

ENVIRONMENTAL LEVELS II --POSTER

BEHAVIOR OF NONYLPHENOL IN WATER ENVIRONMENTS IN THE SETO INLAND SEA, JAPAN

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Introduction

Alkylphenols have been used as a raw material of non-ionic surfactants throughout the world, and these substances exist most widely in water environments. In the present study, nonylphenol (NP) is known as an endocrine disruptor¹. Sediments and water were collected from Harimanada, which is located in the Seto Inland Sea, Japan to determine for the NP. Gas chromatography/mass spectrometric detection was used for the NP determination. The relation between NP in the sediments and the status of the sediments were explored. In addition, the distribution of NP in water environments of Harimanada was exhibited.

Method and Materials

Materials and reagents The acetone, n-hexane, dichloromethane, methanol, ethanol, sodium chloride, potassium hydroxide, diethyl ether, diethyl sulfate, sodium sulfate, methyl acetate and ethanol suitable for pesticide residue · PCB. Sep-Pack PS-2 (Waters Co.) was use to concentrate water samples. Sep-Pak florisil (Waters Co.) was used to clean the samples. P-nonylphenol as a standard solution and phenanthren-d10 as surrogate substance were used.

Sampling Sediment from the bottom of the sea was collected in April, 2000 from eight different areas around Harimanada, which is located in the Seto Inland Sea in Japan.(Fig.1) The outer layers of the sediment were carried out around Harimanada in glass. The Samples for nonylphenol were stored frozen at -20 °C in the freezer. The outer layers of sediments from eight areas in Harimanada were collected and prepared the three samples each 10g on each area. These samples were dissolved with methanol and added to 1.0 ml of conc. HCl and 1 g of ascorbic acid. The samples were added to hexane to remove the lipids and to reextract the dichloromethane and were concentrated to approximately 0.1 ml.

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Derivatization The samples added with 1mol/L-KOH/ethanol solution (0.5mL) and diethyl sulfate (0.2mL) were stabilized for 30minutes. Next, the samples with about 4mL 1mol/L-KOH/ethanol solution were held in 60°C water bath for 60minutes and extracted by 1mL hexane containing 0.05ml internal standard to monitor fluctuations and correct the data accordingly. After the separation, the organic phases were corrected and cleaned up by Sep-Pak florisil with 10mL of 4%ether/hexane. The samples were concentrated to 0.5mL, except where high concentrations of NP were encountered before the gas chromatographic determination.

NP determination The final extracts were analyzed by gas chromatography/mass spectrometry (GC/MS). The analysis was performed on a Finnigan GCQ equipped with an Xcalibur data system on a Gateway computer. The samples (2 µL) were injected splitless at 300°C. The column was an Rtx-5MS (30m, 0.25mm i.d.). Helium was used as the carrier gas (30cm/min). The temperature program was 60°C (1min) – 10°C /min – 300°C (10min). Mass spectrometric detection carried out by electron impact (EI) ionization on full scan mode ($m/z=50-650$) to monitor the ions. Nonylphenol is known to have the following fragment ions ($m/z=107,121,135,150,177$ and 220) and the molecule peak of phenanthrene-d10 is $m/z=188$. (Fig.2) Therefore, these fragment-ions were monitored from the data measured on the full scan mode. Quantitative analysis of NP was based on five points in the curves of response (peak area) for known amount of compound, in the 0.1µg~0.5 µg range. For water, the detection limits were in the 0.16µg/L range depending on the individual 4-NP oligomers used for the selected ion mode acquisition. The final real concentrations measured for the procedural blank were corrected by using the average concentration measured for the procedural blanks and the recovery achieved from the spiked samples of all oligomers; recoveries of 90%-100% were obtained.

Measurement of the specific surface areas of the sediments The sediments collected from Harimanada in the Seto inland sea were cleaned with methanol. The sediments were dried in vacuumed desicator. The specific surface areas(SA) in the sediments were measured by Omunisorp100. These specific surface areas were determined by the adsorption method. To obtain monolayer capacity and cross-sectional area of the adsorbate molecules were used under N₂ gas. The specific surface areas of sediments were calculated by the BET equation². The detection limit was about 0.20 m²/g used by N₂ gas.

