

SEP 1982

American Chemical Society

ACS NEWS SERVICE

1155 SIXTEENTH STREET, N.W.
WASHINGTON, D.C. 20036
Phone (202) 872-4450

DIVISION Environmental Chemistry

PAPER # 37 / 2⁰⁵pm Tues

AMERICAN CHEMICAL SOCIETY'S 184TH NATIONAL MEETING

KANSAS CITY, MISSOURI

SEPTEMBER 12-17, 1982

AUTHOR RAPPE Christopher
(Last Name) (First)
JOB TITLE Professor, Chairman
AFFILIATION Department of Organic Chemistry
ADDRESS University of Umea S-901 87 Umea Sweden
BUSINESS PHONE 46-90-1652 66 HOME PHONE 46-90-134480
TITLE OF PRESENTATION Polychlorinated dioxins, dibenzofurans and
other polynuclear aromatics formed during
incineration and PCB fires
KANSAS CITY ADDRESS DURING MEETING _____
KANSAS CITY PHONE NUMBER _____
ARRIVAL DATE IN KANSAS CITY Sept 13
DEPARTURE DATE FROM KANSAS CITY Sept 16

THIS DOCUMENT IS (Circle One):

1. Paper 2. Summary 3. News Release 4. Other (Specify)

TIME & DATE OF PRESENTATION 205 am/pm Sept. 12, 13, (14) 15, 16, 17
(Indicate hour) (Circle Date)

PLACE OF PRESENTATION Convention Center ROOM # 205 East
Lobby Level

(Note to Correspondents: Release time is the time of presentation)

CONTACTS: Geraldine Sanderson (202) 872-4450
Nancy Enright (202) 872-4448

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POLYCHLORINATED DIOXINS, DIBENZOFURANS AND OTHER POLYNUCLEAR
AROMATICS FORMED DURING INCINERATION AND PCB FIRES

Christoffer Rappe, Stellan Marklund, Per-Anders Bergquist
and Marianne Hansson

*Department of Organic Chemistry
University of Umeå
S-901 87 Umeå, Sweden*

The occurrence of polychlorinated dioxins (PCDDs) and dibenzofurans (PCDFs) in fly ash is well documented. There is much less data reported on levels in other incineration products like flue gas and particulate.

Due to the extreme toxicity of some of the PCDD and PCDF isomers and the large variation in toxicity and biological potency between closely related isomers, a risk evaluation should be based on the levels of the highly toxic isomers. However, isomer specific analyses have only been made in a few cases, in most studies the results have been given in terms of tetra-CDDs, tetra-CDFs, hexa-CDDs etc. The number of isomers in this type of samples is quite large, more than 30 PCDDs and 60 PCDFs have been found.

RESULTS

Municipal incineration, fluidized bed (Sweden)

We have investigated a municipal incinerator working with a fluidized bed. The samples analyzed were extracts of particulates and condensates taken at two different sampling occasions. We found:

1. large variation between the two sampling occasions depending on the conditions in the fluidized bed (temperature, retention time, oxygen excess)
2. higher levels in the condensate than in the particulates indicating that the major source of PCDDs and PCDFs is the flue gas
3. a marked predominance for the tetra-, penta- and hexa-CDFs over the corresponding PCDDs
4. a dominance of octa-CDD over octa-CDF
5. tetra-CDFs is the dominating chlorination level among the PCDFs
6. octa-CDDs is the dominating chlorination level among the PCDDs
7. tetra-CDDs (and 2,3,7,8-tetra-CDD) could only be found in one of the four samples, a condensate. The level of 2,3,7,8-tetra-CDD is about 0.3 ng/m³.
8. a large number of tetra-CDF isomers could be identified
9. in addition to PCDDs and PCDFs we could find other polychlorinated polynuclear aromatics (like chloropyrenes, chlorochrysenes and chlorobenzopyrenes) in these samples. The biological effects of these compounds have not been investigated.

