Distribution of estrogen, nonylphenol and its derivatives in the sediments of a shallow lake

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Abstract To determine the distribution of endocrine disruptors (EDs) in lake water and sediments, field investigation was conducted in Lake Teganuma, which is a shallow eutrophic lake, highly affected by human activities. Concentration profiles with sediment depths were obtained for estrogens, nonylphenol (NP), nonylphenol ethoxylates (NP*n*EO), and nonylphenoxy acetic acids (NPnEC). 17β-Estradiol (E2) was rarely detected, and 17α-ethynylestradiol (EE2) and estriol (E3) were undetected at all depths (0–98 cm) in any of the sediment core samples. The sediment concentrations of estrone (E1) ranging from <0.05 to 3.5 μg/kg-dry wt. and NP from 11.8 μg/kg-dry wt. to 21 mg/kg-dry wt. were obtained. The maximum concentrations of NP*n*EO and NP*n*EC in the core sediments were 2.5 mg/kg-dry wt. and 1.4 mg/kg-dry wt., respectively. The EDs concentrations are higher at the inlet than at the outlet (except for NP) in the sediments near the surface. The longitudinal distributions of E1, NP*n*EO and NP*n*EC in the benthic sediments show that the concentrations are highest at the inlet, and are fairly constant at lower levels towards the downstream. The obtained results also indicate that NP tends to be adsorbed to the organic particulates produced by algae, followed by sedimentation near the outlet of the lake.

Keywords Endocrine disruptors; estrone; nonylphenol; particulate phase; sediment

Introduction

Nonylphenol ethoxylates (NP*n*EO) are nonionic surfactants, widely used in industrial and domestic applications. In Japan, alkylphenol polyethoxylates have been used since the 1950s (Okuda *et al*., 2000), and their production in 1998 was approximately 50 thousand tons. In a sewage treatment plant, NP*n*EO can be degraded biologically to nonylphenol (NP) (Giger *et al*., 1984); thus, NP*n*EO is a precursor of NP. The high levels of NP in sediments and historical sediment profiles in relationship to the production of NP*n*EO were reported (Khim *et al*., 1999; Okuda *et al*., 2000; Yamashita *et al*., 2000; Isobe *et al*., 2001). NP was recently reported to cause endocrine disruption in aquatic wildlife (White *et al*., 1994), in addition to its inherent toxicity and persistency in the environment. This emphasizes the importance of understanding its effects, fate, and transport in the aquatic environment.

In addition to the man-made EDs, natural hormones are also of concern. Purdom *et al*. (1994) reported that sewage treatment plant (STP) effluent was estrogenic to fish. The estrogenic chemicals including 17β-estradiol (E2), estrone (E1), and 17α-ethynylestradiol (EE2), were isolated from domestic sewage, and identified by a fractionation system combined with an in vitro assay technique in detecting estrogenic activity (Desbrow *et al*., 1998).

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The field investigation was conducted in Lake Teganuma, a shallow eutrophic lake, in Japan. Lake Teganuma has been highly affected by man's activities. Li *et al.* (2003) attempted to relate the sediment E1 near the outlet of the lake to the historical changes in waste loadings and sewerage population in the watershed. The objectives of this study are to determine: 1) longitudinal distributions of estrogens [E1, E2, estriol (E3) and EE2], NP and its derivatives [i.e., NP*n*EO and nonylphenoxy acetic acids (NP*n*EC)] in water and benthic sediments along the flow path of the lake; and 2) vertical distributions of the respective compounds in sediments near the inlet and outlet of the lake.

Methods

Study sites and sampling

Lake Teganuma was selected as a typical urban lake, which is one of the most polluted lakes in Japan. The lake is located in the east of Tokyo. Locations of sampling stations are shown in Figure 1. The area of the lake is 6.5 km^2, its average depth is 0.86 m, and its perimeter is approximately 38 km. The watershed area of the lake is 160 km^2, and the population within the watershed is approximately 500,000. Eutrophication was not evidenced in Lake Teganuma until the 1960s. The rapid deterioration of the lake water due to the urbanization of the lake basin became evident in the 1970s. Recently, the water quality of the lake has shown some improvement due to the development of sewerage systems and the introduction of cleaner water from an adjacent river basin.

