FATE OF ENDOCRINE DISRUPTORS CONTAINED IN COMPOSTED SLUDGE AFTER LAND APPLICATION

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ABSTRACT

Many environmental problems caused by endocrine disruptors (EDs) are reported. Little is known about the fate of EDs accumulated in sewage sludge, and we carried out research to make clear the fate of EDs in composted sludge after it is applied to soil. Nonylphenol (NP) and 17β-estradiol (E2) were measured for leachate and soil. High concentrations of NP and E2 were detected in the leachate at the early stage, but they decreased rapidly. Also, high amount of NP and E2 contents in soil decreased significantly. Because the amount of the decrease of NP and E2 in the soil was much larger than the amount of NP and E2 in the leachate, there must be physicochemical or biological decomposition mechanism in the soil layer.

KEYWORDS

Endocrine Disruptors, Composted Sewage Sludge, Lysimeter.

INTRODUCTION

In recent years, there have been many reports on environmental problems caused by endocrine disruptors (EDs) discharged as trace-chemicals in many countries and regions. The Japanese Ministry of Construction carried out a national survey on the EDs pollution of river waters and treated wastewater in FY1998 (MOC, 1999). Some trace-chemicals suspected to be EDs were detected at almost all surveyed points showing relatively higher concentration in treated wastewater. A further survey was carried out by the Ministry of Land, Infrastructure and Transport in FY 2000 showed that removal ratios of these EDs in wastewater treatment process were 70 - 99 % (MLIT, 2001). On the other hand, little was known about the fate of EDs in the sludge treatment process and the fate of EDs accumulated in sewage sludge when the sludge is used for agriculture. Therefore, research and investigation were needed to reveal the fate of EDs and to study countermeasures against EDs in the sewerage system.

METHODS

To make clear the fate of EDs in composted sludge after it is applied to soil, lysimeter method was used. Four lysimeters made of stainless steel were set outside (Photo 1). The schematic diagram of a lysimeter is shown in Figure 1. These lysimeters differed in soil layer conditions such as addition of sewage sludge compost or chemicals (Table 1). Nonylphenol (NP) and 17β-estradiol (E2) were selected as additive chemicals because these

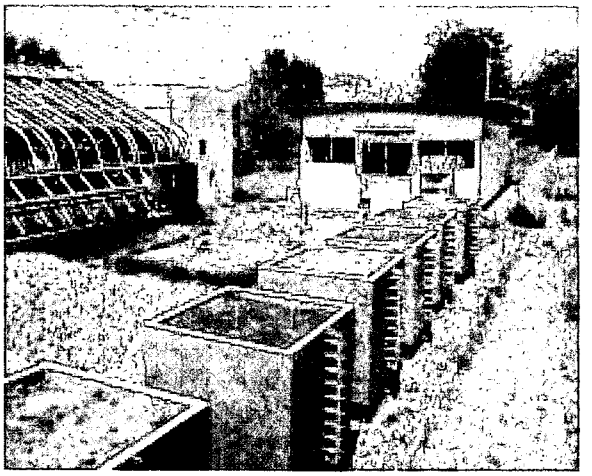


Photo 1 Lysimeters for This Experiment

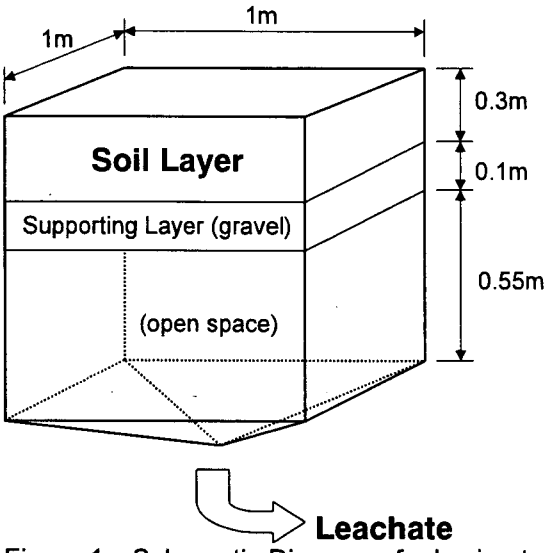


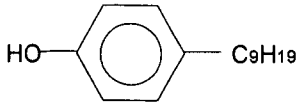
Figure 1 Schematic Diagram of a Lysimeter

