RELATIONSHIP BETWEEN DIOXINS IN FRESH BLEACHING EARTHS AND RESIDUAL DIOXIN LEVELS IN PROCESSED VEGETABLE OILS AND SPENT BLEACHING EARTHS

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Introduction

2001-02 production of fats and oils totaled 119 million metric tons (MMT) worldwide[1]; ~ 14 MMT were produced in the United States, the world's second largest producer. Bleaching earths derived from bentonite are used as an integral part of the process for preparing edible fats and oils[2]. Typically, they are added at low dosages (0.3 –3 wt%, based on oil) during processing to absorb traces of organic colored pigments, phospholipids, and trace metals. Some of these constituents are pro-oxidants; if not removed, the resultant oil will be oxidatively unstable and prone to rapid rancidification. Worldwide production of bleaching clays was estimated at about 700,000 tons in 2001[3]; based on typical usage levels versus oil type, ~66,000 tons of bleaching clays were probably used in the United States during the period 2001-02.

Studies by Ferrario[4] and Rappe[5] have clearly established that various clays (including bentonite and montmorillonite) contain detectable levels of dioxins. Depending on type and source, levels can be quite high; for some ball and kaolin clays, dioxin levels in the range 200-1600 ppt TEQ_{WHO} have been reported. More typically, dioxins levels are similar to background in soils (5-10 ppt TEQ_{WHO})[4, 6]. PCDDs/PCDFs profiles derived from anthropogenic sources (e.g. – fly ash[7, 8, 9]) typically contain relatively high levels of PCDFs as compared to clays. There is, by now, general agreement that the dioxins in clays are derived by natural (albeit poorly understood) mechanisms.

Isosarri, et al.[10] has shown that olive oil can be used to extract dioxins from contaminated soils. Even though bentonite-based (bleaching) clays are orders of magnitude less contaminated than the most highly contaminated balls clays, a question arises as to the fate of dioxins present in bleaching clays[‡] during vegetable oil processing. This question is herein addressed by examining the movement of dioxins during processing of vegetable oils under laboratory conditions that approximate commercial reality. Also some data are reported for dioxin levels in commercially processed oils and spent bleaching earths after the use of commercial bleaching earths.

Methods and Materials

Bleaching earths are sold and used in their powdered state. "Bleaching" involves mixing "fresh" bleaching earth (FBE) with liquid oil and heating the mixture under partial vacuum (~28" Hg) at 90-120 °C for 15-30 min. and then filtering the clay/oil mixture. The oil at this point is referred to as refined-bleached (RB) oil. Spent bleaching earth (SBE), a by-product, is often simply hauled away to landfill; however, in by fully integrated oil-seed crushing/ refining operations it can be incorporated back into the seed meal. In this case, the seed meal containing the SBE typically becomes a component in animal feed. The final step in edible oil processing involves subjecting the RB oil to high-temperature, vacuum distillation to remove relatively lower boiling components and various odoriferous impurities that would otherwise reduce palatability and stability. The resultant deodorized oil is referred to as refined-bleached-deodorized (RBD) oil and the small amount of overhead (0.25-0.5%) is referred to as deodorizer distillate (DD).

[‡] Note: ball clays and kaolin clays are not used for processing (bleaching) edible oils.

Laboratory bleaches: Commercially available FBEs (three different manufacturers) were used to bleach caustic-refined canola oil in a series of back-to-back bleaches using a 2000 mL three-necked flask fitted with thermometer, 3-way inlet valve (N_2/vac) and addition funnel (for admitting clay/oil slurry). The initial charge, 1200 g fresh canola oil, was heated to 230 °F (25-27" Hg) before addition of the first clay/oil aliquot (45 g clay/300 g oil) and then maintained at 235 °F ± 5.5 °F for the remainder of the run. After 10 min., the first 450 g aliquot of bleached oil was removed and a fresh clay/oil aliquot (14 g clay/450 g oil) added. This process mimics continuous mode of operation in modern-day plants and was repeated at 10 min. intervals with withdrawals and FBE/oil additions until a total of 100 g clay and ~3330 ±30 g oil had been processed (i.e. ~3 wt% clay dosage). Mass balance between input (FBE + starting oil) and output (SBE + RB oil) was quite good (>99.7%). SBE samples were obtained by vacuum filtration of the clay/oil slurry using a Buchner funnel; they were found to retain 36-46% oil (basis gravimetric analysis). RB oils were then deodorized in a laboratory deodorizer to yield samples of RBD oil.

According to manufacturer's literature, bleaching clays (AM_1, AM_2) are characterized as acid-activated montmorillonite clays. Bleaching clays (AH_1, AH_2) were characterized as acid-enhanced "hormite"[3] (naturally occurring mixture of bentonite and attapulgite clay). Finally, two additional samples (AM_3, AM_4) were prepared by blending small amounts (4% and 6%, respectively) of a dried and ground naturally-contaminated high-dioxin montmorillonite with bleaching clay AM_2.

