

# FORMATION AND SOURCES II –POSTER

## PCDDs IN GEOLOGICALLY OLD SAMPLES FROM QUEENSLAND, AUSTRALIA

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### Introduction

Polychlorinated dibenzo-*p*-dioxins (PCDDs) have recently been detected in a number of mined clay products including kaolinite clay from Germany<sup>1</sup> and ball clay samples from the US<sup>2</sup>. Similar PCDD/F congener and isomer profiles have been identified in these clay samples which are unlike known anthropogenic PCDD/F profiles. A lack of anthropogenic PCDD/F sources that could explain the observed patterns in these cases has led to suggestions that the contamination may be the result of natural formation processes.

Recent investigations in Queensland, Australia have identified elevated levels of PCDDs in soils and sediments in the coastal region<sup>3,4</sup>. The PCDD/F congener profiles of these samples show strong similarities to kaolinite samples previously analysed from Queensland<sup>4</sup> and Germany<sup>1</sup> as well as ball clay samples from the US<sup>2</sup>. In addition, a preliminary investigation of PCDD/Fs in a shale oil sample from the Queensland coastal region also indicated elevated levels of OCDD (unpublished data). Thus, the aim of this study was to determine PCDD/F contamination in geologically old samples from Queensland including kaolin and oil shale in order to assess possible source and formation of PCDD/Fs.

### Materials and Method

#### *Sampling*

Oil shale samples S1 – S7 were collected from various depths within a mine exploration core (ranging from 17.25m – 76.9m). Oil shale is a kerogenous claystone, the kerogen being solid organic matter accumulated during periods of productive algae growth<sup>5</sup>. The oil shale deposit where the samples were collected is considered to have formed during a shallow, fresh-water, lacustrine environment, fluctuating between open water, swamp and anoxic mudflat subenvironments<sup>6</sup>. The oil shale in this deposit is estimated to have formed in the mid-late Eocene period, approx. 40 – 50 million years ago<sup>5</sup>. The exploration core was drilled in 1998 with a tungsten core sampler (119mm dia.) using water for lubrication. The core was stored in steel core holder trays. To avoid possible contamination during storage, the exterior surface of sample sectors chosen for analysis was removed. Samples were ground with a tungsten grinder and air-dried prior to analysis.

# FORMATION AND SOURCES II -POSTER

Kaolin samples K1 – K6 were collected from a previously excavated surface from various sites and depths within a mine deposit in central Queensland. Kaolin is a soft, fine clay comprising mainly of kaolinite ( $\text{Al}_2\text{Si}_2\text{O}_5(\text{OH})_4$ )<sup>7</sup>. Kaolin is formed by two key processes i.e. weathering and chemical alteration of a parent rock, referred to as 'kaolinisation'. Parent rocks are typically feldspar-rich and when they undergo 'kaolinisation', most other elements deplete leaving behind silicon, aluminium, oxygen and hydrogen (i.e. kaolinite). There are primary and secondary kaolin deposits, the former are the result of in situ weathering of feldspar-rich rock and the later are sedimentary deposits of transported kaolinite material. Individual kaolin deposits differ in many respects due to variations in their physiochemical properties. Due to these properties kaolin has a variety of usages and are commonly named with respect to their use. For example, kaolin clay is often referred to as kaolinite, the main element of kaolin, and ball clay (a secondary kaolin) is named with respect to its use as a coagulating agent. The kaolin deposit sampled in Queensland was formed approximately 20 – 25 million years ago. It comprises of kaolinite and a small quantity of resistant parent rock material. Sample K4 was separated based on the colour, into two subsamples, (i) the kaolinite clay (K4a) and (ii) the parent rock material (K4b). A soil sample collected from above the kaolin deposit was also included (K1). All samples were collected using stainless steel sampling equipment. To avoid contamination from recent atmospheric exposure, samples were collected from at least 10cm below the exposed surface. At each of the sites 2-5 sub-samples were homogenised and freeze-dried prior to analysis.

## *Analysis*

The majority of samples were analysed at the Queensland Health and Scientific Services (QHSS) laboratories, Brisbane Australia, using a method developed to screen for OCDD<sup>8</sup>. In addition a selection of kaolin samples were analysed for the 2,3,7,8-substituted and sums of non-2,3,7,8 substituted PCDD/Fs at Ergo Forschungsgesellschaft mbH in Hamburg, Germany (ERGO) using a standardised method<sup>9</sup>. Detailed analytical methodologies are described elsewhere<sup>3,4</sup>. Sub-samples of K2, K4 and K7 were analysed using both methods thus providing a QC/QA that allows comparison of the results from the two laboratories.

## Results and Discussion

### Reproducibility and inter-laboratory collaboration

In this study, the sample (and inter-laboratory) reproducibility was tested with samples K2, K4 and K7. Overall, the variation in replicate samples analysed in the two laboratories ranged from 10 – 15%, which has been considered acceptable for the purpose of this study.

### OCDD in oil shale

In this study, OCDD was detected in only 3 of the 7 oil shale samples analysed (Table 1). The OCDD concentrations were relatively low in all samples, OCDD concentrations ranged from below the limit of detection to 170  $\text{pg g}^{-1}$  dw. The highest concentration was detected in the sample J1 (OCDD concentration 170  $\text{pg g}^{-1}$  dw), the upper most sample analysed, which originated from a depth of approximately 17 m. The results from this study did

Table 1 – OCDD ( $\text{pg g}^{-1}$  dw) in the oil shale exploration core samples

	Depth (m)	OCDD ( $\text{pg g}^{-1}$ dw)
J1	17.25m	170
J2	30.6m	Nd
J3	45.65m	Nd
J4	48.63m	12
J5	55.59m	Nd
J6	60.47m	Nd
J7	76.97m	15

# FORMATION AND SOURCES II -POSTER

not confirm preliminary findings of OCDD concentrations up to 1000 pg g<sup>-1</sup> dw in shale oil samples from the same mine. Hence, the authors did not find evidence for a significant PCDD formation process in the oil shale samples.

