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Item ID Number 01419

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Report/Article Title Analytical Chemistry and Source Notes Gathered
During Meetings of World Health Organization Held in
Naples and Copenhagen March 17-16, 1986.

Journal/Book Title

Year 1986

Month/Day March 29

Color

Number of Images 5

Description Notes

3/29/86

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ANALYTICAL CHEMISTRY AND SOURCE NOTES
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INTRODUCTION

The European Regional Office of the World Health Organization (WHO-EURO) held meetings on the above dates to consider two aspects of a three-year effort on "dioxins" and PCBs (see separate report for more extensive information this larger effort):

- A. The health implications of the emissions of CDDs/CDFs from municipal waste combustors (MWCs) and municipal sewage sludge combustors (MSSCs).
- B. Additional information which should be gathered prior to conducting an assessment of the risk of breast feeding newborns with milk contaminated with CDDs/CDFs and PCBs.

The major points of these meetings were contained in a trip report submitted on March 28, 1986. The summary below, dealing with analytical chemistry and sources, is one of several summaries promised in the trip report which amplify on certain aspects of and information gleaned from the WHO meetings.

Technique

Sampling spikes:

- a. Following Rappe, Sweden has dictated that CDD/CDF analysis should include addition of a labelled spike to the sampling equipment (e.g., XAD-2 resin or urethane foam plug). Final analytical results will be corrected for the percent recovery of this spike, in a fashion analogous to the correction made for the recovery of spikes during the extraction and clean-up phase. Rappe generally finds that the recovery is in the 30-60% range, but see below. Therefore, there are three spikes in the life history of every sample: the one in the sampling device (4 congeners), the one added prior to extraction and clean-up (3 congeners), and the one added as a concurrent internal standard.
There was some discussion of the effectiveness of this procedure, but, in summary, it did highlight the question of the adequacy of the sampling phase of the analysis -- which we often assume to be 100%.
- b. Some investigators report that ambient air monitoring for CDDs/CDFs has been effective only during the winter months. Apparently, during the warmer periods of the year, the sorbant material (e.g., urethane foam) does not retain the analyte of the sampling spike which has been added to check for efficiency of sampling.

Feeding studies

One lab took a large volume of flyash and homogenized it. Repeated sampling from the large mass showed variations in CDD/CDF content in excess of 100X.

Analysis of PCBs

- a. Analysis of the PCBs is even more difficult than that analysis of the CDDs/CDFs. The lack of standards for the congeners, the difficulty in identifying the toxic congeners, and the variable methods of analysis have made it difficult to develop a standardized approach. However, within recent years there is an emerging consensus about how many and which congeners to quantitate and to use as a basis for quantitating the amount of PCBs; e.g., 11-12 peaks, as opposed to 2-3 peaks. Therefore, the reported results of some labs have decreased by a factor of about 2, simply due to a different approach to analysis. Consequently, one needs to closely examine reports of reductions in PCB levels to be assured that these are not simply a reflection of altered analytical approaches.
- b. A WHO meeting in February recommended quantitating PCBs based on about 7 peaks. However, only three of these peaks have been found to any significant extent in human milk; therefore, including the other four in the procedure may be irrelevant, if not expensive and damaging.

Laboratory capabilities

- a. It is estimated that there are roughly 10 labs in Europe which have the ability to measure CDDs/CDFs at very low levels. These labs are found in Sweden, the Netherlands, Denmark, Germany, Norway, Italy (3-4), and Finland.

Media

- a. Rappe reports successful analysis of CDDs/CDFs in blood in the low ppt range, starting with 150 ml of blood.
- b. Rappe is conducting an inter-lab validation study for the analysis of CDDs/CDFs in human milk. They have collected a homogeneous sample of 10 liters of milk. Given the complexity of uniformly spiking this much material, each investigator will prepare his/her own samples, using prepared aliquots of spiking solution provided by the referee lab.
- c. Cows grazing in the plume of MWCs are reported to have higher levels of CDDs/CDFs than those grazing outside the plume. However, there is some question about the significance of this difference since the number of cows is small and the difference between the two groups of cows is not as great as one might think.
- d. Rappe finds that the HxCDD/F fingerprinting found in human samples matches the isomer pattern found in cows

milk.

