undetectable concentrations. The dominant homologue is the OCDD, followed by the HpCDDs or HxCDDs. PeCDDs and TeCDDs show the lowest values. These patterns are not comparable with anthropogenic sources ¹⁻¹⁰. There are few explanations for the occurrence of such dioxin associations in clays. The enzymatic natural formation of dioxin under laboratory conditions was described by Öberg et al. (1992) and Wagner et al. (1990) ^{11,12}. A formation by prehistoric bush- or forest fires ⁶ as well as the burning of coal seams or peat is unlikely, but may not be excluded.

Materials and Methods

Origin of the clay:

During the Upper Cretaceous and Lower Tertiary a kaolinitic weathering crust of considerable thickness (> 15m) was developed on top of the pre-Tertiary basement rocks in Central Europe and adjoining regions ¹³ (Fig.1a). Southeast German sections of this crust were partially eroded (Fig. 1b) during the Oligocene due to the uplift of the Bohemian Massif in the south. The kaolinitic material was transported by rivers to the north and deposited in sequences of clays and sandy layers (Fig.1c). During the Middle Miocene extensive swamps developed within the sedimentary basins and humic acids migrated downwards from the swamps into the kaolinitic clay, the sand and the older weathering crust, which caused reducing conditions (Fig.1d) ¹⁴.

Sampling:

The investigated profile consists of four different horizons (Fig.2). In a first campaign 24 samples were taken to distinguish the mineralogical composition of the horizons. In a second campaign five composite samples were taken for dioxin as well as mineralogical analysis. One sample was taken in the upper clay layer, one in the lignite interlayer and one sample in each zone of the lower clay layer. The lignite seam was not sampled.

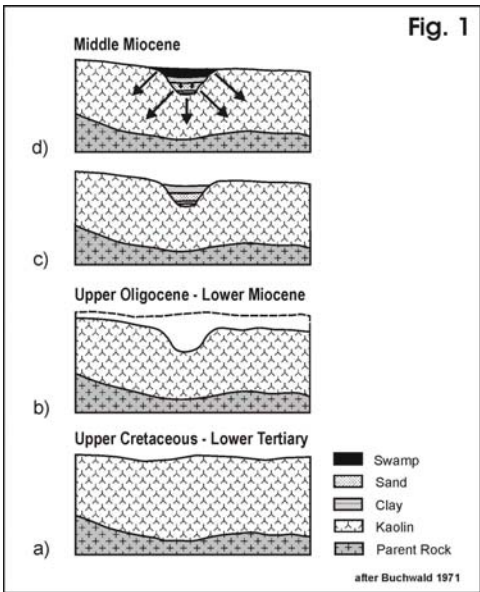


Fig. 1. Formation of kaolinitic clays in Southeast Germany during the Tertiary (after Buchwald 1971¹⁴)

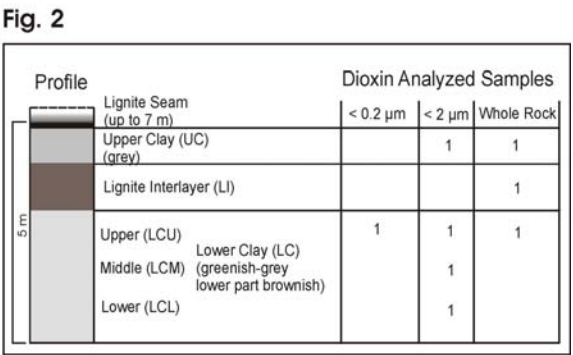


Fig. 2. Sketch of the sampled profile, number of analyzed dioxin samples per horizon and explanation of horizon name abbreviations

Preparation:

The samples were dried and one part was ground in a disk vibratory mill. Another part was sieved through a 63 μm mesh and the finer fraction was further separated to fractions $< 2 \mu\text{m}$, $2 - 20 \mu\text{m}$ and $20 - 63 \mu\text{m}$ via Atterberg sedimentation cylinders. In addition, a fraction $< 0.2 \mu\text{m}$ of the upper part of the lower clay layer was separated by centrifuge.

Analysis:

To identify the mineral content the whole rock samples (WH) and the samples $< 2 \mu\text{m}$ were analyzed with X-Ray diffraction by a Philips PW 1710 (Cu-K α , 50 kV, 30 mA). TOC measurements were made by burning composite samples of every horizon at 350°C and by LECO CS-200 Analysis.

Eight samples, three whole sediment samples (UC, LI, LCU), four samples $< 2 \mu\text{m}$ (UC, CU, LCM, LCL) and one sample $< 0.2 \mu\text{m}$ (LCU) were analyzed for dioxin (Fig.2). 100g of each sample were spiked with ^{13}C labeled PCDD/PCDF standards and afterwards Soxhlet-extracted for 20 hours with 300 ml of toluol. The cleaning of the extract was made via a basic alumina column followed by a multistep modified silica column. The last treatment was the purification in a basic alumina column again. The resulting extracts were measured by HRGC/LRMS with a 60m x 0.25 mm SP2331 fused silica capillary column and attached HP-MSD 5973. The determination of PCDDs and PCDFs is described in DIN 38414-S24¹⁵.