Industrial boiler (USA) - PCP incineration

Samples of bottom ash and baghouse ash from an industrial boiler burning pentachlorophenol (PCP) contaminated waste were analyzed. A multitude of PCDDs and PCDFs were identified and the total levels of PCDDs were about 5 ppm and of PCDFs about 2.5 ppm. In this case 2,3,7,8-tetra-CDD is only a very minor peak and more than 90% of the PCDDs are lower chlorinated congeners than octa-CDD, the expected PCP-dimerization product. The pattern of the tetra-, penta and hexachloro dioxins is in good agreement with the dioxin pattern found in samples of European fly-ash.

Rotatory cement kiln (Norway) - PCB incineration

We have analyzed a series of samples taken during a test study of thermal destruction of PCB in a rotatory cement kiln in Norway. The kiln is 150 m long with a diameter of 3.5 m. It has a so called "wet" oven operating at 1450 °C in the solid material and at 2000 °C in the flames. During the test period 4 m³ of PCB was burned at a feeding rate of 50 kg/h. The samples analyzed include condensates, particulates and cement. All the samples were negative for PCDFs and PCDDs.

Accidental PCB-fires

a) Capacitor fire, Skövde, Sweden

In March 1982 a fire broke out in a capacitor battery (400 V) serving a high-frequency oven. The dielectricum in the capacitors consisted of mineral oil or PCB and the two types of capacitors were

mixed at random. The fire started in a capacitor containing mineral oil, and about 2 h elapsed until the fire was completely extinguished. The building, a foundry, was very well ventilated. Wipe tests were taken and analyzed. The results show that levels exceeding 100 ng/m² could only be found in an area close to the fire. The highly toxic 2,3,7,8-tetra-CDF is one of the major dibenzofuran isomers.

In addition to the PCDFs the samples contained a series of polychlorinated pyrenes, but no dioxines or biphenylenes could be found in the samples from this fire.

b) Capacitor fire, Stockholm, Sweden

Soot samples were collected from an accidental PCB-fire in Stockholm, Sweden, in August 1981. Here, capacitors filled with PCB was ignited probably due to electrical misfailure (10 kV). The extract containing the planar polychlorinated polynuclear aromatics was analyzed and the major peaks were a series of chlorinated biphenylenes, but other compounds found were the highly toxic 2,3,7,8-tetra- and 2,3,4,7,8-penta-CDF. No dioxines could be found.

c) Transformer fire, Binghamton, USA

The dielectricum in the Binghamton fire was a mixture of 65% Aroclor 1254 and 35% chlorobenzenes. Soot samples from this fire were analyzed and the dominating products were the PCDFs, more than 2000 ppm of total PCDFs. The highest levels were found for penta- and hexa-CDFs, 700 ppm and 1000 ppm respectively. The highly toxic isomers were the dominating isomers.

In addition to PCDFs we also found a series of PCDDs, the dominating

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isomers were the highly toxic 2,3,7,8-tetra-CDD (0.6 ppm) and 1,2,3,7,8-penta-CDD (2.5 ppm).

CONCLUSIONS

In addition to polychlorinated dioxins and dibenzofurans, we have found several other products like polychlorinated biphenylenes, pyrenes, benzopyrenes and chrysenes.

Much interest has been given the observation of polychlorinated dioxins in incineration products. It has been suggested by Dow Chemicals that dioxins are ubiquitous and formed in de novo reactions. The data reported here shows a much more complicated picture.

1. The dioxins are only one part of the problem of the formation of toxic polychlorinated polynuclear aromatics (PCPNAs) during incineration and other thermal reactions. The same interest should be given to the polychlorinated dibenzofurans.
2. The highest levels of PCPNAs are found when technical products are thermally converted directly into dioxins or dibenzofurans. Examples of precursors are:
chlorophenols - dioxins
PCBs - dibenzofurans, biphenylenes
chlorobenzenes - dioxins, dibenzofurans
chlorodiphenyl ethers - dioxins, dibenzofurans
3. Dechlorination of octachlorodioxin to hepta-, hexa- and other lower chlorinated dioxins is another major pathway.
4. Lower chlorinated compounds like mono-, di- and trichloro derivatives of dioxins, dibenzofurans, pyrenes, benzopyrenes and

chrysenes can be formed in a de novo formation similar to the formation of benzo(a)pyrene and other polynuclear aromatics in most incineration reactions.

5. Under special conditions flue gas is the major source of PCPNAs.

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