## PCDDs in kaolin samples

In contrast to the results from analysis of shale oil, OCDD was detectable in all of the samples collected from the kaolin deposit at concentrations ranging from about 10 pg g<sup>-1</sup> dry weight (dw) in sample K5 to approx. 2800 pg g<sup>-1</sup> dw in sample K4 (Table 2). There was no clear trend of OCDD concentration within the deposit and both the highest and lowest OCDD concentrations were observed in the 1-2 m deep layer. The samples obtained from the soil above the core (K1) and a sample collected from a depth of about 10 m (K7) showed 460 and 85 pg g<sup>-1</sup> dw OCDD respectively. Hence, OCDD is distributed throughout the kaolin deposit and can be found in the soil above the deposit at elevated levels. The un-homogenous distribution of the OCDD in the kaolin is further evident from a large difference in the OCDD concentration between samples K3 (540 pg g<sup>-1</sup> dw) and K4 (2800 pg g<sup>-1</sup> dw) both of which were collected in close proximity at similar depth within a given area. (Note that samples were collected during two sampling events).

Table 2 – OCDD concentration (pg g<sup>-1</sup> dw) in samples collected from the kaolin deposit

	Depth (m)	OCDD (pg g <sup>-1</sup> dw)
K1	surface	460
K2	1-2m	120 ± 10
K3	1-2m	540
K4	1-2m	2800 ± 250
K4a	Kaolinite	3200
K4b	Parent rock	140
K5	1-2m	10
K6	3-4m	100
K7	8-10m	85 ± 5

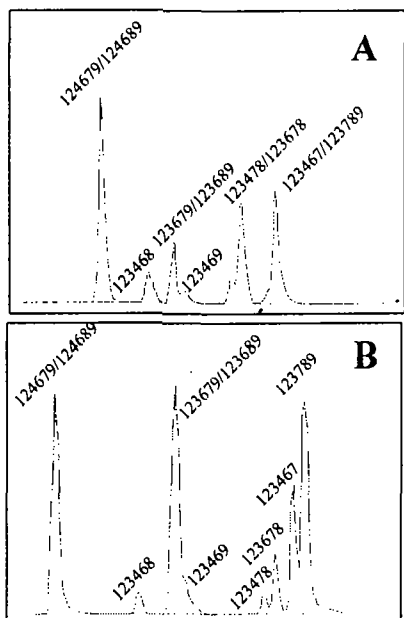


Figure 1 – Typical HxCDD isomer pattern in the kaolin samples from Queensland (A) and ball clay samples from US (B) (note: graph B is based upon and re-drawn from ref<sup>2</sup>)

These

samples showed variation in total organic carbon (TOC), (although % TOC was extremely low) and thus TOC may explain the variation in the OCDD concentration between samples. Analytical results of K4 subsamples consisting primarily of the kaolinite clay fraction (K4a) and the remnant parent rock material (K4b) showed the OCDD is primarily associated with the kaolinite fraction (96 %).

Full PCDD/F congener analysis was performed for five of the kaolin samples and the profiles were similar in all samples analysed (including sample K1). The congener pattern is consistently dominated by OCDD. Further, the HpCDD is dominated by the 1,2,3,4,7,8,9 HpCDD isomer, (1.2 and 2.8 times greater compared to 1,2,3,4,6,7,8 HpCDD), whereas among the HxCDD, 1,2,3,7,8,9 HxCDD is the dominating toxic (2,3,7,8) HxCDD isomer. PCDF concentrations in all samples were low or not detected (maximum value 0.8 pg g<sup>-1</sup> dw). The congener profile and HxCDD isomer patterns are very similar to those observed in soil and sediment samples in Queensland<sup>3,4</sup> and those detected in ball clay and kaolin samples from elsewhere<sup>1,2</sup> (Figure 1).

## FORMATION AND SOURCES II -POSTER

There are number of possibilities that may explain the origin of PCDDs in kaolin samples from Queensland: i.) PCDDs were present in original parent rock material; ii.) PCDDs are formed either during or after formation of the kaolin itself and iii.) PCDDs are formed elsewhere and the high surface area of kaolin acts as a sink for lipophilic chemicals such as PCDDs.

The data from this study does not provide conclusive evidence regarding the source of PCDDs in kaolin, however the data does provide some clues to the nature of the formation process. The sub-sampling of kaolin sample K4 indicated that the PCDD contamination is associated primarily with the kaolinite fraction, taking into consideration that the elemental composition of kaolinite ( $\text{Al}_4\text{Si}_4\text{O}_{10}(\text{OH})_8$ ) does not include carbon, it seems unlikely that the formation of PCDDs is related to the formation of the kaolin. In addition, if the PCDDs are formed in the kaolin, the highest PCDD levels would be expected in these deposits. However, the concentrations of OCDD in the kaolin deposit analysed in this study were not elevated when compared to other media previously analysed in Queensland and in fact comparable OCDD concentrations to the kaolin samples were evident in the soil overlying the deposit. Furthermore the similarities in the PCDD/F congener profiles in the kaolin samples, the material overlying the kaolin deposit and the topsoil samples previously analysed in the coastal Queensland environment, suggests that the kaolin acts as a sink for these chemicals which are formed by unidentified processes.

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