Sampling efforts were made in June 2002 and March 2003. Sediment core (98 cm in depth) samples and benthic (10 cm in depth) sediment samples were collected by a diver using acrylic tubes (10 cm × 100 cm length) under minimal disturbance. Lake water and benthic sediment samples were collected along the flow path from the mouth of the Ootsu River (one of the inlets of the lake) to the headwater of the Tega River (the outlet of the lake).

Preparation of sediment core samples and analysis

Each sediment core sample (87 cm in depth) was divided into layers of 1 cm in depth. All 1 cm layers from the surface to a depth of 50 cm were analyzed separately. The 1 cm layers from the depths of 50 to 87 cm were analyzed every 10 cm in depth.

The 1 cm thick sediment samples were analyzed for estrogens (E1, E2, E3 and EE2), NP, NP*n*EO, NP*n*EC, and conventional parameters (TOC, total nitrogen, total phosphorus, total sulfur, sediment water content, bulk density, ignition loss). NP was analyzed by GC/MS (JEA, 1998), NP*n*EO was measured by GC/MS (JSWA, 2001), and NP*n*EC was determined by GC/MS (Komori *et al.*, 2001b). E1, E2, E3, and EE2 were measured using LC/MS/MS (Komori *et al.*, 2001a). The river water samples were analyzed for estrogens (E1, E2, E3 and EE2), NP, NP*n*EO, NP*n*EC, and traditional water quality parameters. E1, E2, E3 and EE2 were analyzed using the LC/MS/MS method described by Komori *et al.*

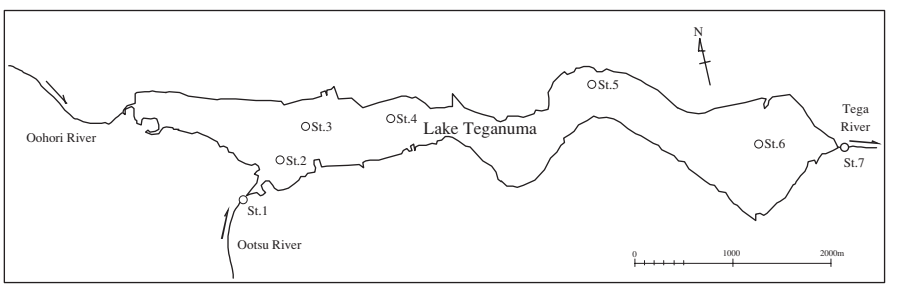

Figure 1 Location of sampling stations in Lake Teganuma, Japan

(2002). NP and NP*n*EO in water samples were analyzed by HPLC (JSWA, 2002). NP*n*EC was measured using the LC/MS/MS method (Yasojima *et al*., 2002).

Results and discussion

Longitudinal distributions of estrogens, NP and its derivatives in water and surface sediments

The water column and surface sediment samples collected were analyzed for estrogens, NP and its derivatives (NP*n*EO and NP*n*EC), and results are shown in Figure 2. The graphs on the left-hand side present the results of the water column analysis for E1, NP, NP*n*EO (n = 1–4), NP*n*EO (n = 5–15), and NPnEC (n = 1–3), while the graphs on the right-hand side present the results of the sediment analysis for the respective compounds. E2, EE2, and E3 were either rarely detected or not detected at all in the water column and surface sediments at the selected sampling sites. Note that the concentrations of these compounds adsorbed on particulates are presented based on 1 litre of water sample (μg/L); thus, summation of the dissolved concentration (μg/L) and particulate concentration (μg/L) gives total concentration in a water column (μg/L). From Figure 2, it can be seen in the water column that: 1) the dissolved fraction of E1 accounts for nearly the total amount of E1 detected; and 2) larger fractions of NP and its derivatives are in a dissolved form. The sediment concentrations of E1, NP*n*EO, and NP*n*EC are highest at St.2 (except for the concentrations at St.1 at the discharge point of the Ootsu River). The NP concentration in the sediment becomes higher at

