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## Contamination of nonylphenolic compounds in creek water, wastewater treatment plant effluents, and sediments from Lake Shihwa and vicinity, Korea: Comparison with fecal pollution

Minkyu Choi<sup>a,\*</sup>, Edward T. Furlong<sup>b</sup>, Hyo-Bang Moon<sup>c</sup>, Jun Yu<sup>d</sup>, Hee-Gu Choi<sup>a</sup>

<sup>a</sup> Marine Environment Research Division, National Fisheries Research and Development Institute (NFRDI), 152-1, Haeanro, Gijang-eup, Gijang-gun, Busan 619-705, Republic of Korea

<sup>b</sup> National Water Quality Laboratory, U.S. Geological Survey, Denver Federal Center, P.O. Box 255857, Building 95, Denver, CO 80225-0046, United States

<sup>c</sup> Department of Environmental Marine Sciences, College of Science and Technology, Hanyang University, Ansan 426-791, Republic of Korea

<sup>d</sup> Marine Environment Impact Assessment Center, NFRDI, 152-1, Haeanro, Gijang-eup, Gijang-gun, Busan 619-705, Republic of Korea

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### ABSTRACT

Nonylphenolic compounds (NPs), coprostanol (COP), and cholestanol, major contaminants in industrial and domestic wastewaters, were analyzed in creek water, wastewater treatment plant (WWTP) effluent, and sediment samples from artificial Lake Shihwa and its vicinity, one of the most industrialized regions in Korea. We also determined mass discharge of NPs and COP, a fecal sterol, into the lake, to understand the linkage between discharge and sediment contamination. Total NP (the sum of nonylphenol, and nonylphenol mono- and di-ethoxylates) were 0.32–875  $\mu\text{g L}^{-1}$  in creeks, 0.61–87.0  $\mu\text{g L}^{-1}$  in WWTP effluents, and 29.3–230  $\mu\text{g g}^{-1}$  TOC in sediments. Concentrations of COP were 0.09–19.0  $\mu\text{g L}^{-1}$  in creeks, 0.11–44.0  $\mu\text{g L}^{-1}$  in WWTP effluents, and 2.51–438  $\mu\text{g g}^{-1}$  TOC in sediments. The spatial distributions of NPs in creeks and sediments from the inshore region were different from those of COP, suggesting that Lake Shihwa contamination patterns from industrial effluents differ from those of domestic effluents. The mass discharge from the combined outfall of the WWTPs, located in the offshore region, was 2.27  $\text{kg d}^{-1}$  for NPs and 1.00  $\text{kg d}^{-1}$  for COP, accounting for 91% and 95% of the total discharge into Lake Shihwa, respectively. The highest concentrations of NPs and COP in sediments were found in samples at sites near the submarine outfall of the WWTPs, indicating that the submarine outfall is an important point source of wastewater pollution in Lake Shihwa.

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### 1. Introduction

Lake Shihwa, an artificial saltwater lake (surface area = 56.5  $\text{km}^2$ , drainage basin = 476.5  $\text{km}^2$ ), is located on the west coast of South Korea (Fig. 1) where the tidal flats are developed and the lake provides habitat for aquatic animals and birds. There are large industrial complexes in the Lake Shihwa region (total industrial area = 31  $\text{km}^2$ ), where more than 8500 companies produce metal products, machinery, equipment for industry, and chemicals and chemical products. The cities of Shiheung and Ansan (total population exceeds 1 million) are located on Lake Shihwa. Rapid growth of the population and industrial development has led to deterioration of water quality and biodiversity in this region (Li et al., 2004a,b; Kim et al., 2009; Yoo et al., 2009).

In 2000, the South Korean government designated Lake Shihwa as a special management coastal zone and constructed a water gate

to promote exchange of water with the adjacent Yellow Sea. However, many studies continue to report substantial contamination in Lake Shihwa water, sediment, and biota from trace metals and toxic organic contaminants such as polychlorinated biphenyls, polycyclic aromatic hydrocarbons, perfluorinated compounds, and nonylphenols (NPs) (Li et al., 2004a,b; Koh et al., 2005; Kim et al., 2009; Yoo et al., 2009; Hong et al., 2010). In particular, it was reported that Lake Shihwa was one of the most contaminated areas in Korea for nonylphenol (Li et al., 2004a,b; Koh et al., 2005; Choi et al., 2009). Although many studies have investigated the contamination of Lake Shihwa by chemicals from industrial wastewater pollution, little attention has been focused on pollution from wastewater treatment plants (WWTPs). WWTPs treat approximately  $5 \times 10^8 \text{ kg d}^{-1}$  of wastewater and discharge the effluent and any associated chemical or fecal contamination through an underground pipeline to Lake Shihwa (MOE, 2009). We assessed contamination from wastewater discharge by using chemical wastewater indicators such as NPs and comparing with fecal sterols. To our knowledge, this is the first report on the contribution of these WWTP-derived compounds to wastewater pollution in the coastal industrialized region of Korea.

\* Corresponding author at: 152-1, Haeanro, Gijang-eup, Gijang-gun, Busan 619-705, Republic of Korea. Tel.: +82 51 720 2531; fax: +82 51 720 2515.

E-mail address: [mkchoi@nfrdi.go.kr](mailto:mkchoi@nfrdi.go.kr) (M. Choi).