Table 1 Experimental Condition of Soil Layer in Each Lysimeter

	Condition of Soil Layer	Legend for Fig.4,5,6
Case 1	Soil (control)	■
Case 2	Soil + Chemicals(NP, E2)	◆
Case 3	Soil + Compost	□
Case 4	Soil + Compost + Chemicals(NP, E2)	◇

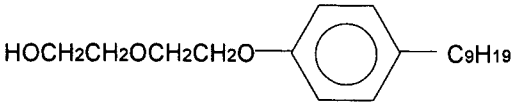
Added chemicals: NP=500mg/lysimeter, E2=17mg/lysimeter

An example of Nonylphenols (NP)



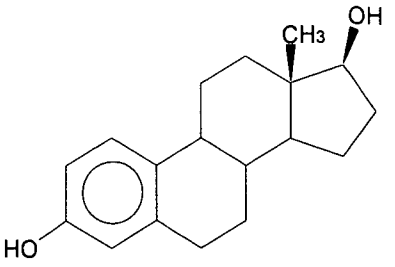
4-nonylphenol

An example of Nonylphenol-poly-ethoxylates (NPnEO)

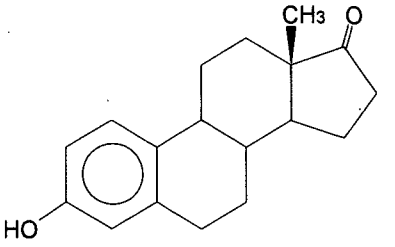


4-nonylphenol-di-ethoxylate

Figure 2 Examples of Nonylphenols



17ß-estradiol (E2)



Estrone (E1)

Figure 3 Examples of Estrogens

trace-compounds were detected in higher amounts at many surveyed points during the national survey.
Figure 2 shows examples of structural formula of NP, which is a chemical that is strongly suspected as EDs. NP is also known as an end product of degradation of nonylphenol polyethoxylates (NPnEO) (Giger *et al.*, 1984) that have been widely used as a detergent. Figure 3 shows structural formula of E2, which is one of human female estrogens.

Samples were taken from leachate and soil for two year and eight months, and NP and E2 were measured. The JSWA analytical methods for wastewater and sewage sludge (JSWA, 2001) were applied, in which NP in soil was extracted with a reflux method and detected with GC/MS, on the other hand, E2 was extracted with an ultrasonic extraction method and detected with enzyme linked immunosorbent assay (ELISA).
According to recent studies, analytical methods used in this experiment have some problems. For example, ELISA must be applied to limited cases, because it reacts with other substances such as estrone (E1) (Komori *et al.*, 2003). When amounts of estrogens in sewage sludge compost were measured using LC/MS/MS, E2 was not detected but E1 was detected from the compost sample. However, because of continuousness of analyzed data, the values obtained using ELISA were treated as amounts of E2.

RESULTS AND DISCUSSION

The total amount of leachate during the experiment was 6.3 - 8.2 times of the soil layer volume.

Figure 4 shows the concentration of total organic carbons (TOC). The concentration of TOC was high until about 100 days. At that time, the total amounts of leachate were approximately 100L.

High concentrations of NP and E2 were detected in the leachate at the early stage of the experiment, and they decreased rapidly along time (Figure 5). These trends were similar to that of TOC in the leachate. The maximum concentration of NP (2.7 µg/L) obtained in this

