INVESTIGATION OF MONO-ISOPROPYLNAPHTHALENE, DI-ISOPROPYLNAPHTHALENE AND TRI-ISOPROPYLNAPHTHALENE IN THE ENVIRONMENT AROUND THE PAPER RECYCLING PLANT

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Abstract

Mono-Isopropylnaphthalene (MIPN), Di-Isopropylnaphthalene (DIPN) and Tri-Isopropylnaphthalene (TIPN) have been widely used for PCBs substitutes. The concentration and the fingerprints of their isomers in the environment around the paper recycling plant were investigated. 1-MIPN, 2-MIPN and major 8 isomers of DIPN were assigned with GC/MS. It was found that the river water, the sediment, the algae and the air were polluted with DIPN by the wastewater and the exhaust from the paper recycling plant. Moreover, another pollution source of DIPN and TIPN was considered because the unusual fingerprint of DIPN isomers and high concentration of TIPN were detected from the sediment which was not influenced by the wastewater from the paper recycling plant. It was considered that DIPN in the sea bass was metabolized and the rates of decomposition of DIPN were different with each isomers.

Introduction

Mono-Isopropylnaphthalene (MIPN), Di-Isopropylnaphthalene (DIPN) and Tri-Isopropylnaphthalene (TIPN) as PCBs substitutes have been increasingly used from 1970's in Japan. However they are concerned to have harmful influences to health and environment because of their high persistent and accumulating properties¹. Because of their usage for ink solvent, there is a concern that their compounds contaminate widely in the environment. The foods contaminations of DIPN from the wrapping with recycled paper were reported ². MIPN and DIPN in the environmental water, the sediment and the biological samples have been measured in Japan, however, there are some analytical problems that DIPN isomers peaks have not been separated and assigned enough. MIPN, DIPN and TIPN are usually used as isomer mixtures. It is important to assign MIPN, DIPN and TIPN isomers for investigating their fates in the environment. Recently, DIPN isomers were separated and assigned in the field of chemosynthesis ³. On the other hand, DIPN and TIPN isomers have not been assigned in the environmental field yet.

In this study, to reveal the pollution of MIPN, DIPN and TIPN in the environment, their simultaneous analytical method was developed and their concentration and isomer fingerprints were investigated in the environmental samples around the paper recycling plant.

Materials and Methods

1. Sampling

The river water, the sea water, the sediment, the algae and the sea bass were sampled. Sampling points were indicated in Fig.1. 1L river waters were sampled from point B (water B), point D (water D), point D' (water D'), point E (water E) and point F (water F). Point B is about 10km upstream from the mouth of Ibo River. Point E is about 2km downstream of point B. Point F is about 1km downstream of point E. Point D and Point D' are upstream and downstream of waterway from the paper recycling plant.

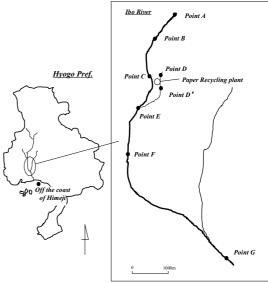


Fig.1 The map of sampling point.

The waterway was jointed at point E in the Ibo River. 1L sea water was sampled off the coast of Himeji. 20g wet sediments were sampled from Point A (sediment A), Point B (sediment B) and Point E (sediment E). As the biological sample, 20g wet algae were sampled from Point B (algae B), Point E (algae E) and Point F (algae F). And a few Sea bass were sampled off the coast of Himeji and their bodies were mixed and homogenized to 20g-wet. The air was sampled from Point C (air C) near by the paper recycling plant and the roof of our institute as a control. $0.5 \text{ m}^3 \sim 10 \text{m}^3$ air were introduced into PS-Air cartridge which have been conditioned by acetone washing and drying with N_2 gas. As the other sample, 1.2g waste newspaper was sampled and cut like as finger tip.

2. Analytical procedure

MIPN, DIPN and TIPN in the water samples were extracted by shaking with 10mL hexane in 1L glass bottle. As to the sediment, the biological sample and the newspaper, they were extracted by alkaline degradation with 50mL KOH/MeOH for about 12 hours. After the solvent have been changed to Hexane, the extract was cleaned up by the silica gel containing 5% water or sulfuric acid. As to the air samples, they were extracted by 10mL dichloromethane from PS-Air cartridge. After these pre-treatments of samples, MIPN, DIPN and TIPN were analyzed by GC/MS using a Agilent6890N/JMS-Q1000GC equipped with SPELCOWAX-10 capillary column(30m, 0.32mm i.d., 0.25 μ m film sickness). The m/z for quantification of MIPN, DIPN and TIPN were 170, 212 and 254, respectively.