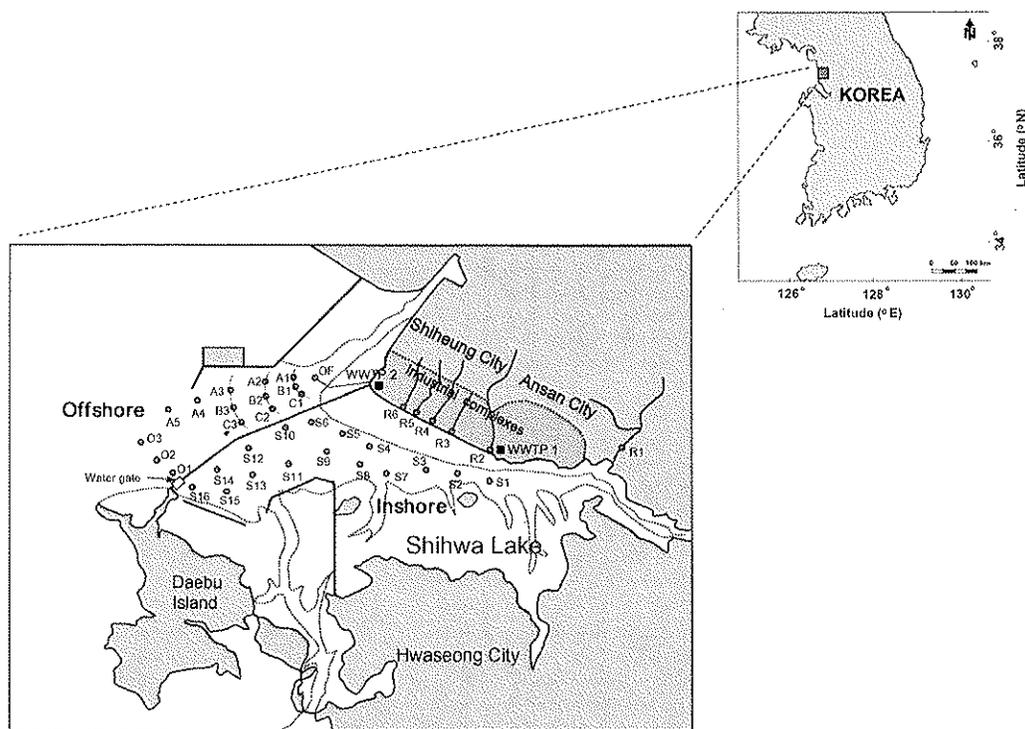


Fig. 1. Sampling locations of creek water (R1–R6), wastewater treatment plant effluent (WWTP1 and WWTP2), and surface sediment samples [S1–S16, OF (the outfall of WWTPs), A1–C3, O1–O3] from the artificial seawater Lake Shihwa, Korea.

NPs are metabolites of nonionic surfactants widely used in a variety of industrial processes and residential and commercial cleaning products since the 1940s. These contaminants are commonly found in effluents from industrialized areas (Bennie et al., 1997; Kannan et al., 2003; Li et al., 2004a,b; Choi et al., 2009) and have been used as markers for industrial contamination (Diez et al., 2006; Lara-Martin et al., 2008). Coprostanol (COP), a fecal sterol, has been widely used as an indicator of fecal pollution in the aquatic environment because of its occurrence at high concentrations in human feces (40–60% of total fecal sterols excreted; Chan et al., 1998). Distribution profiles of COP together with other fecal sterols such as cholestanol (CHOA) can provide useful information on urban sewage pollution in the marine environment. Grimalt et al. (1990) suggested a range of 0.7–1.0 for COP/(COP + CHOA) as characteristic of urban sewage polluted sediments and <0.3 as unpolluted sediments. High COP/(COP + CHOA) ratios of approximately 0.6 also were found in locations adjacent to a sewage outfall (Jeong and Han, 1994) and a sewage sludge disposal site (Chan et al., 1998).

The present study investigated current contamination of NPs in sediments from Lake Shihwa region compared to the distribution of fecal sterols. We also investigated creek surface water and wastewater treatment plant effluents (WWTPEs) and their mass discharge into the Lake Shihwa, to understand the linkage between discharge and sediment contamination.

## 2. Materials and methods

### 2.1. Sample collection

The sampling locations for creek water, WWTPEs, and sediment from Lake Shihwa in Korea are presented in Fig. 1. Surface sedi-

ment samples (0–4 cm depth) were collected using a box core sampler at 16 stations (S1–S16) in the inshore region and 15 stations in the offshore region of the lake in March 2008 (Fig. 1). The collected samples were individually wrapped in aluminum foil and immediately frozen. The sediment samples were transported to the laboratory, stored at  $-20\text{ }^{\circ}\text{C}$ , and subsequently freeze dried.

Water samples were collected monthly between June 2008 and May 2009 from six creeks (R1–R6) discharging from the inshore industrialized region and from two WWTPs (WWTP1 and WWTP2) whose outfalls discharge at depth further offshore in Lake Shihwa. WWTP1 and WWTP2 treat  $2.77 \times 10^8\text{ kg d}^{-1}$  and  $2.14 \times 10^8\text{ kg d}^{-1}$  of wastewaters, respectively (MOE, 2009). Influent volumes received by the plants are derived from both industrial (55%) and domestic (45%) sources. Both WWTPs use an activated sludge for biological treatment, followed by a biological aerated filtration for WWTP1 and sand filtration for WWTP2 (MOE, 2009). The creek water sample collection was conducted at low tide in the surveyed area by using a bucket sampler and flowmeter (BFM001, Valeport, England) to estimate flow rate and mass discharge. Samples were filtered in the laboratory using GFF filters ( $0.7\text{ }\mu\text{m}$ , Whatman, Maidstone, England) within 2 d of collection.

### 2.2. Analytical procedures

The water and sediment samples were analyzed for NPs [nonylphenol (NP) and nonylphenol mono- and di-ethoxyliates ( $\text{NP}_{1,2}\text{EO}$ )] and two fecal sterols (COP and CHOA) according to the method of Choi et al. (2007, 2009) and Li et al. (2007). For NPs (NP and  $\text{NP}_{1,2}\text{EO}$ ; pure standards from Cambridge Isotope Laboratories, Andover, MA, USA), the filtered water samples were extracted three times by liquid–liquid extraction, and the filter and freeze-dried sediment samples were extracted twice with a mechanical

shaker using dichloromethane (ultra residue analysis; J.T. Baker, Phillipsburg, NJ, USA). A surrogate standard, nonylphenol- $^{13}\text{C}_6$  (Cambridge Isotope Laboratories, Andover, MA, USA) was added to each sample before extraction. The extracts were concentrated to about 1 mL under a gentle stream of dry nitrogen. Water and sulfur were removed from the extract using anhydrous sodium sulfate (Kanto, Tokyo, Japan) and activated copper (Sigma-Aldrich, St. Louis, MO, USA), respectively. The extract was concentrated to 0.5 mL, derivatized using N,O-bis [trimethylsilyl] trifluoroacetamide (BSTFA, Sigma-Aldrich), and interferences were removed by fractionation through a Florisil (1 g, 60–100 mesh, reagent grade, Sigma-Aldrich) chromatography column. After the addition of internal standards, the concentrated eluents were transferred to vials for instrumental analysis.