Samples of FBE, SBE, and fresh, RB and RBD canola oil from the laboratory bleaches were submitted to Paradigm Analytical Laboratories, Inc. (2627 Northchase Parkway, S.E., Willmington, NC 28405) for dioxins analysis by EPA method 1613b. Data are shown in Table 1.

Commercial bleaches: Samples of FBE, SBE, starting (unbleached) oil, and RB oil from three commercial edible oil refiners were obtained over a short period (< 2hours) such that RB oil and SBE were associated with the input materials (i.e. – FBE and starting oil). All trials were conducted with acid-enhanced hormites. SBE from these runs was found to retain 32.1-33.6% oil based on weight loss after hexane extraction. As before, these samples were submitted to Paradigm Analytical Laboratories. Data are shown in Table 2.

Results and Discussion
Commercial bleaching earths utilized in this study were grab samples; it is not known if the dioxin levels reported here (0.45 – 6 ppt TEQ_{WHO}) are representative of these products in general. Furthermore, although it is assumed differences in dioxin levels between products are associated with differences in the raw clays from which they were manufactured, it must be noted that most manufactures use direct, open flame[2] drying during manufacturing and contributions to PCDDs/PCDFs as a result cannot be entirely ruled out. However, PCDFs in all samples were quite low and it seems most likely that contributions from combustion sources are relatively minor. PCDD profiles are, moreover, similar to those reported for other raw and processed clays[4].

As is clear from the data in Table 1, dioxins present in FBE are leached into the oil under the conditions employed during vegetable oil bleaching. Without exception, SBE is found to contain significantly less dioxin than the starting material after bleaching. By considering levels of H_PCDD and OCDD in FBE versus SBE (corrected for retained oil), it can be calculated that 90-95% of these congeners are released into the oil. Because levels of less-substituted congeners in FBE are much lower to start with, they often could not be detected in SBE; whether they would leach more or less efficiently is unknown.

Table 1. Lab Bleaches: Dioxin levels[a] (pg/g)- before and after bleaching (3% FBE dosage)

PCDD Congeners	Fresh oil	AM₁ FBE	AM₁ SBE	AM₁ RB oil	AM₂ FBE	AM₂ SBE	AM₂ RB oil	AH₁ FBE	AH₁ SBE	AH₁ RB oil	AH₁ RBD oil
2,3,7,8-TCDD	0.02	0.01	0.01	0.01	0.02	0.02	0.03	**0.88**	0.04	0.03	0.01
1,2,3,7,8-Pe	0.03	**0.10**	0.04	0.05	0.45	0.02	0.03	**2.13**	0.08	0.03	0.05
1,2,3,4,7,8-Hx	0.03	**0.12**	0.04	0.05	0.62	0.03	0.03	**1.82**	0.07	0.04	0.05
1,2,3,6,7,8-Hx	0.03	**0.54**	0.07	0.03	0.86	0.04	0.03	**2.48**	0.09	0.04	**0.01**
1,2,3,7,8,9-Hx	0.03	**0.31**	0.07	0.05	2.03	0.03	0.08	**3.70**	0.23	0.04	0.05
HpCDD	0.15	13.8	1.3	0.5	19.5	0.6	0.5	27.6	1.4	0.3	0.2
OCDD	0.7	114	15	4	175	6	4	121	8	2	0.09
Σ (PCDD/DFs)	0.85	141	18.2	5	200	7.1	4	160	10.3	2	0.3
TEQ[b] WHO '98	0.09	0.45	0.12	0.12	1.15	0.09	0.11	4.16	0.20	0.11	0.12

PCDD Congeners	AH₂ FBE	AH₂ SBE	AH₂ RB oil	AH₂ RBD oil	AM₃ FBE	AM₃ SBE	AM₃ RB oil	AM₃ RBD oil	AM₄ FBE	AM₄ SBE	AM₄ RB oil	AM₄ RBD oil
2,3,7,8-TCDD	**1.17**	0.04	0.02	0.01	**0.36**	0.04	0.02	0.01	**0.53**	**0.04**	0.03	0.01
1,2,3,7,8-Pe	**3.29**	0.03	**0.05**	**0.01**	**2.85**	**0.33**	**0.05**	**0.04**	**4.04**	**0.24**	0.03	**0.06**
1,2,3,4,7,8-Hx	**2.26**	0.03	0.03	**0.03**	**6.20**	**0.57**	**0.08**	**0.06**	**9.22**	0.03	0.03	**0.10**
1,2,3,6,7,8-Hx	**2.81**	0.03	0.03	**0.02**	**3.21**	**0.31**	0.03	**0.05**	**4.01**	**0.16**	0.03	**0.05**
1,2,3,7,8,9-Hx	**7.25**	**0.24**	**0.13**	**0.04**	**6.00**	0.03	**0.15**	**0.07**	**7.90**	0.03	0.03	**0.12**
HpCDD	24.0	0.7	0.3	0.3	40.1	2.9	0.6	0.5	51.2	1.6	0.8	0.05
OCDD	107	6	2	3	169	9	3	4	168	5	5	3
Σ (PCDD/DFs)	148	6.8	2	3.5	228	13.1	4	4.8	246	7.1	6	3.7
TEQ[b] WHO '98	5.97	0.14	0.12	0.07	5.23	0.52	0.13	0.12	7.33	0.35	0.11	0.14