Results and Discussion

The chromatogram of the MIPN, DIPN and TIPN standard which were the stock solutions for industries was shown in Fig.2. The amount of 2ng of MIPN, DIPN and TIPN were injected to GC/MS, respectively. Their isomers were separated very well by using polar column. 1-MIPN and 2-MIPN were assigned according to the reference to Dr.Brozozouski³. The major eight isomer peaks of DIPN were assigned by the individual isomer stock solutions of DIPN provided by Dr.Brozozouski. The six isomer peaks of TIPN were detected though they were not assigned.

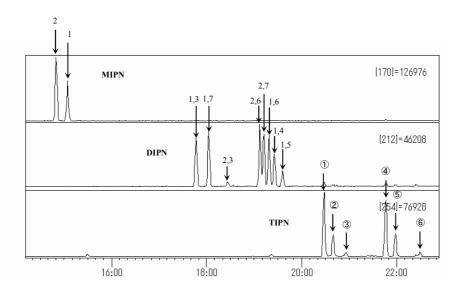


Fig.2 The chromatogram of MIPN, DIPN and TIPN standard. The amount of 2ng of MIPN, DIPN and TIPN were injected to GC/MS.

The concentrations of MIPN, DIPN and TIPN in the environmental samples are summarized in Fig.3. MIPN was not detected from all samples. DIPN was detected from all samples. TIPN was detected some sediments and algae.

The concentration of DIPN in the river water, the sediment and the algae increased at the point E and decreased gradually in the downstream direction. Because the water samples have been sampled by waterway too, it could be known that the concentration of DIPN was diluted with water from the water D'. The water D' was most influenced by the wastewater from the paper recycling plant. DIPN in the newspaper was detected with the order of magnitude of 100ng/g. DIPN in the air C was detected about ten times concentration as high as the roof of the institute. In the sediment A, DIPN and TIPN were detected with the order of magnitude of 1ng/g and 100ng/g, respectively although the sediment A was not influenced by the wastewater from the paper recycling plant. Off the coast of Himeji, DIPN was detected at trace level (0.8ng/L) from the sea water and the order of magnitude of 1ng/g from the sea bass. The concentration level of DIPN in the sea bass was the same as the national investigation in 1980.

The fingerprints of MIPN, DIPN and TIPN isomers detected from the samples were almost same as the standard. However the fingerprints of DIPN detected from the sediment A and the sea bass were different from others. The fingerprints of DIPN isomers in some samples were shown in Fig.4. 1, 3-DIPN and 1, 7-DIPN in the sediment A were relatively smaller than others. 1, 7-, 2, 6- and 2, 7-DIPN in the sea bass were relatively smaller than others.

It was found that the wastewater and the exhaust from the paper recycling plant were one of loading sources of DIPN. It was considered that there was another pollution resource of DIPN and TIPN in the Ibo River because high concentration of TIPN and the unusual fingerprint of DIPN isomers were detected from the sediment which was not influenced by the wastewater from the recycled paper factory. And it was considered that DIPN in sea bass was metabolized and the rates of decomposition were different by isomers.

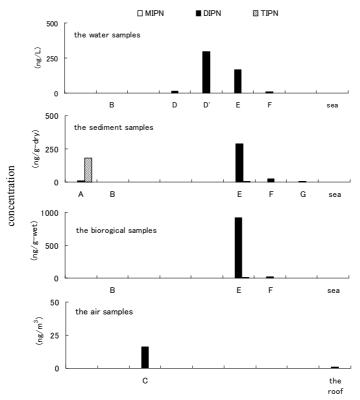


Fig.3 The concentrations of IPNs in samples. X axis indicates sampling point.

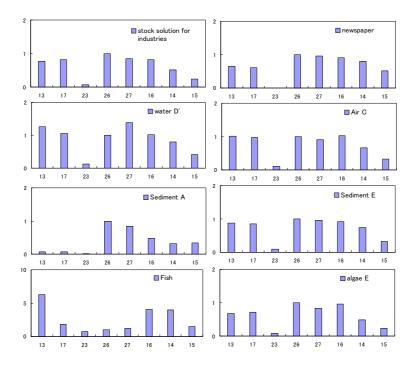


Fig.4 The fingerprints of DIPN isomers in samples. Y axis indicates a ratio to 26-DIPN. X axis indicates DIPN isomer.

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References

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