Results:**Granulometry:**

The clays are very fine grained, containing 98 wt % (Lower Clay) and 95 wt % (Upper Clay) of the fraction $< 2 \mu\text{m}$. Only 2 wt % (UC) and 1 wt % (LC) are of sizes coarser than 20 μm .

Mineralogy:

The upper clay is more dominant in kaolinite, whereas the lower clay contains more illite and montmorillonite (Tab.1). Quartz, pyrite, anatase, feldspar and zircon are the detectable accessory minerals of the clays. The organic carbon content differs between 2-3 wt % for the upper clay and 1-2 wt % for the lower clay. The content of quartz, feldspar, zircon and organic carbon increases with the coarsening of the grain size (Tab.1, 2a).

The lignite interlayer consists of 75 % organics with smaller amounts of kaolinite. Illite, quartz, anatase and pyrite are the main accessory minerals (Tab.1.). Coal petrographic analyses of the lignite interlayer and the organics of the clays show that they contain no fusinite components.

Tab. 1. Mineral composition of whole rock samples and the fraction > 63 µm (LC)

Whole Rock Samples (wt %)	Kaolinite (%)	Illite (%)	Montmorillonite (%)	Quartz (%)	Pyrite (%)	Anatase (%)	Org. Carbon (%)
Upper Clay	82	10	< 2	< 3	< 2	1	2 (LECO)
Lignite Interlayer	18	3	-	< 3	3	0.5	75
Lower Clay (Upper)	66	24	< 5	3	< 2	2	1 (LECO)
Lower Clay (Middle)	72	19	< 5	< 3	< 2	1.5	1
Lower Clay (Lower)	72	19	< 5	< 3	< 2	1.5	2

Fraction >63 µm (wt %)	Kaolinite (%)	Illite/Muscovite (%)	Feldspar (%)	Quartz (%)	Pyrite (%)	Anatase (%)	Org. Carbon (%)
Lower Clay (composite)	18	4	2	28	< 2	0.5	47 (LECO)

Dioxin:

PCDDs are dominant in all samples whereas PCDFs are undetectable with the exception of extremely low values in the upper clay. Therefore, only the results from 2,3,7,8-substituted PCDDs and the homologue group concentrations and distribution patterns of PCDD are presented.

Tab. 2. a) Organic carbon content and b) I-TEQ values for different horizons and grain sizes

Organic Carbon (wt %)	< 2 µm (LECO)	20 – 63 µm (T 350°C)	> 63 µm (LECO)	I-TEQ (pg/g dw)	< 0.2 µm	< 2 µm	Whole Rock
Upper Clay	3	30	33	Upper Clay		15	21
Lignite Interlayer	34	-	-	Lignite Interlayer			39
Lower Clay (Upper)	1.2	17	-	Lower Clay (Upper)	50	80	125
Lower Clay (Middle)	1.0	28	47 (composite)	Lower Clay (Middle)		25	
Lower Clay (Lower)	1.6	58	-	Lower Clay (Lower)		47	

The highest concentrations of dioxin were found in the samples of the upper part of the lower clay (LCU). The overlying lignite interlayer and the upper clay show lower values. The dioxin content of the clays is decreasing with fining grain size. The < 2 µm fractions of the different zones of the lower clay do not show any regular distribution of dioxin (Tab.2b, Fig.3, 4). OCDD is the prevailing

contaminant. The HxCDD value is higher than the amount of the 1,2,3,4,6,7,8-HpCDD with the exception of the whole rock samples of the upper clay and the lignite interlayer.

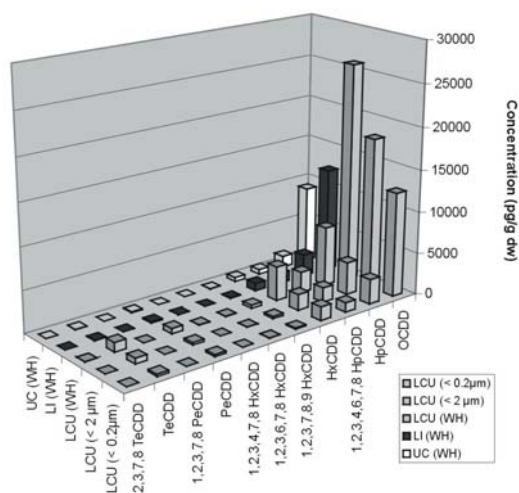


Fig 3. 2,3,7,8–substituted PCDDs and homologue group concentration of the whole rock samples and of the different grain size fractions of the upper part of the lower clay (LCU)