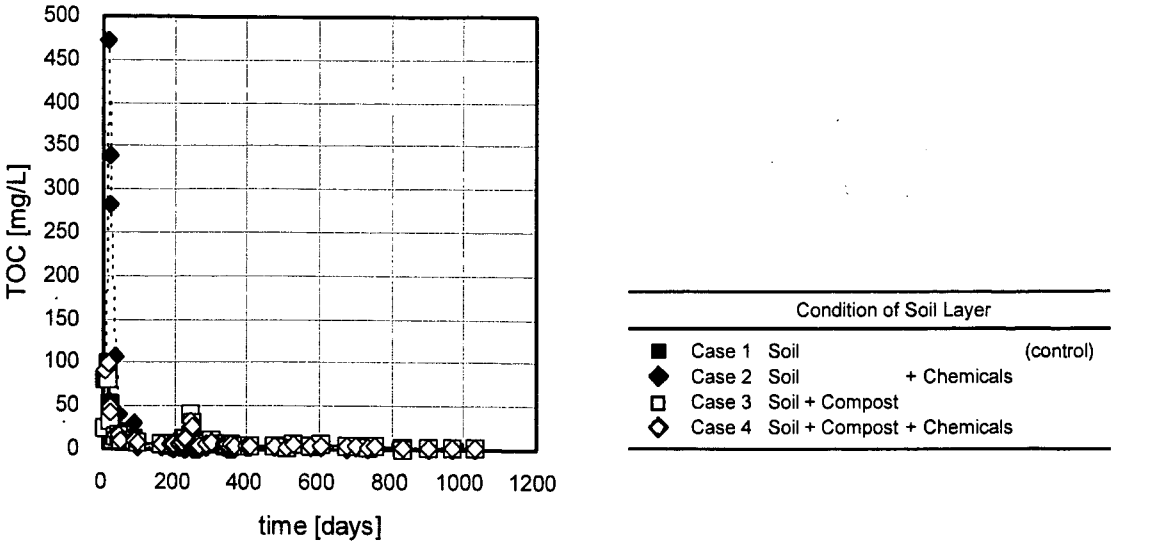


Figure 4 TOC in the Leachate from Lysimeter

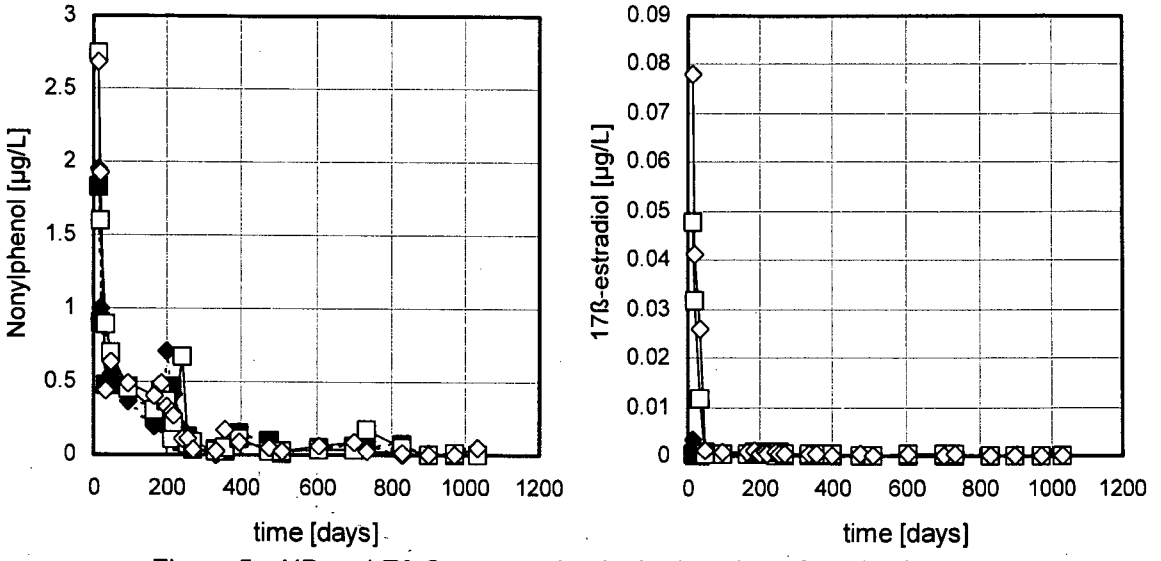


Figure 5 NP and E2 Concentration in the Leachate from Lysimeter

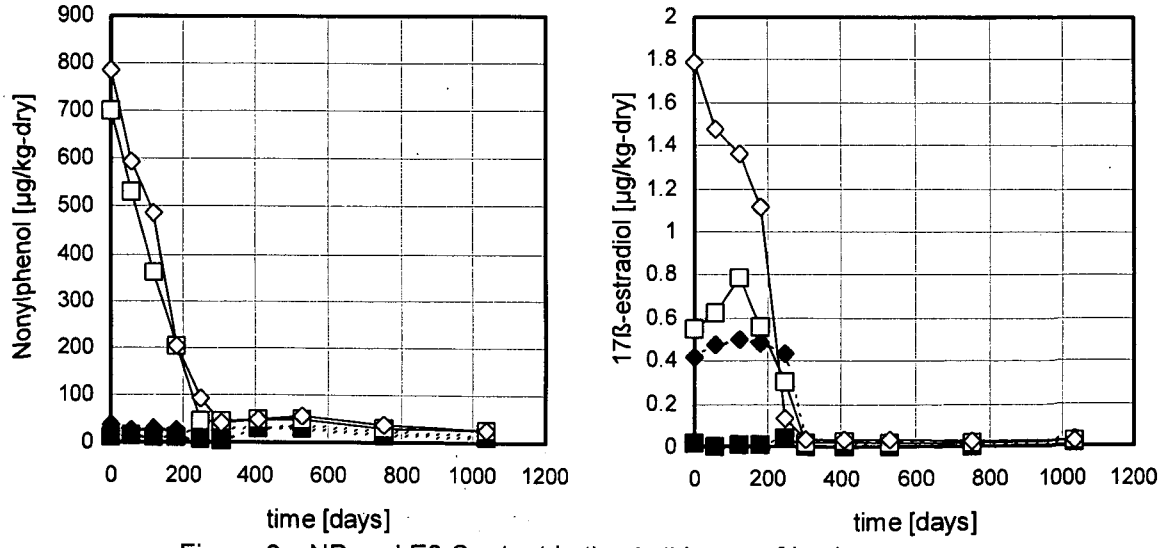


Figure 6 NP and E2 Content in the Soil Layer of Lysimeter

experiment was slightly lower than the proposed water quality criteria of NP for aquatic life (5.9 μg/L for freshwater organisms) that was based on acute and chronic toxicity of NP (U.S.EPA, 2003).
The concentrations of E2 in Cases 3 and 4 with compost was extremely (over 20 times) higher than those in Cases 1 and 2 without compost at the early stage of the experiment. On the other hand, the concentrations of NP in Cases 3 and 4 with compost was only 1.4 - 1.9 times of those in Cases 1 and 2 without compost.
The total amount of NP and E2 which leaked out during the experiment of Cases 3 and 4 were 0.34 - 0.69% and 1.6 - 5.3% of the initial content in the soil layer, respectively. Very small amount of NP and E2 leaked out from the soil layers with showing a lower leakage ratio for NP.

The NP and E2 contents in the soil layer of each lysimeter are shown in Figure 6. High amount of contents were observed in the cases with compost, but they decreased significantly to the almost same level as those of the control after 300 days.

Because the amount of the decrease of NP and E2 in the soil layer was much larger than the amount of NP and E2 that leaked out with rainfall, there must be physicochemical or biological decomposition mechanism in the soil layer.

CONCLUSIONS

To make clear the fate of EDs in composted sludge after it is applied to soil, lysimeter experiment was carried out. By the two year and eight month experiment, it was revealed that very small amount of NP and E2 leaked out from the soil layers and there must be physicochemical or biological decomposition mechanism in the soil layer.