Table 2. Commercial Trials: Dioxin levels[a] (pg/g) of bleaching earths & vegetable oils

PCDD Congeners	#1 – Soy Oil (0.35% dosage) FBE 1	SBE 1	Start oil	RB oil	#2 – Corn Oil (0.40% dosage) FBE 2	SBE 2	Start oil	RB oil	#3 – Palm Oil (1.0% dosage) FBE 3	SBE 3	Start oil	RB oil
2,3,7,8-TCDD	**0.41**	0.04	0.02	0.01	**0.34**	0.05	0.06	0.04	**0.56**	0.03	0.03	0.05
1,2,3,7,8-Pe	**1.19**	**0.04**	0.03	0.03	**1.18**	0.06	0.04	0.04	**1.17**	**0.06**	0.12	0.25
1,2,3,4,7,8-Hx	**1.10**	0.07	0.03	0.03	**1.35**	**0.24**	0.08	0.08	**1.20**	**0.09**	0.09	0.25
1,2,3,6,7,8-Hx	**1.37**	0.06	0.03	0.03	**1.70**	**0.20**	0.08	0.08	0.72	**0.15**	**0.09**	0.25
1,2,3,7,8,9-Hx	**1.88**	0.05	0.03	0.03	**2.29**	**0.34**	0.08	0.08	**2.14**	**0.13**	0.12	0.18
HpCDD	14.2	0.49	0.19	0.26	21.7	0.64	0.07	0.06	17.5	0.82	0.12	0.73
OCDD	60.8	3.50	1.56	2.20	107	4.9	0.12	0.16	88	9.9	1.16	5.26
Σ (PCDD/DFs)	82	4	2.0	3.45	136	6.3	0.13	0	111	12.2	1.7	7.2
TEQ[b] WHO '98	2.30	0.15	0.08	0.08	2.31	0.28	0.20	0.15	2.57	0.21	0.26	0.61[c]

[a] Because any individual contribution to TEQ by PCDFs was always below 0.02 ppt , PCDF values are omitted from the tables. Values in *italics* are *estimated detection limits* for non-detected congeners.

[b] TEQ$_{WHO\ '98}$ values were calculated using 1 times detection limit for non-detected congeners.

[c] TEQ$_{WHO\ '98}$ value overstated because of high estimated detection limits (see data).

The situation in going from starting $\Rightarrow$ RB $\Rightarrow$ RBD oil is more problematic. In spite of the (deliberately) high FBE dosage level employed for the lab bleaches, differences between starting and processed oils in terms of TEQ values are barely discernible, probably because of the large dilution effect by the oil itself. Because deodorization conditions (230-260 °C / 1-3 mm Hg) are conducive, tetra-and penta-substituted congeners should volatilize easily during the deodorization step (e.g. - vapor pressure 2,3,7,8-TCDD = 21.4 mm Hg @ 200 °C[11] compared to fatty acids = 4.3 mm Hg @ 200 °C[12]) and their levels would be expected to drop in going from RB $\Rightarrow$ RBD oil. The data are, however, inconclusive in this regard.

Data in Table 2 (commercial operations spanning a range of bleaching dosages and oil types), duplicates the results from the laboratory experiments (i.e., 92-96% of dioxins leached from starting bleaching earth; almost no change in TEQ values for starting as compared to RB oil).

Conclusions

These data show that vegetable oils solvate most (90-95%) of the dioxins present in bleaching earths under the conditions typically employed during edible oil processing. It is also clear that residual dioxin levels in the spent bleaching earth and processed oils are extremely low, even after having employed (relatively) high clay dosages. Based on physical principles, it is expected that RBD oils would contain near-zero levels of lower congeners after deodorization; conversely, the small amount of DD produced should be concentrated in these congeners. Noteworthy in this respect is a recent EPA/FDA paper[13] reporting deodorizer distillates obtained from various US refiners possessed relatively high levels of dioxins (range 1.4 – 7.1 ppt TEQ) as compared to oil.

These data are also relevant with regard to European legislation[14] which stipulates < 0.75 ppt TEQ dioxins for edible oils and oil by-products. They show bleaching earths containing dioxins in the range 5-10 ppt TEQ (i.e. – background levels) as used in edible oil processing will yield oils and spent cakes possessing TEQ values well below current European regulatory limits. In fact, by extrapolation, even higher dioxin levels (i.e. >10 ppt TEQ) can be tolerated without issue when processing with lower (more typical) clay dosages.

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