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Response to Comment on "Evidence for the Presence of PCDD/Fs in the Environment Prior to 1900 and Further Studies on Their Temporal Trends"

SIR: We thank Baker and Hites (*1*) for their interest in our paper (*2*) and are glad to have an opportunity to clarify and expand a little on some issues.

As has been pointed out previously (*1*−*5*), time trend information can give important clues about the relative importance of different sources of PCDD/Fs to the environment. However, it has proved very difficult for scientists to find definitive evidence for the presence/absence of PCDD/Fs in the environment more than several decades ago (see ref *3* for review; also *5*−*8*). For example, in some studies with sediment cores, preserved human tissues, foodstuffs, etc. PCDD/Fs have been detected at or very close to the analytical detection limits (*5*−*8*). If PCDD/Fs were present in the environment a long time ago, however, surface soil is a good matrix to study because its concentrations will reflect cumulative deposition (minus any losses due to volatilization, biodegradation, leaching, or subsurface mixing) over many years/decades and possibly centuries (*4*). In contrast, each dated layer of a sediment core represents a much shorter, discrete time interval and therefore will have lower masses of PCDD/Fs present for the analyst to detect (*3*, *5*).

Because the analyst is looking for ultra low concentrations, questions of sample contamination and integrity are crucial. We were acutely aware of these issues when we undertook the study on Rothamsted soil, because of our previous work showing the ease with which samples can become contaminated with PCBs (*9*) and the literature dealing with potential PCDD/F contamination (see ref *3*).

The 1881 sample selected for study had been stored in a glass jar; the jar contained ∼5 kg of soil and had been unopened since 1881. It had a cork bung driven into the lip of the glass, and wax was used to seal the top of the cork and fill the depression between glass and cork. We consider this to have been an airtight method of storage. We described previously our efforts to ensure no contamination after the jar had been opened and our experiment to test for potential contamination with modern laboratory air and the potential impact of contact with dust (*2*). The method of taking and preparing the samples until the early 1990s has also been described in detail (*10*).

There were clearly a wide range of readily detectable PCDD/Fs present in the sample taken from the sealed jar of 1881 soil; how did they get there? There are four possibilities: (i) some or all of them were present when the sample was collected; (ii) some or all of them were formed in the sealed jar during storage; (iii) some or all of them entered the jar after collection (by diffusion through the wax/cork); (iv) some or all of them entered the sample after it was taken from the jar.

If they occurred, cases ((ii)−(iv)) would all be compound-specific or compound-selective processes (e.g. (iii) would favor the lighter compounds which are predominantly in the gas-phase in air; (iv) would favor those in the dust samples). However, the range and mixture of PCDD/Fs detected in the soil sample is quite typical of that from contemporary UK background soil (*4*).

We believe that case (i) applied; we believe that of cases (ii)−(iv) only case (iv) might be relevant for some of the congeners, i.e. contamination with traces of dust. As our Table 3 calculation showed (ref *2*), relatively small quantities of dust would significantly influence the concentrations of the Hx to OCDFs, if they had somehow become incorporated into the jar. Given that the jar contained ∼5 kg of soil, PCDD/Fs from tens of milligrams of dust would have had to somehow reach the soil stored in the deeper parts of the jar where we took our sample, despite all our best efforts to prevent this. However, for the tetra- and pentahomologues, PCDD/Fs from tens of grams of dust would have been needed. We believe this could not have happened. When we collected the jar from the Rothamsted store it did, of course, have a thin layer of dust on it. However, the jar was not opened until the outside had been scrupulously cleaned. In our opinion the only other possible explanations for the presence of lighter homologues in the soil are therefore cases (i) or (ii). Biologically-mediated formations and conversions of PCDD/Fs have been reported (e.g. ref *11*) where lower chlorinated compounds have been formed from anaerobic dechlorination of heavier homologues. However, this is unlikely to have resulted in the pattern found in the soil or to have been able to occur efficiently in a sealed jar of dried soil. It was, in fact, quite difficult to collect enough dust from the shelves and storage jars in the archive to yield the samples for PCDD/F analysis.

In summary, the study was carefully performed and the data cannot easily be dismissed. As such, it makes an important contribution to the information on the historical occurrence and levels of PCDD/Fs. Nonetheless, our study is just one piece of evidence, and further work is required to contribute to the database on historical PCDD/F levels and trends. It is worth emphasizing again (*2*) that the data originates from a country with a centuries-long history of industrial activity, including metal refining and smelting and combustion of coal/wood and is therefore unlikely to be representative of PCDD/F emissions in many other parts of the world.

On a separate issue we confirm that Table 7 does contain an error in the units; it should read pg; we thank Baker and Hites for drawing attention to this.

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