In order to further clarify of the fate of EDs in the sludge treatment process and in the soil with sewage sludge compost, it is necessary to understand the material balance including EDs' relating substances such as NPnEO, nonylphenol carboxylic acids (NPnEC), and E1. However, there is still much to be investigated in relation to analysis of EDs and its relating substances in the sewage sludge samples such as low and unstable extraction efficiency from sludge samples and extremely high amount of other organic substances. Appropriate analysis methods for sewage sludge sample need to be established and further investigation is required to reveal the fate of EDs and to study countermeasures to deal with EDs in the sludge treatment process.

REFERENCES

Giger W., Brunner P.H., and Schaffner C. (1984). 4-Nonylphenol in Sewage Sludge: Accumulation of Toxic Metabolites from Nonionic Surfactants. *Science*, **225**, pp.623-625.

Japan Sewage Works Association, JSWA (2001). *Manual of Water Quality Analysis for Endocrine Disrupting Chemicals on Sewerage System*, Japan Sewage Works Association (*in Japanese*).

Komori K, Tanaka H., Okayasu Y., Yasojima M., and Sato C. (2003). Analysis and Occurrence of Estrogen in Wastewater in Japan. *Proceedings of the 4th IWA Specialized Conference on Assessment and Control of Hazardous Substances in Water - ECOHAZARD 2003-*, pp.45/1-45/8.

Ministry of Construction, MOC (1999). *FY1998 Interim Report on Countermeasures for Endocrine Disruptors in Sewage System*, Ministry of Construction (*in Japanese*).

Ministry of Land, Infrastructure and Transport, MLIT (2001). *FY2000 Final Report on Countermeasures for Endocrine Disruptors in Sewage System*, Ministry of Land, Infrastructure and Transport (*in Japanese*).

United States Environmental Protection Agency, U.S.EPA (2003). *Ambient Aquatic Life Water Quality Criteria for Nonylphenol - Draft*, p.17, United States Environmental Protection Agency.