Briefly, for fecal sterol analysis, filter and freeze-dried sediment samples were placed in 50-mL Teflon centrifuge tubes with Teflon caps. A surrogate standard, 1-nonadecanol (Dr. Theodor Schuchardt & Co., Hohenbrum, Germany), was added to each tube, and the samples were extracted twice with a mechanical shaker using 50:50 dichloromethane-chloroform (ultra residue analysis; J.T. Baker). The extracts were concentrated to about 1 mL under a gentle stream of dry nitrogen and transferred to hexane (ultra residue analysis; J.T. Baker). The extracts were then passed through a Florisil chromatography column. The eluents were concentrated and derivatized using BSTFA. The concentrated eluents were transferred to vials for instrumental analysis after the addition of the internal standards.

NPs and fecal sterols were quantified using a gas chromatograph (GC-6890 series; Agilent, Wilmington, DE, USA) equipped

with a mass spectrometer (MS; Agilent Model 5973 N, Palo Alto, CA, USA). A DB-5MS (30-m length, 0.25-mm inner diameter, 0.25- $\mu\text{m}$  film thickness; J&W Scientific, Palo Alto, CA) was used with helium as the carrier gas at  $1.2\text{ mL min}^{-1}$ . The injection port was maintained at  $280\text{ }^\circ\text{C}$ . One microliter of sample was injected in the splitless mode. The GC oven temperature for NPs was initially  $50\text{ }^\circ\text{C}$  for 2 min, and then was raised to  $200\text{ }^\circ\text{C}$  at  $30\text{ }^\circ\text{C min}^{-1}$ , to  $230\text{ }^\circ\text{C}$  at  $2\text{ }^\circ\text{C min}^{-1}$ , to  $310\text{ }^\circ\text{C}$  at  $30\text{ }^\circ\text{C min}^{-1}$ , and held for 10 min. For fecal sterols, the oven temperature was initially  $85\text{ }^\circ\text{C}$  for 3 min, and then was raised to  $130\text{ }^\circ\text{C}$  at  $10\text{ }^\circ\text{C min}^{-1}$ , to  $310\text{ }^\circ\text{C}$  at  $3\text{ }^\circ\text{C min}^{-1}$ , and held for 7 min. Auxiliary temperature was  $280\text{ }^\circ\text{C}$ . The MS was operated at 70 eV of ionization potential with ion source temperature at  $230\text{ }^\circ\text{C}$  and electron multiplier voltage at 1800 eV. The analytes were analyzed in the selected ion monitoring mode.

The total organic carbon (TOC) content in sediments was determined using a CHN Elemental Analyzer (PerkinElmer, Model 2400; Boston, MA, USA) after removal of calcium carbonate with 1 N HCl (Kim et al., 2006; Choi et al., 2007).

### 2.3. Quality assurance

All of the surrogate standards were detected with no interferences. Solvents injected before and after the injection of standards showed negligible contamination or sample-to-sample carryover. Procedural blanks for sediment, water, and filter were processed in the same way as the samples. The blanks did not contain quantifiable amounts of the target compounds. The limits of detection (LOD) were calculated as three times the signal-to-noise ratio,

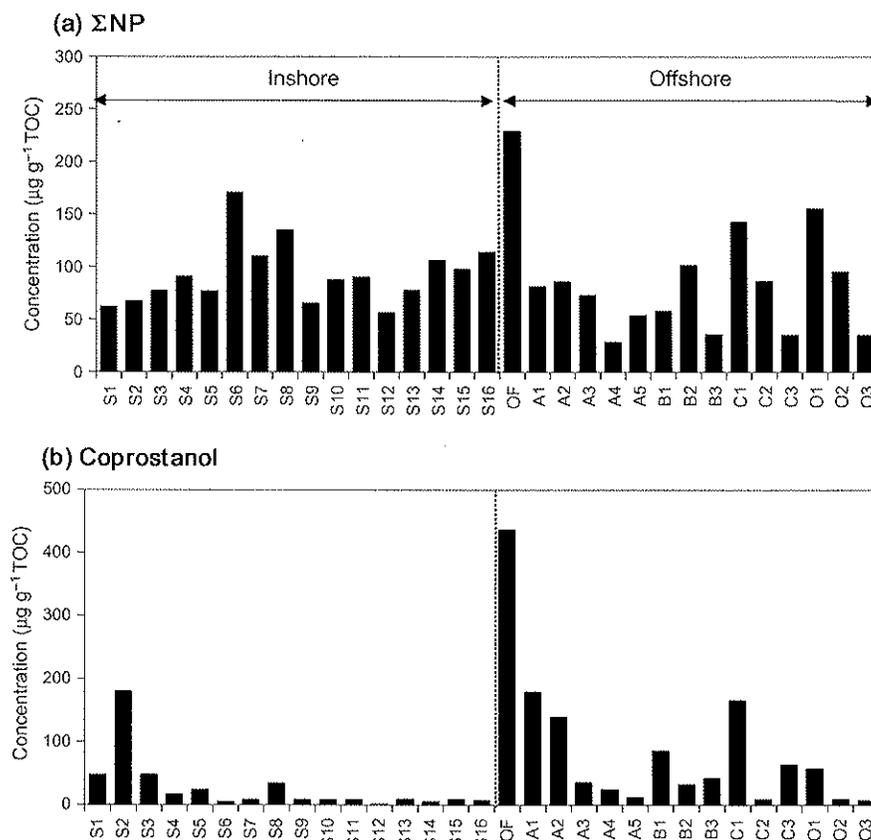


Fig. 2. Spatial distribution of concentrations of (a) total nonylphenolic compounds (the sum of nonylphenol and NP $_{1-2}\text{EO}$ ) and (b) coprostanol in sediments from Lake Shikwa, Korea.

which were from 4 to 5 ng g<sup>-1</sup> dw (dry weight) in sediments and 8–10 ng L<sup>-1</sup> in water for the two sterols, and from 1 to 4 ng g<sup>-1</sup> dw in sediments and 2–8 ng L<sup>-1</sup> in water for NPs.

