

Relation between Isomer Compositions of Polychlorinated Naphthalenes and Congener Compositions of PCDDs/PCDFs from Incinerators

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1. Introduction

Polychlorinated naphthalenes (PCNs) are composed of as many isomers as PCDDs. We have already identified all di- through penta- isomers¹⁾ and all isomers of hexachloronaphthalenes (HxCN) were identified by Nikiforov et. al.²⁾. PCNs are often found in the flue gas of incinerators together with PCDDs and PCDFs³⁾. However, the compositions of PCNs from incinerators and the mechanisms of their formation are not clear.

The objective of this study is to clarify the isomer composition of PCNs in relation to PCDDs/PCDFs formation. Isomer specific analysis of PCNs and congener specific analysis for PCDDs/PCDFs were carried out for fly ash samples from twelve municipal incinerators.

2. Materials and Methods

Fly ash samples were collected from municipal incinerators listed in Table 1. Five of them are stoker type and the others are fluidized bed incinerators. Air-dried fly ash samples were digested with hydrochloric acid and was Soxhlet extracted with toluene for 24 h. Toluene was removed by evaporation and the residue dissolved in n-hexane was washed by aqueous sodium hydroxide and concentrated sulfuric acid. Further purification was performed by activated copper, silica gel column and alumina column.

Table 1 Incineration plants where fly ash samples were collected

Sample	Type of incinerator	Capacity
A	Stoker (Continuous)	400 t/day
B	Stoker (Continuous)	200
C	Stoker (Continuous)	150
D	Stoker (Mechanical batch)	20
E	Stoker (Mechanical batch)	80
F	Fluidized bed	- *
G	Fluidized bed	40
H	Fluidized bed	20
I	Fluidized bed	50
J	Fluidized bed	100
K	Fluidized bed	130
L	Fluidized bed	- *

* : No information

PCNs, PCDDs and PCDFs in fly ash were analyzed by selected ion monitoring using double focusing GC/MS (Hitachi M-80B). Silicone OV-1701 column (GL Science Inc.) was used for determination and isomer specific analysis of PCNs¹⁾ and DB-5 column (J&W Scientific) was used for determination of PCDDs/PCDFs congeners.

3. Results and discussions

Correlation between PCNs and Dioxins on their concentrations

Concentrations of total PCDDs and total PCDFs was compared with total PCNs. Total PCDDs and PCDFs are sum of tetra- through octa- isomers. In the case of PCNs, the concentrations of tri- through hepta- congeners were summed. The result is shown in Fig. 1. The concentrations of PCNs have strong correlation with those of PCDDs and PCDFs.

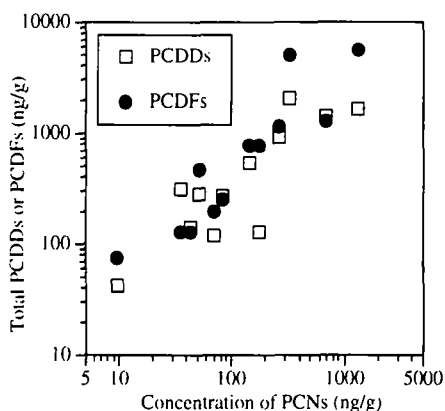


Fig.1 Relationship between PCNs and PCDDs/PCDFs

Classification of isomer compositions

Six typical patterns of isomer composition of PCNs from incinerators are shown in Fig. 2. Iso-mer composition of tetrachloronaphthalenes (TeCNs) and pentachloronaphthalenes (PnCNs) shows significant difference between the samples from fluidized bed incinerators and those from stoker incinerators. Samples from stoker incinerators have a pattern in which lateral positions are mainly substituted except for trichloronaphthalenes (TrCNs). Dominance of 1,2,6,7-TeCN, 1,2,3,6,7-PnCN and 1,2,3,4,6,7-/1,2,3,5,6,7-HxCN among each congeners are specific to this pattern (pattern I). For the majority of the samples from fluidized bed incinerators, different pattern (pattern II) appeared. In pattern II, 1,2,6,7- and 1,2,3,6,7- isomers are not always major constituents. Instead, 1,2,8-TrCN, 1,2,3,4- and 1,2,4,8-TeCN, 1,2,4,7,8- and 1,2,3,4,5-PnCN were dominant isomers. Thus chlorine substitution occurs mainly on successive positions including 1,8- positions. All five samples (A - E) from stoker incinerators and one sample (F) from fluidized bed incinerators were classified to pattern I. Among seven samples from fluidized bed incinerators, five samples (H - L) were showing pattern II pattern and one sample (G) had a pattern Like a mixture of I and II.

1,3,6-TrCN and 1,3,6,8-TeCN, which appeared in two samples (B and E), were supposed to be thermal decomposition products of polyvinylidene chloride.

For all samples analyzed here, concentration of 1,2,3,4,5,6,7-HpCN was higher than that of 1,2,3,4,5,6,8-HpCN.