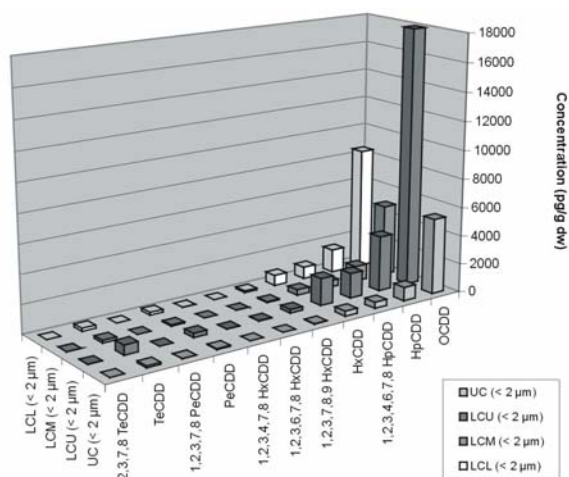


Fig 4. 2,3,7,8–substituted PCDDs and homologue group concentration of the fraction < 2 μm

The 1,2,3,7,8,9-HxCDD is the dominant toxic HxCDD with a ratio 1,2,3,7,8,9-HxCDD/1,2,3,6,7,8-HxCDD from 5.0 to 8.0. The high toxic 2,3,7,8-TeCDD is found in low concentrations between 1.0 and 21.0 pg/g dw (Fig.3, 4).

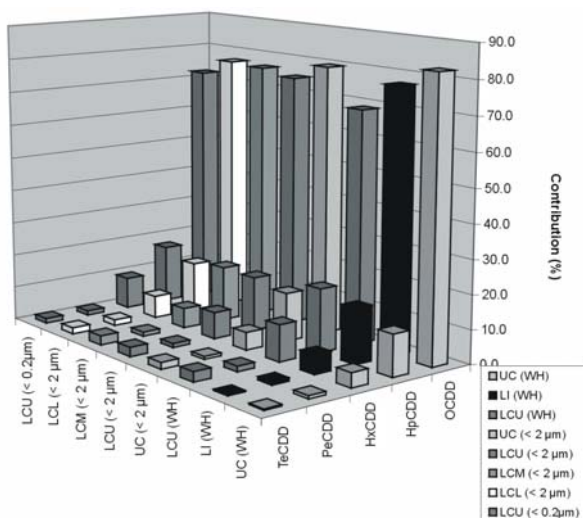


Fig. 5. Homologue group contribution

All samples show the same homologue group contribution dominated by OCDD (65 to 82%), followed by lower amounts of HpCDD and HxCDD. TeCDD is dominant in relation to PeCDD, with the exception of the whole rock samples of the upper clay and the lignite interlayer (Fig.5).

Discussion:

- The similarity of the PCDD homologue contribution patterns (Fig.5) shows that there is only one dominant process responsible for dioxin formation.
- The difference of the homologue group contribution pattern of our study, compared to that of former studies ^{2,6,7}, could be an indication for different stages or processes of chlorination or dechlorination.
- There is no statistic correlation between mineralogy and dioxin content in the clays and the lignite. Consequently, the mineralogy is not controlling the dioxin concentration
- Dioxin concentration increases with coarser grain size of the samples. Therefore the dioxin could hardly be adsorbed on the surface of clay minerals. Consequently, a secondary migration of dioxin adsorbed on small organic particles down from the hanging wall of the profile is unlikely.
- The coarser fractions are enriched in organic carbon. This implies an adsorption of dioxin on coarse grained organic particles (Fig.2 a,b).

- The lignite interlayer shows a lower dioxin concentration than the lower clay. Therefore the organic carbon content of the clays could not be the only reason for dioxin enrichment. For this reason we will focus future research on the composition and degradation stage of organics in different grain size fractions.
- No fusinite was found in the organic components, which means that burning of organic material as a reason for dioxin formation can be excluded.

Conclusion:

The PCDD/PCDF concentration, the distribution and the homologue contribution patterns in the sedimentary clays, lead to the conclusion that the dioxin has been formed by one dominant natural process closely related to the geological origin of the clay.

A hypothetical model for natural dioxin formation, which still has to be verified by further work, could stem from the following basic conditions:

- Dioxin is enriched in kaolinitic clays because kaolinite formation takes place under climatic conditions which force the growth of terrestrial plants. The upper sequence of kaolinitic weathering crusts is eroded together with the overlying organic-rich soils. After transportation they are deposited in basins.
- The concentration, the distribution and the homologue group contribution of dioxin in clay depends on the content and the composition of the organic material and is controlled by biochemical processes.

Acknowledgements:

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