The recovery of the target compounds in the absence of TOC or other sample matrix components was based on five replicate analyses of sea sand (washed sea sand; Fisher Scientific, Phillipsburg, NJ, USA, used as received) spiked with fecal sterols or NPs and five replicate analyses of purified water (HPLC grade; J.T. Baker) spiked with NPs. The recoveries of fecal sterols were 77 ± 14% for the sea sand, and the recoveries of NPs were 104 ± 15% for sea sand and 81 ± 12% for purified water. The performance of actual sample analyses was monitored with the recovery surrogates. Recoveries of nonylphenol-<sup>13</sup>C<sub>6</sub> were 80 ± 13% for sediment samples, 69 ± 14% for filtered water samples, and 82 ± 11% for particle-bearing samples. Recoveries of 1-nonadecanol were 109 ± 8.8% for sediment samples and 113 ± 13% for filter samples.

### 3. Results and discussion

#### 3.1. Distribution in surface sediment

TOC content in sediments from Lake Shihwa ranged from 0.20% to 1.45%. The TOC content in sediments differed between the inshore and offshore regions of Lake Shihwa (*t*-test, *p* < 0.001). TOC concentrations in the inshore sediments were approximately two times higher (mean ± std; 0.94 ± 0.33%) than in the offshore region sediments (0.54 ± 0.20%). The highest content of TOC was found at station S5, and TOC contents higher than 1% were observed at all the inshore sites (stations S1–S6, S9, S11, and S12). These locations also contained high total NP concentrations. Total NP concentrations in the inshore region correlated significantly with sediment TOC (*r* = 0.564, *p* < 0.05), confirming the observations of other studies in Lake Shihwa (Khim et al., 1999; Koh et al., 2005). Koh et al. (2005) and Oh et al. (2010) also reported a significant relationship between TOC contents and other organic contaminants (PCBs, organochlorine pesticides, bisphenol A, and methylmercury) in Lake Shihwa sediments. This correlation indicates that TOC in Lake Shihwa is an important factor influencing the distribution of organic contaminants, although their sources in Lake Shihwa are thought to be localized. In this study, NPs and COP were normalized to TOC to assist in identifying potential sources or contaminated areas (Fig. 2).

Concentrations of NP, NP<sub>1+2</sub>EO, and ΣNP (the sum of NP and NP<sub>1+2</sub>EO) were 14.2–91.8 μg g<sup>-1</sup> TOC (mean: 46.1 μg g<sup>-1</sup> TOC), 15.1–138 μg g<sup>-1</sup> TOC (mean: 44.3 μg g<sup>-1</sup> TOC), and 29.3–230 μg g<sup>-1</sup> TOC (mean: 90.4 μg g<sup>-1</sup> TOC) in sediments, respectively. The concentrations of NPs varied within a narrow range, suggesting widespread occurrence of NPs in Lake Shihwa sediments. The compositions of NP and NP<sub>1+2</sub>EO in sediments were 33.8–68.4% (mean: 52.1%) and 31.6–66.2% (mean: 47.9%), respectively. Fig. 3a) shows box plots that compare NP concentrations from this and other studies (Khim et al., 1999; Li et al., 2004a,b; Choi et al., 2009) that sampled Lake Shihwa sediments over a 10-year period. The observed NP concentrations (10–90 μg g<sup>-1</sup> TOC and/or 100–1030 ng g<sup>-1</sup> dw) were not significantly different from those previously measured in 1998, 2002, and 2006 (*t*-test, *p* = 0.150–0.428), except for in 2000 (*t*-test, *p* < 0.01). This suggests that NP concentrations in sediments have not substantially changed since the earliest of the prior studies.

The South Korean government has been trying to reduce contamination from NP by designating it as a priority chemical, prohibiting its use as a component of household cleaners in 2001, and prohibiting its use for all domestic applications in 2007, and prohibiting its use for some industrial applications such as paints and inks in 2010 (MOE, 2007). However, NP concentrations are

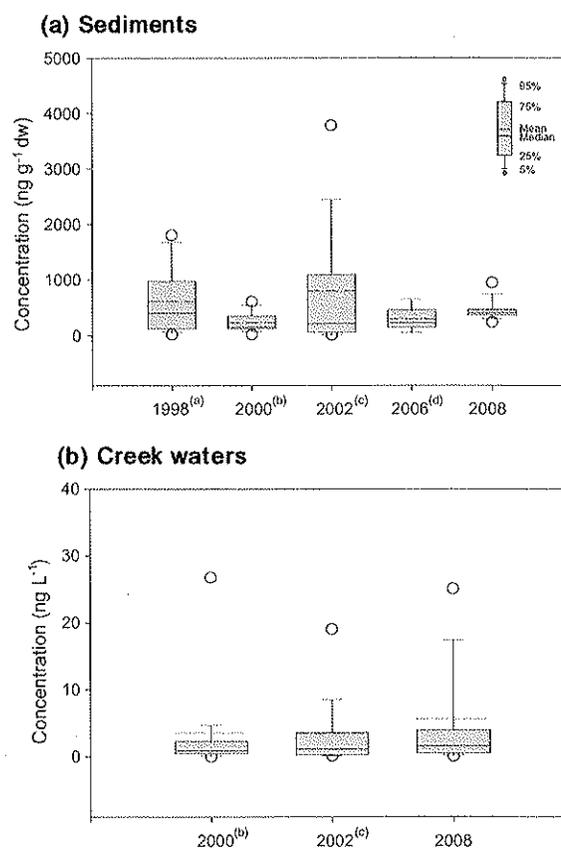


Fig. 3. Comparison of nonylphenol concentrations with previous studies in (a) sediments and (b) creek water from Lake Shihwa. In each figure, superscript "(a)" are results from Khim et al. (1999), superscript "(b)" are from Li et al. (2004a), superscript "(c)" are results from Li et al. (2004b), and superscript "(d)" are results from Choi et al. (2009).

not reduced in the sampled creeks discharging to Lake Shihwa, suggesting that efforts to control NP use in household products have not been effective at mitigating NP concentration in potential sources of these compounds to the sediment in Lake Shihwa.