Sources

- a. Air sampled in a Hamburg auto tunnel is purported to display CDD/CDF emissions similar to those from MWCs -- in fact, from any combustion source. This includes the 1,2,3,7,8-PeCDD, which had been thought to be a marker for MWC emissions. At best, it is now a marker for emissions from combustion sources, in general.
- b. The three main contenders for the "Major CDD/CDF Contributor" in the environment seem to be: a) MWCs, b) automobiles, and c) PCP.
- c. Several of the analysts believe that PVC will serve as a legitimate source of CDD/CDF emissions in a MWC. This is in contrast to the position set forth by FDA in a recent EIS, in which they cite primarily one study in which increased amounts of PVC in the waste stream did not seem to materially elevate the CDD/CDF emissions. I have conveyed this information to Paul Kaldjian of the Federal Activities Office, who is coordinating the EPA response to the FDA EIS. Note that an increased possibility of CDD/CDF emissions is not equivalent to a conclusion of a significant increase in health risk.
- d. The pulp and paper industry in some parts of the world are using an NO₂ based bleaching process, which apparently is associated with CDDs/CDFs as well. In addition, there is indication that some parts of the industry use bromine-based slimicides; again, potential sources of halogenated dioxins and furans.
- e. I read the Hites article in the recent Environmental Science and Technology and found it wanting. Allegedly, the article provides further evidence for the combustion of chloro-organics as the source of the CDDs/CDFs in the sediments of the Great Lakes. I did not find the evidence of the explanation convincing. First, the data displayed in the articles seemed, to me, to argue strongly for a significant admixture of higher CDDs/CDFs from pentachlorophenol to any contribution from combustion sources. Second, I found some of the argument lack the clear compelling logic one looks for in a scientific exposition. Instead, it seemed that possibility and speculation in early parts of the paper transmuted into "fact" later in the paper. Further, I understand that there is some question about the investigator's clean up procedures.
Hagenmaier (German analyst) still feels that the data say "PCP" to him.
- f. The Stiglitz experiment described in Bayreuth has been investigated by Hagenmaier. He has found a lot of strangeness going on as he heats flyash at elevated temperatures for a matter of hours. For example, spikes disappear and there is a decrease in some CDDs/CDFs and an increase in others. There is evidence of the flyash's acting as a catalyst to facilitate

transformation of the higher CDDs/CDFs to the lower ones.

- g. Rappe has found that the homologue profiles may differ from one combustion source to the next. However, he has found that the isomer pattern (e.g., the distribution of the TCDDs) is the same from one combustion source to the next.

Note: This has implications for the application of the estimation of 2,3,7,8-TCDD equivalents in risk assessment. Ballschmiter says that "Everyone knows" the percent of 2378-isomers within each homologous group that are sampled from a combustion source. He will send me what "everyone knows".

Note: This may raise questions about the Townsend explanation (cf., Bayreuth) for the origin of the CDDs/CDFs in Midland soil samples.

- h. Some folks feel that day-to-day variations at the same plant could be 10X, making an assessment of the effect of conditions and controls very difficult. Others did not agree.
- i. The general consensus is that, with current sampling methods, it is futile to discuss the percent partitioning between gaseous and particulate phases.
- j. Rappe has not seen an increase in the CDD/CDF contamination of the Baltic Sea organisms that matches the increase of in the number of MWCs. This could argue against MWC as the significant source, or it could reflect more recent improvements in combustion efficiency. Other potential sources include a) autos, b) wire reclamation plants, and metal mills burning off "cutting oils"; i.e., chlorinated paraffins.
- k. I understand that Hagenmaier reported finding 2,3,7,8-TCDD in NaPCP produced by Dynamit-Noble at a plant where trichlorophenol was produced. Further, he has found 2,3,7,8-TCDD and 1,2,3,7,8-PeCDD in a sample of Dowicide G. Finally, he found 2,3,7,8-TCDD in a sample of 2,4-D. I have a preprint of the report which has been submitted to Chemosphere.
- l. Emissions from all kinds of incineration processes are considered to be likely sources; e.g., hospital incinerators, crematoria, and supermarket incinerators. These are likely to be small in volume, but their levels could be high.
- m. OCDD has been found in essentially all samples of house dust at a combined level of 70 ppb. A likely source is PCP which is rather pervasive; e.g., these Hx-, Hp- and OCDD have been found in toilet paper.
- n. New automobile engine oil is reported has containing Hx-, Hp- and OCDD. Again, this is suspected as having a PCP origin.
- o. An estimate of Hx-, Hp- and OCDD contributions to the German environment:
800 kg/yr from MWC
250 Kg/yr from PCP use

More than 1000 kg/yr from PCP waste

Controls

Metals emissions from MWCs and MSSCs could be troublesome. Swedish work seems to confirm our understanding that most metals emissions will be significantly reduced by the controls designed to reduce acid gases, particulate, and CDD/CDF emissions. Sweden is developing a method to control mercury emission, which seem to be among the most difficult to control.

It would seem that metals control at the front end could be more effective than currently practiced. Even though some authorities have implemented input controls (primarily on batteries coming into the water stream), these attempts have not met with resounding success. Where are we in moving ahead on this issue via RCRA, TSCA, and CPSC?

Nomenclature

Rappe calls the "fingerprint" based on homologue-specific data the "CDD/CDF profile" of the sample. The "fingerprint" of the isomer-specific data, he calls the "pattern" of the sample.

Tidbits

There is some indication of covalent reactions between PCP and fat in vivo.

On a fat basis there is little, if any difference, in the CDDs/CDFs or the PCB levels in fat, organ, milk, or blood.

Folks are investigating the transformation between homologues.

IPCS has apparently published a report on "Principles of Risk Assessment in Infants".

Canada is doing flyash leachate studies.

Levels

- a. Average PCB in background human milk fat: .5-1.5 ppm
" " " workers' " " " : 3-15 ppm

The most prominent congener in milk fat is the 2,2',2,4,4',5-HxPCB

- b. See attached list for the major and minor components of PCDDs and PCDFs in human milk.
- c. Reggiani, J. of Appl Tox 1, 323 (1981) cites three analyses of human milk by McKinney. We need to find the original report.
- d. Netherlands data on human milk will be released in April and should add to the current picture.
- e. PCP workers show an 85% decrease in their blood level of OCDD within one year.