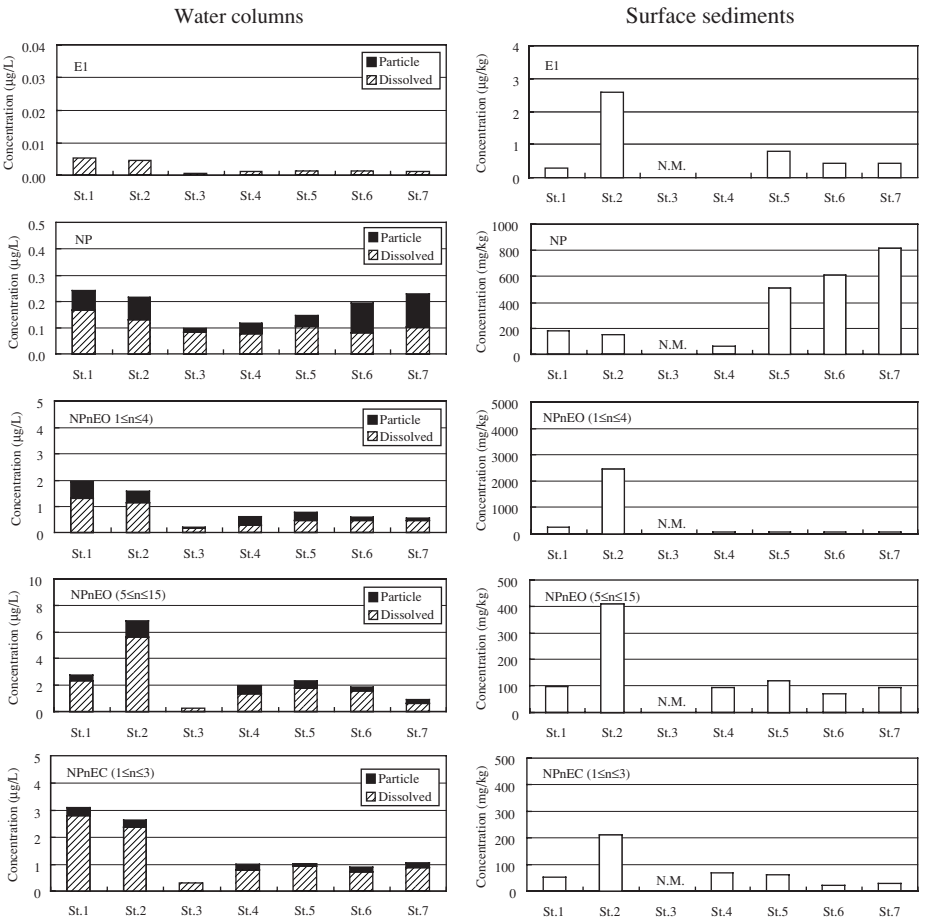

Figure 2 Concentrations of E1, NP, NP*n*EO, and NP*n*EC in the longitudinal direction of the flow path. N.M. = not measured

the sampling locations near to the outlet of the lake. The computed concentration ratios of E1, NP and its derivatives in sediments to those in water are large, suggesting that these compounds are adsorbed by suspended particles followed by settling and sedimentation.

Figure 3 shows the concentrations of VSS and chlorophyll *a* in the water along the flow path. As seen, both VSS and chlorophyll *a* (i.e., algae) increase towards the outlet of the lake.

The results suggest the formation scenario of the distributions of E1, NP and its derivatives, as shown in Figure 4. The scenario is as follows.

1. In wet weather, large amounts of SS are delivered into the lake by flushing out from the watershed. Velocity of flow slows down and the flux of SS into sediments becomes higher at the mouth of the lake. E1, NP and its derivatives, adsorbed by the particulates, settle down into sediment near the inlet of the lake, as shown in Figure 4A.
2. In dry weather, much nitrogen and phosphorus are delivered into the lake continuously. Algal growth is gradually accelerated in a water column toward the downstream. NP remaining in the water column tends to be adsorbed on organic particulates produced by algae. The SS flux into the sediments becomes higher toward the downstream. Finally these particles tend to settle in the water column to become organic sediments, and the NP concentration in the sediments becomes higher toward the outlet of the lake, as shown in Figure 4B.