Concentrations of COP in sediments were 2.51–438 μg g<sup>-1</sup> TOC (mean: 56.7 μg g<sup>-1</sup> TOC). The range of COP in the present study (30–2200 ng g<sup>-1</sup> dw) was higher than, or comparable to, those in Gyeonggi Bay (3–3800 ng g<sup>-1</sup> dw; Li et al., 2007) and in Masan Bay, Korea (280–5300 ng g<sup>-1</sup> dw; Li et al., 2008), in the Pearl River estuary, China (nd–50 μg g<sup>-1</sup> TOC; Peng et al., 2005), and Mekong Delta, Vietnam (5–4800 ng g<sup>-1</sup> dw; Isobe et al., 2002). However, the concentrations of COP in the present study were much lower than those reported in Boston Harbor (260–12,000 ng g<sup>-1</sup> dw; Eganhouse and Sherblom, 2001), Cootes Paradise of Ontario, Canada (150–38,000 ng g<sup>-1</sup> dw; Mayer et al., 2007), Santa Monica Bay, USA (70–45,000 ng g<sup>-1</sup> dw; Venkatesan et al., 2010), and Guanabara Bay, Brazil (330–40,000 ng g<sup>-1</sup> dw; Carreira et al., 2004), which contain sampling sites at nearby WWTP outfalls.

On a TOC normalized basis, concentrations of ΣNP in the offshore region of Lake Shihwa (87.1 ± 54.7 μg g<sup>-1</sup> TOC) were comparable to those in the inshore region (93.5 ± 29.7 μg g<sup>-1</sup> TOC). However, for Cop, the offshore region showed three times higher concentrations (87.9 ± 112 μg g<sup>-1</sup> TOC) than those in the inshore region (27.5 ± 43.6 μg g<sup>-1</sup> TOC). The distribution pattern for NPs differed substantially from the pattern observed for COP in the same set of samples. ΣNP/COP ratio in the inshore also showed

three times higher values ( $9.32 \pm 7.48$ ) than those in the offshore ( $2.65 \pm 2.88$ ; *t*-test,  $p < 0.01$ ). These results suggest that inshore region of Lake Shihwa is substantially more contaminated by NPs than COP, while contamination by NPs and COP in the offshore region is comparable.

In the offshore region, a significant correlation between COP and  $\Sigma$ NP in sediments ( $r = 0.591$ ,  $p < 0.05$ ) was observed. The highest concentrations of  $\Sigma$ NP and COP were found at the sample from station OF, the outfall of both WWTP1 and WWTP2, and their concentrations sharply decreased with distance from the outfall of WWTPs (Fig. 2). A high correlation between COP concentration and ratios of (COP/COP + CHOA) was observed in the offshore ( $r = 0.734$ ,  $p < 0.01$ ). These results indicate that predominant sources of NPs and COP in the offshore region are WWTP effluents. If NPs are presumed to derive primarily from industrial sources while COP and CHOA derive primarily from wastewater, then this observation suggests that the sources of contamination from industrial effluents were consistent with domestic effluents in the offshore region. However, a poor correlation in the inshore region ( $r = -0.272$ ,  $p = 0.31$ ) was observed for these same contaminants, suggesting different sources or pathways of introduction for industrial and domestic effluents.

### 3.2. Occurrence in creeks

Concentrations of NPs (NP and NP<sub>1+2</sub>EO) and fecal sterols (COP and CHOA) in creek water and WWTPs are summarized in Table 1. The concentrations of NP, NP<sub>1+2</sub>EO, and  $\Sigma$ NP were 0.05–50.4  $\mu\text{g L}^{-1}$  (median: 1.66  $\mu\text{g L}^{-1}$ ), 0.22–872  $\mu\text{g L}^{-1}$  (median: 4.44  $\mu\text{g L}^{-1}$ ), and 0.32–875  $\mu\text{g L}^{-1}$  (median: 7.81  $\mu\text{g L}^{-1}$ ) in creek water, respectively. The levels of NP in the present study are comparable to those previously reported in Lake Shihwa [*t*-test,  $p = 0.421$ – $0.451$ ; Fig. 3b]; 0.1–41.3  $\mu\text{g L}^{-1}$  in 2000 (Li et al., 2004a), and 0.12–4.32  $\mu\text{g L}^{-1}$  in 2002 (Li et al., 2004b). Total NP concentrations in creek water have not decreased appreciably since NP concentrations were reported in 1998.

Concentrations of COP and CHOA ranged from 0.09 to 19.0  $\mu\text{g L}^{-1}$  (median: 1.99  $\mu\text{g L}^{-1}$ ) and 0.18–2.35  $\mu\text{g L}^{-1}$  (median: 0.47  $\mu\text{g L}^{-1}$ ) in creek water. The median COP/(COP + CHOA) ratios were 0.69–0.85 in creeks, indicating substantial fecal pollution. COP contamination in creeks discharging to Lake Shihwa fall within the range of concentrations in reports from other locations: Santa Ana River, USA (not detected to 0.026  $\mu\text{g L}^{-1}$ ; Noblet et al., 2004), St. Lawrence River, Canada (0.002–0.067  $\mu\text{g L}^{-1}$ ; Cathum and Sabik, 2001), Pearl River Delta outlets, China (not detected to 0.52  $\mu\text{g L}^{-1}$ ; Wang et al., 2010), Po River, Italy (8.30–9.20  $\mu\text{g L}^{-1}$ ; Gilli et al., 2006), Mokpo Bay (0.09–7.57  $\mu\text{g L}^{-1}$ ; Choi et al., 2007) and Masan Bay, Korea (2.03–23.1  $\mu\text{g L}^{-1}$ ; Choi et al., 2005), and Mekong Delta, Vietnam (below detection to 97.1  $\mu\text{g L}^{-1}$ ; Isobe et al., 2004).