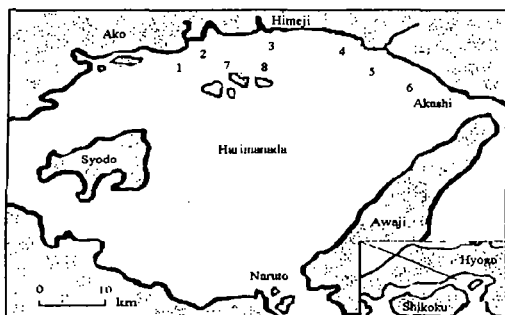


Fig.1 Sampling points(1~8) in Harimanada

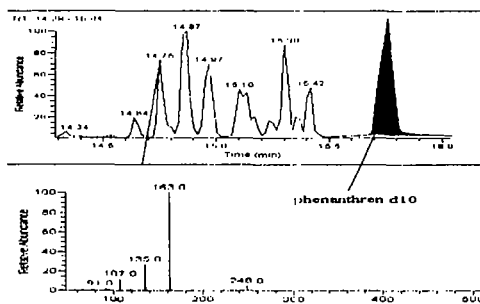


Fig.2 Chromatograms and Spectra of NP in sediment

Result and Discussion

The weights of the sediments were determined and the amount of NP per gram calculated. NP is a hydrophobic substance and most of NP does not exist as a dissolved substance in a water environment. It was thought that most of the NP existed as an adsorptive substance on the specific surface of the sediment. Therefore, to examine the relation between the specific surface area of the sediment and the NP concentration, the specific surface areas of these sediments were examined. The results obtained indicate that the amount of specific surface area has a strong influence on the concentrations of NP. It was found that the sediments had large amount of specific surface areas and thus contained a high concentration. The amount in NP was in area 29; 0.06 $\mu\text{g/g}$, SA(Non Detection), and the 4, 5, 6, and 8 were very little amount detection(0.06~0.14 $\mu\text{g/g}$). The amount in areas 1,2,3 and 7 were 0.21 $\mu\text{g/g}$, SA(18.33 m^2/g), 0.50 $\mu\text{g/g}$, SA(16.07 m^2/g), 0.28 $\mu\text{g/g}$ SA(13.94 m^2/g) and 0.38 $\mu\text{g/g}$, SA(16.67 m^2/g), respectively. About the problem of the concentration of sediment in water environment, while very small amounts of NP were detected in areas 4,5,6, and 8 in Harimanada, it was found that the specific surface areas in these areas were smaller than those of the sediments from areas 1,2,3 and 7. Accordingly, the highest concentrations of NP were detected in areas 1, 2, 3 and 7. It appears that the amount of NP did not depend on the amount of sediment but rather the specific surface area of sediments (Fig.3-4). It is also important to consider that NP is a hydrophobic substance and that most NP does not exist as a dissolved substance in water environments. When the NP per each specific surface area of the samples was calculated. It was found that the amount of NP in area 2 was three times higher than that in area 1 and that the values in other samples were nearly equal value except for sample 6. Our results indicate that, in the seas of the Himeji areas, the pollution levels are high in areas of high population, where as they are small in low-population areas.

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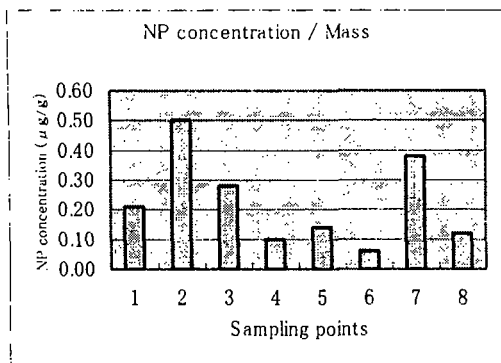


Fig.3 NP concentration in sediments in Harimanada

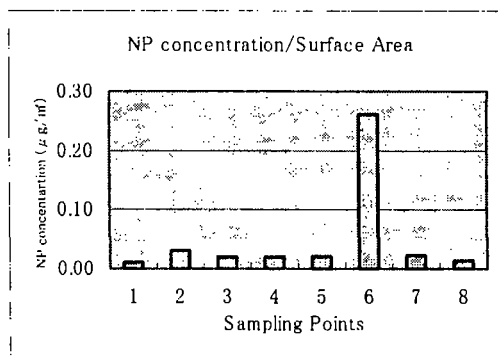


Fig.4 The relation between NP and specific surface area in Sediments (No.6 is reference value)

References

1. Tom, T., Greet, D., and Willy V.,(1999) Nonylphenol and Estrogenic Activity in Aquatic Environmental Samples, Published in J. Environ. Qual. 28, 702-709
2. K, Gotoh., H, Masuda., and K, Higashitani., (1997) Powder Technology Handbook, MARCELL DEKKER, INC, USA. 337-349