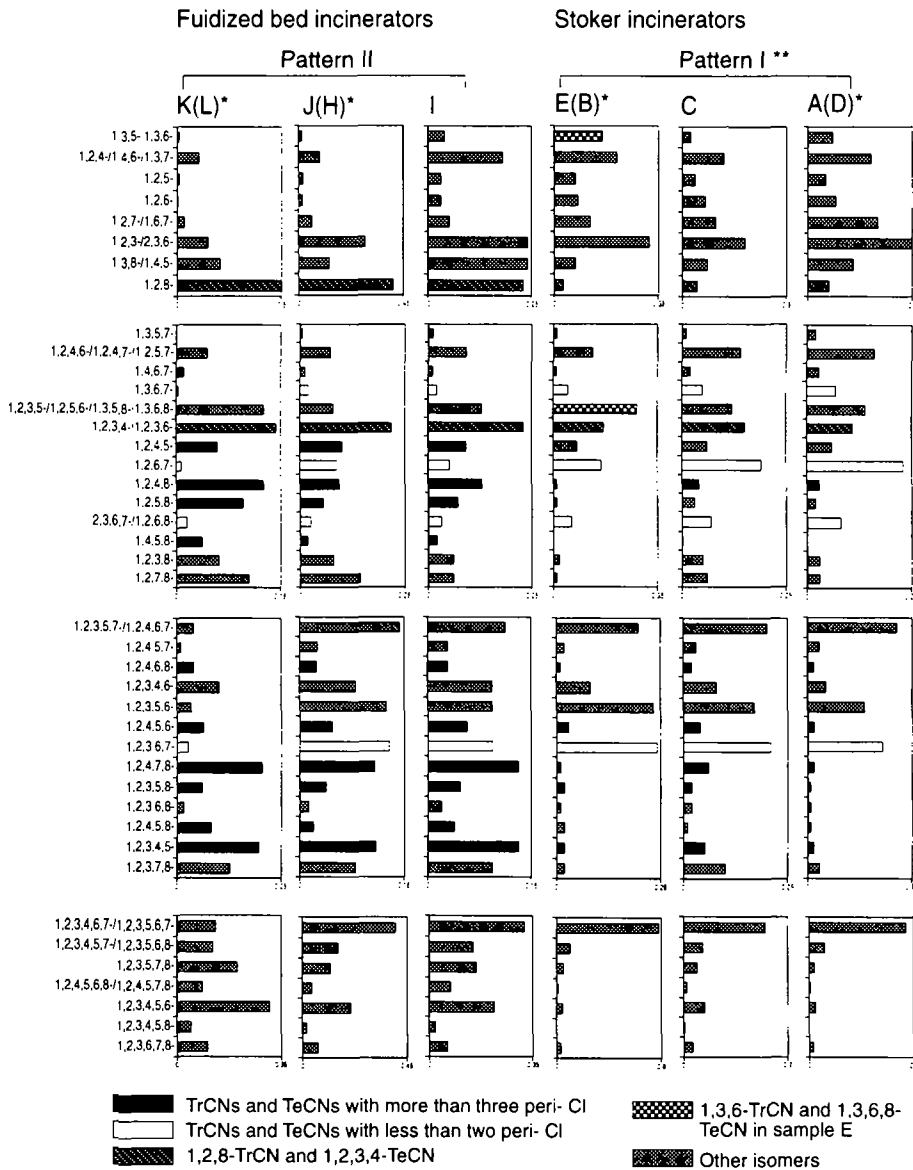


Fig. 2 Isomer composition of PCNs from municipal incinerators

* Name of the sample which has similar isomer composition are indicated in parentheses

** 1,3,6-TrCN and 1,3,6,8-TeCN are ignored in this classification

Congener composition of PCDDs and PCDFs

For samples H - L (PCNs: pattern II) and G (partially pattern II), congener compositions of PCDDs and PCDFs are shown in Fig. 3. Except for sample H, PCDFs are found in greater amount than PCDDs. The content of congeners increase upon the elevation of the degree of chlorine substitution up to hepta- congener. On the other hand, samples those have PCNs pattern I give various congener composition (Fig. 4). These results imply that there exists a certain reaction which is common to the generation of PCNs of pattern II and PCDDs/PCDFs of Fig.3 (I - L). Peri- position has higher reactivity than lateral positions for chlorine substitution on naphthalene nucleus. According to this orientation, chlorination reaction is likely to have occurred in the condition when pattern II appears in PCNs. This assumption can explain the reason why higher chlorinated PCDDs/PCDFs are dominant for these samples. By this property, composition of PCNs (especially TeCNs and PnCNs) may become an indicator of reaction conditions in which PCDDs and PCDFs are generated.

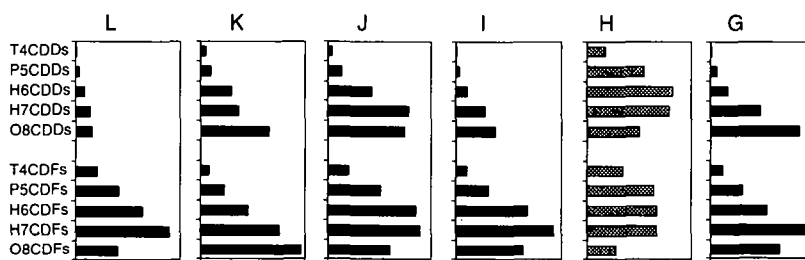


Fig.3 Congener compositions of PCDDs/PCDFs - samples with PCNs pattern II and sample G

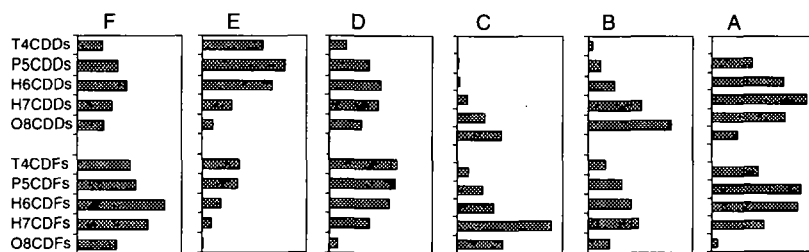


Fig.4 Congener compositions of PCDDs/PCDFs - samples with PCNs pattern I

Acknowledgment

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4. References

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