Among six creeks, the highest concentrations of NP and NP<sub>1+2</sub>EO were from samples from Okgu Creek (R6, median: 11.5  $\mu\text{g L}^{-1}$  for NP) and Jeongwang Creek (R4, median: 7.42  $\mu\text{g L}^{-1}$  for NP<sub>1+2</sub>EO), respectively, which receive wastewater from industrial complexes (Fig. 4a). The lowest concentrations of NP and NP<sub>1+2</sub>EO were all from Ansan Creek (R1, 0.39  $\mu\text{g L}^{-1}$  for NP and 1.08  $\mu\text{g L}^{-1}$  for NP<sub>1+2</sub>EO), which receives wastewater from residential areas. Similar results were also reported by Hong et al. (2010) and Li et al. (2004a). However, elevated median concentrations of COP, defined in this study as greater than the median of all creeks (1.99  $\mu\text{g L}^{-1}$ ) were detected at R2 (2.55  $\mu\text{g L}^{-1}$ ), R3 (3.07  $\mu\text{g L}^{-1}$ ) and R4 (2.78  $\mu\text{g L}^{-1}$ ), and COP concentration patterns at these sites were different from those for NPs (Fig. 4b). Low ratios of  $\Sigma$ NP/COP was observed in samples from R1 (median: 1.84), R2 (median: 2.28), and R3 (median: 1.41), whereas high ratios were observed in samples from R4 (median: 7.11), R5 (median: 9.06) and R6 (median: 17.2). These ratios indicate that the processes producing spatial distributions of contaminants in Lake Shihwa from industrial effluents may differ from those of domestic effluents. Industrial complexes were developed along the lake from 1977 to 1987, whereas construction of massive residential apartment complexes was started far from the lake in mid-1990. The human

**Table 1**

Summary of concentrations ranges, median concentrations, and mass discharge of nonylphenolic compounds and fecal sterols in creek waters and wastewater treatment effluents that contribute to Lake Shihwa.

Creek or effluent	Mean discharge (million L d <sup>-1</sup> )	Concentration ( $\mu\text{g L}^{-1}$ )					Mass discharge (g d <sup>-1</sup> )	
		NP <sup>a</sup>	NP <sub>1+2</sub> EO <sup>b</sup>	$\Sigma$ NP <sup>c</sup>	COP <sup>d</sup>	CHOA <sup>e</sup>	$\Sigma$ NP	COP
Ansan (R1)	3.43–22.9 (5.63) <sup>f</sup>	0.05–21.9 (0.39)	0.22–20.8 (1.08)	0.32–23.7 (1.58)	0.13–14.4 (1.97)	0.24–1.75 (0.60)	2.71–221 (12.8)	0.67–87.2 (9.64)
Shiheung (R2)	1.93–13.9 (3.43)	0.29–14.2 (1.48)	0.54–21.2 (3.58)	2.18–25.3 (6.53)	0.20–19.0 (2.55)	0.24–2.06 (0.46)	5.34–208 (25.0)	0.62–48.1 (10.9)
Singil (R3)	0.52–1.74 (0.89)	0.17–25.5 (1.66)	0.52–8.75 (4.11)	2.70–29.3 (4.87)	0.66–5.64 (3.07)	0.29–1.43 (0.50)	2.38–15.4 (5.13)	0.59–5.03 (2.36)
Jeongwang (R4)	5.37–15.5 (8.73)	0.12–18.9 (2.36)	1.15–872 (7.42)	4.87–875 (14.3)	1.04–15.2 (2.78)	0.31–2.35 (0.58)	42.5–8654 (134)	14.7–132 (30.5)
Gunja (R5)	0.69–5.39 (1.43)	0.22–13.5 (1.38)	0.94–173 (6.96)	1.37–175 (9.44)	0.09–9.93 (0.98)	0.23–1.56 (0.35)	4.03–598 (15.2)	0.32–12.5 (1.74)
Okgu (R6)	0.40–7.33 (2.07)	0.46–50.4 (11.5)	0.70–11.0 (4.83)	5.58–55.0 (16.4)	0.36–6.98 (0.93)	0.18–1.44 (0.28)	10.1–138 (32.5)	0.26–11.3 (1.51)
Subtotal	22.2						224	56.7
WWTP1	235–343 (274)	0.13–54.6 (0.57)	0.38–11.8 (0.97)	0.61–60.7 (1.64)	0.11–4.77 (0.64)	0.22–2.02 (0.38)	168–2882 (526)	30–1333 (193)
WWTP2	188–259 (214)	0.14–68.8 (1.01)	1.78–18.1 (6.56)	2.82–87.0 (7.57)	0.46–44.0 (3.53)	0.29–2.02 (1.09)	671–2872 (1742)	95–9269 (798)
Subtotal	488						2268	991
Total	510						2492	1048

<sup>a</sup> NP: nonylphenol.

<sup>b</sup> NP<sub>1+2</sub>EO: nonylphenol mono- and di-ethoxylates.

<sup>c</sup>  $\Sigma$ NP: the sum of NP and NP<sub>1+2</sub>EO.

<sup>d</sup> COP: coprostanol.

<sup>e</sup> CHOA: cholestanol.

<sup>f</sup> Values in parentheses are medians.