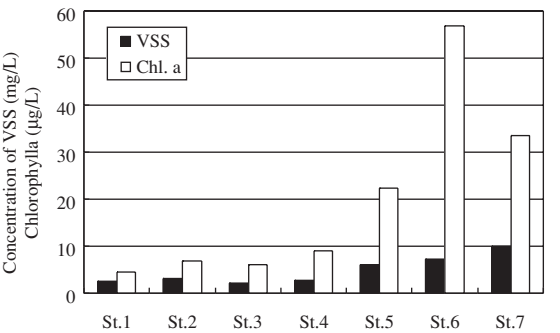

Figure 3 Concentrations of VSS and chlorophyll *a* in the longitudinal direction of the flow path

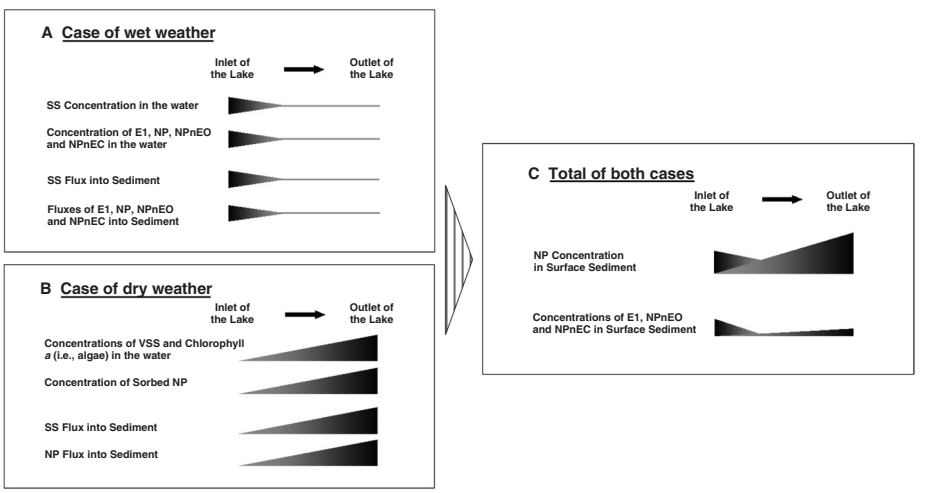

Figure 4 Formation scenario of the distributions of E1, NP, NP*n*EO and NP*n*EC

3. Combining both of the above cases, longitudinal distributions of E1, NP, NP*n*EO and NP*n*EC in surface sediments are formed, as shown in Figure 4C. It seems that the differences between the distribution of NP and those of the other selected chemicals are made by the differences in their hydrophobicity.

Takahashi *et al*. (2002) reported that NP and estrogens in water tend to be highly accumulated in periphytons. Although their data support our scenario for NP, they do not always support the scenario for estrogens. A further investigation is needed to understand their fate and transport mechanisms, including discrete mechanisms such as rainstorm events, to identify their sources, and to evaluate current remediation efforts.

Vertical distributions of estrogens, NP and its derivatives in the sediments

Figure 5 shows the concentrations of estrogens at various depths of the sediment core samples.

Near the mouth of the Ootsu River (at St.2), there exist three prominent peaks of E1 at depths of 55 cm, 27 cm, and the surface sediments. Near the outlet of the lake (at St.6), only one prominent peak of E1 is present at a depth of 20 cm. The presence of E1 in the deep sediments suggests that E1 is likely refractory in deposited sediments. Except for the sediment depths of ~20 cm, the concentrations of E1 are consistently higher at St.2 than at St.6. The highest sediment concentrations of E1 at St.2 and St.6 are 3.5 and 1.8 μg/kg-dry wt., respectively. These concentrations are an order of magnitude lower than the levels observed in Tokyo Bay (Nakada *et al*., 2001).

EE2 and E3 were not detected and E2 was rarely detected from any of the sediment samples. These results are different from Nakada *et al*. (2001) who reported the existence of E2 at depths of approximately 10 to 80 cm.

Figure 6 shows the concentrations of NP and its derivatives (NP*n*EO and NP*n*EC) at various depths of the sediment core samples.