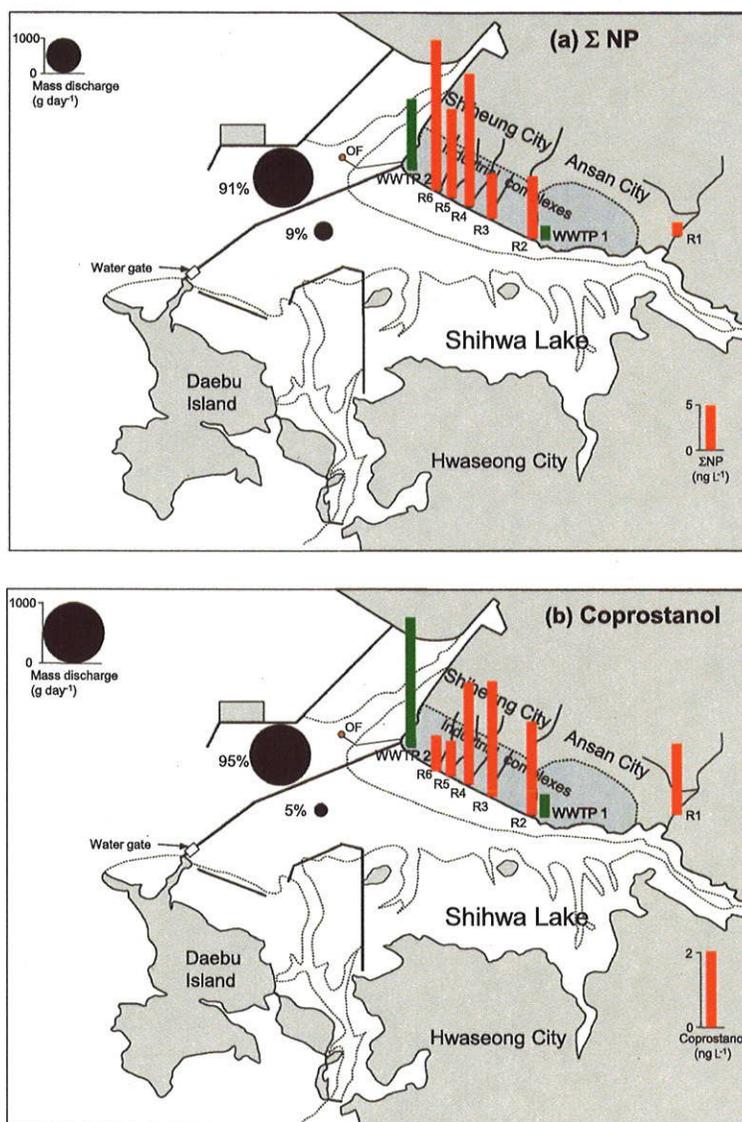


Fig. 4. Spatial distribution of concentrations and mass discharge of (a) total nonylphenolic compounds (the sum of nonylphenol and NP<sub>1+2</sub>EO) and (b) coprostanol in creek water and wastewater treatment plant effluents from Lake Shihwa, Korea. ng L<sup>-1</sup>, nanograms per liter.

population has increased from approximately 400,000 people in 1990 to 1.1 million people in 2008, made possible by an increasing supply of apartments (AMG, 2009; SMG, 2009). The separation of industrial complexes and residential districts in the Lake Shihwa region may reflect the different distribution between NPs and COP.

### 3.3. Occurrence in wastewater treatment plant effluents

Concentrations in WWTPs were 0.13–68.8 μg L<sup>-1</sup> (median: 0.81 μg L<sup>-1</sup>) for NP, 0.38–18.1 μg L<sup>-1</sup> (median: 2.68 μg L<sup>-1</sup>) for NP<sub>1+2</sub>EO, and 0.61–87.0 μg L<sup>-1</sup> (median: 3.62 μg L<sup>-1</sup>) for ΣNP, respectively (Table 1). The concentrations of ΣNP were approximately half of those in creeks but were seven times higher than those in WWTPs of Masan Bay, Korea (median: 0.48 μg L<sup>-1</sup>; Li et al., 2008), where 10% of the influent is from an industrial source. The concentrations of ΣNP in WWTP2 (median: 7.57 μg L<sup>-1</sup>) were

four times higher than those in WWTP1 (median: 1.64 μg L<sup>-1</sup>) (Table 1, Fig. 4a). The ratio of NP<sub>1+2</sub>EO/NP is a useful indicator to assess pollution by NPs that have not been exposed to biological treatment processes (Ferguson et al., 2001; Li et al., 2008; Choi et al., 2009), although additional NP ethoxomer data are helpful for confirming biological treatment exposure. The ratio of NP<sub>1+2</sub>EO/NP in WWTP2 (median: 4.79) was twice as high as that in WWTP1 (median: 2.39), indicating that WWTP1 may treat wastewater more efficiently than WWTP2.

Concentrations of COP and CHOA ranged from 0.11 to 44.0 μg L<sup>-1</sup> (median: 1.82 μg L<sup>-1</sup>), and 0.22–2.02 μg L<sup>-1</sup> (median: 0.53 μg L<sup>-1</sup>) in the WWTPs, respectively. The concentrations of COP in WWTPs were lower than those in WWTPs from other locations; 36–183 μg L<sup>-1</sup> (Beck and Radke, 2006) and 5.2–154 μg L<sup>-1</sup> (Venkatesan et al., 2010). The concentrations of COP in WWTP2 were four times higher than those in WWTP1 (Table 1),

and COP/(COP + CHOA) ratios in WWTP 2 (median: 0.78) were also higher than those in WWTP1 (median: 0.57). Similarly, NP concentrations from WWTP2 exceeded those from WWTP1.

3.4. Mass discharge through creeks and wastewater treatment plants

Mean flows and mass discharge (grams per day) of six creeks and WWTPs into Lake Shihwa over the time period of the study were estimated (Table 1). Flow rates were calculated by multiplying the measurement of flow velocity by area components of a measurement section in a stream (Soupir et al., 2009). Mass discharge was calculated by multiplying the water flow rate by the corresponding concentration of each compound, multiplied by a units conversion factor. Because samples were collected at the mouth of these creeks, these loads represented the amount of contaminants entering the lake estuarine system.