We observed NP at levels ranging from 11.8 μg/kg-dry wt. to 21 mg/kg-dry wt. In the sediment samples at depths deeper than 20 cm, the NP concentrations at St.2 are higher than those at St.6. However, at depths less than 20 cm, the concentrations are reversed (i.e., the NP concentration is higher at St.6). The maximum concentrations of NP*n*EO and NP*n*EC in the core sediments are 2.5 mg/kg-dry wt. and 1.4 mg/kg-dry wt., respectively. The

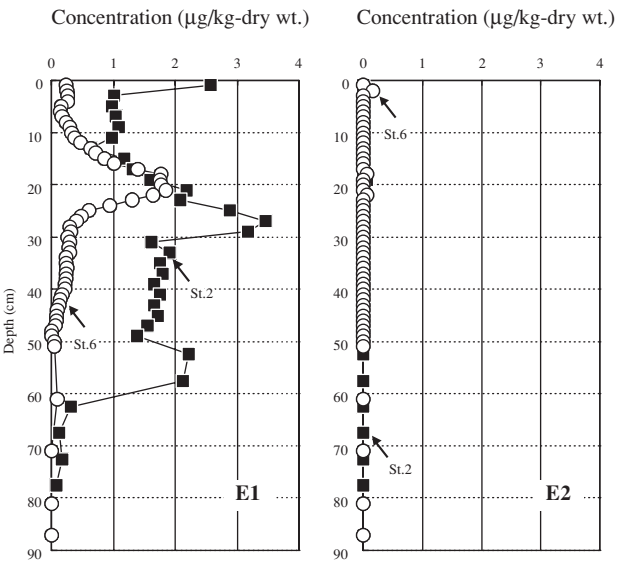

Figure 5 Vertical concentration profiles for E1 and E2 in sediments of Lake Teganuma

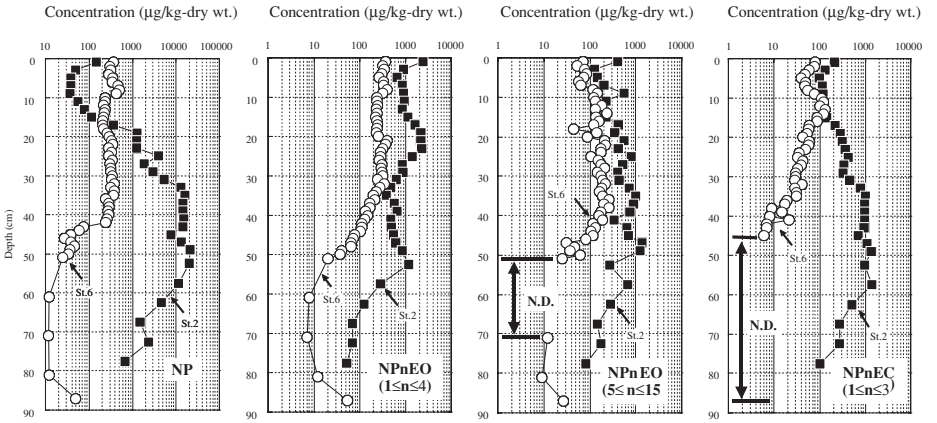

Figure 6 Vertical concentration profiles for NP, NP*n*EO and NP*n*EC in sediments of Lake Teganuma

concentrations of NP*n*EO and NP*n*EC are consistently higher throughout the sediment depths at St.2 than at St.6. Further, the ratio of NP to its derivatives varies with the depths at St.2; that is, the ratio of NP to its derivatives is smaller in the upper sediments, and larger in the deeper sediments.

Conclusions

We investigated the distribution of estrogens (E1, E2, E3 and EE2), NP and its derivatives (NP*n*EO and NP*n*EC) in water columns, benthic (10 cm in depth) sediments, and deep (98 cm in depth) sediments in Lake Teganuma. The results obtained suggest the following.

1. The concentrations of the target EDs in the deep sediments are higher near the mouth of the Ootsu River (i.e., the inlet of the lake) than at its outlet (except for NP in sediments near the surface).
2. The concentrations of E1, NP*n*EO, and NP*n*EC in benthic sediments are highest at the inlet, and relatively constant at lower levels toward the downstream.
3. The sediment NP level tends to decrease in the middle of the lake, and then increases towards the outlet of the lake, indicating that NP tends to be adsorbed by organic particles produced by algae, followed by sedimentation near the outlet of the lake.

More studies should be undertaken to clarify the EDs' fate and transport mechanisms (e.g., rain storm events), identify their sources, and evaluate current remediation efforts.

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