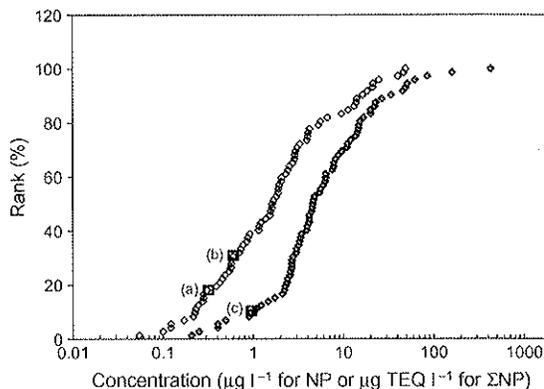
Total input of NPs from the two WWTPs was 2270 g d<sup>-1</sup> (526 g d<sup>-1</sup> for WWTP1 and 1740 g d<sup>-1</sup> for WWTP2), approximately 10 times higher than from the total input from six creeks (224 g d<sup>-1</sup>) (Table 1, Fig. 4a). For COP mass discharge, the total input from the two WWTPs was 991 g d<sup>-1</sup> (193 g d<sup>-1</sup> for WWTP1 and 798 g d<sup>-1</sup> for WWTP2), which was approximately 20 times higher than input from the six creeks (56.7 g d<sup>-1</sup>) (Table 1, Fig. 4b). The WWTPs appear to be the largest contributors of NPs and COP on a gram-per-day basis, although high concentrations of NPs and COP were detected in the creeks. This indicates that WWTP discharge is the main contributor of the wastewater pollution to the Lake Shihwa. In addition, the contribution of the mass discharge through the six creeks was about four times higher for NPs than for COP, indicating that wastewater from industrial sources is less efficiently controlled than wastewater from domestic sources.

The rankings of median mass discharge of NPs from creeks were R4 > R6 > R2 > R5 > R1 > R3 while for COP the rankings were R4 > R2 > R1 > R3 > R5 > R6 (Table 1). Except for R4, which had the greatest mass discharge for both contaminants, the mass discharge of NPs from creeks was different from that of COP. High mass discharge of NPs was observed at R5 and R6, whereas COP discharge was higher at R1, R2, and R3 and was similar to the concentration pattern in the creeks. These differences in compound-specific discharge may result in different contamination patterns between NPs and COP in sediments of the inshore region.

3.5. Ecotoxicological concern

Trace levels of NPs can cause chronic effects and disrupt the endocrine systems of aquatic organisms (Soares et al., 2008). Guidelines have been proposed in various countries for nonylphenol or ΣNP in sediments to protect aquatic life (Environment Canada, 2002; Furuichi et al., 2004; Jonkers et al., 2005). The NP concentrations measured in the present study were compared to screening and ecotoxicological values in water (Fig. 5a). In the 72 water samples analyzed from creeks draining into Lake Shihwa, the NP concentrations in 68% and 81% of the samples were higher than the predicted no-effect concentration of NP reported by the Japanese Ministry of the Environment (0.608 μg L<sup>-1</sup>; Furuichi et al., 2004) and the maximum permissible concentration (MPC) in The Netherlands (0.33 μg L<sup>-1</sup>; Jonkers et al., 2005), respectively. Similarly, the NPs concentrations in 89% of 72 samples exceeded the Canadian water-quality guideline (CWQG) for ΣNP (1.0 μg NP toxic equivalency (NP-TEQ) L<sup>-1</sup>; Environment Canada, 2002). In the sediments of Lake Shihwa, 98% (30 stations) and 13% (5 stations) of 31 samples exceeded the MPC for NP (0.105 μg g<sup>-1</sup> dw) and the CWQG for ΣNP [1.0 μg NP-TEQ g<sup>-1</sup> dw (1% TOC)], respectively (Fig. 5b). This indicates that NP and ΣNP in the Lake Shihwa environment may pose a potential risk to sensitive species. In addition,

(a) Creek waters



(b) Sediments

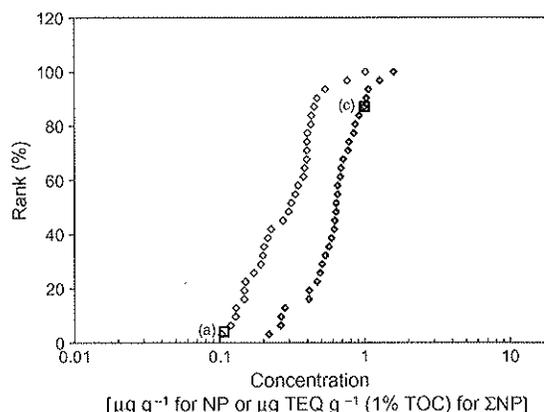


Fig. 5. Ranked cumulative concentrations of nonylphenol and total nonylphenolic compounds (ΣNP) in comparison to screening values reported elsewhere. In each figure, point “a” is the maximum permissible concentration (MPC) for nonylphenol in the Netherlands (Jonkers et al., 2005); point “b” is the predicted no-effect concentration (PNEC) of nonylphenol in Japan (Furuichi et al., 2004); point “c” is the water quality guideline for ΣNP in Canada (Environment Canada, 2002).

tion, NP in sediments was at concentrations highly exceeding the MPC, whereas NP and ΣNP in creek water were at high concentrations exceeding the CWQG. This indicates that NP is a predominant contaminant in sediments and may pose a risk to benthic organisms, while NP<sub>1+2</sub>EO, which can be degraded to NP, predominates in creek water.

4. Conclusions

Sediments and freshwater in Lake Shihwa are contaminated by NPs and COP. Levels of NP observed in creek water and sediments remained high, when compared to previous investigations, and commonly exceeded the screening and ecotoxicological benchmarks. WWTP discharge to Lake Shihwa was a major contributor of industrial wastewater pollution, as evidenced by high concentrations of NPs and COP in sediments close to the outfall and their high mass discharge through a major WWTP outfall. Continuing study on the bioavailability and/or toxicity at the sites near the WWTP outfall and proper management of point sources is needed to protect the aquatic ecosystem of Lake Shihwa.

## Disclaimer

Any use of trade, product, or firm names is for descriptive purposes only and does not imply endorsement by the US or Korean Government.

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