Occurrence and Concentrations of Estrogenic Phenolic Compounds in Surface Waters of Rivers Flowing into Masan Bay, Korea

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The estrogenic phenolic compounds, nonylphenol (NP), octylphenol(OP), bisphenol A (BPA) and nonylphenol mono- and diethoxylate ($NP_{1-2}EO$) were analyzed in 24 surface water samples from six rivers flowing into Masan Bay. All of the phenolic compounds were detected in all six rivers in high concentrations. The most abundant compound was $NP_{1-2}EO$ (86.0%), followed by NP (10.1%), BPA (3.6%) and OP (0.3%). The levels of phenolic compounds were 1.42-22.70 µg/L for $NP_{1-2}EO$, 0.15-1.68 µg/L for NP, 0.024-0.610 µg/L for BPA and 0.003-0.067 µg/L for OP. Especially, high concentrations were recorded in the rivers that pass through industrial complexes. The concentrations of phenolic compounds observed in these river waters were 1-2 orders of magnitude lower than the reported acute toxicity levels (hundreds of micrograms per liter). However, they were only slightly lower than the chronic toxicity levels. Most of the water samples also exceeded the Canadian nonylphenolic compounds water quality guideline, 1 µg/L, for the protection of aquatic life and the maximum permissible concentrations (MPC), 0.33 µg/L for NP and 0.12 µg/L for $NP_{1-2}EO$.

Key words: Nonylphenol, Nonylphenol ethoxylates, Toxicity, River water, Masan Bay

Introduction

Of endocrine disrupting compounds, estrogenic phenolic compounds such as alkylphenolic ethoxylates (APEOs), their degradation products [shorter-chain APEOs and alkylphenols (APs)], and bisphenol A (BPA) have been paid attention recently because of their high production, widespread use and ubiquitous. occurrence in the environment (Kuch and Ballchmiter, 2001; Ying et al., 2002; Berryman et al., 2004; Jonkers et al., 2005a,b). APEOs, nonionic surfactants, have been widely used as industrial, institutional and domestic cleaners since the 1940s. APEOs are also important to a lot of industrial applications, including the production of pulp and paper, textiles, coatings, agricultural pesticides, lube oils and fuels. They have a great tendency to bioaccumulate their toxicity in aquatic life (Lee and Peart, 1995, Ahel et al., 1996). In addition, nonylphenol (NP) has a three times more estrogenic activity than DDT (Soto et al., 1991) and causes deformities and reproductive problems in wildlife and fish (Jobling and Sumpter, 1993).
Estrogenic phenolic compounds such as NP,

shorter-chain NPEOs, BPA, and octylphenol (OP) are frequently detected in various water bodies in Europe North America and Japan (Bennie et al., 1997; Ying et al., 2002). Many countries, including European Union members, Canada and the United States have passed regulations to restrict the use of APEOs in domestic applications (Jeannot et al., 2002; Vitali et al., 2004) and some of them have recently proposed guidelines for NP and NPEOs in water and sediments to protect aquatic life (Environment Canada, 2002; Furarchi et al., 2004; Jonkers et al., 2005b). In Korea, NPEOs are still used legally in domestic and industrial applications and little has been reported on the occurrence of NP in Korean surface waters (Li et al., 2004a,b; Li et al., 2004). Moreover, there are no data on $NP_{1-2}EO$ in Korean surface waters. Therefore, it is very important that Korean surface waters be surveyed to determine aquatic concentrations, investigate inputs and support the risk assessment associated with these substances.

Masan Bay, which is located on the southeastern coast of Korea, is one of the most contaminated estuarine systems in Korea (Fig. 1). Masan Bay was designated as a special management coastal area in
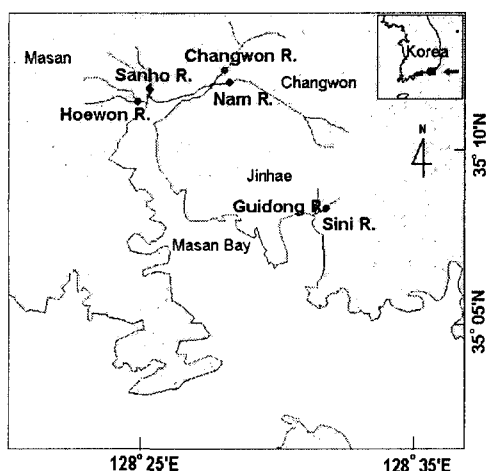
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Fig. 1. Location of Masan Bay and sampling sites.

1983. The Bay supports one of the greatest concentrations of heavy industry in Korea and a large human population. The area is surrounded by the cities of Masan, Changwon, and Jinhae, which are highly urbanized (81% of the total population of over 1 million lives in the drainage basin, with an average population density of 2682 people per km^2) and heavily industrialized (about 1300 industrial plants). Approximately 300,000 tons of domestic and industrial wastewater are discharged daily from these cities and industrial complexes into the coastal region. It has also been estimated that about 39 tons/day of biochemical oxygen demand (BOD) are discharged from these cities into the bay, and approximately 80% of the BOD was discharged through rivers (KMI, 2002). As of 2003, 63% of Jinhae, 80% of Masan, and 95% of Changwon were connected to a sewage system (MOE, 2004). Khim et al. (1999) and Choi et al. (2005) reported that the rivers flowing into Masan Bay are major sources of toxic contaminants. Therefore, the rivers can be considered one of the main routes of organic pollutants into the bay.

We measured the amounts of NP, $NP_{1-2}EO$, OP and BPA in the surface waters of six rivers flowing into Masan Bay, to determine their maximum concentrations in surface waters, and evaluate the human and environmental risks related to these concentrations.

Materials and methods

Sample collection

Surface water samples were collected four times in 2004 (February, June, August, and December) from six rivers (the Hoewon, Sanho, Changwon, Nam, Guidong, and Sini Rivers; Fig. 1) flowing into the bay. Water samples were collected from the mouths of the

rivers using a water sampler and flowmeter (BFM001 Valeport, England) when the tide was at its lowest ebb. Two liters of water were collected at each station in 4-L amber glass bottles, and transported to the laboratory, where the water samples were immediately filtered using precombusted glass fiber filters (GF/F, Whatman). The filtered water samples were acidified with 6 N HCl to depress microbial degradation and stored at 4°C. The filtered water samples were extracted within 3 days. The filters were stored at -30°C until analysis.

Analytical method and Precision

All solvents were purchased from Merck. NP, OP, and BPA standards were purchased from Aldrich, and $NP_{1-2}EO$ was from Chem Service. Internal standards (acenaphthene-d_{10}, phenanthrene-d_{10}, pyrene-d_{10}) and surrogate standards (bisphenol-d_{16}, nonylphenol-$^{13}C_6$) were purchased from Aldrich and Cambridge Isotope Laboratories, respectively. All the glass equipment was washed with solvents and baked before use to remove organic contamination.

All of the dissolved compounds were subject to solid phase extraction using a Waters Oasis HLB (0.2 g, 6 mL) copolymer cartridge according to the Water Oasis applications for EDC analysis (Waters, 2002). The cartridges were first conditioned with 7 mL each of dichloromethane, methyl t-butyl ether, methanol, and ultrapure water. After all of the dissolved waters (500 mL×2) passed through cartridges at a flow rate of less than 5 mL/min under vacuum, the cartridges were dried using vacuum pressure. They were rinsed with 3 mL of methanol-water (40:60, v/v) solution, followed by 3 mL of water, and 3 mL of methanol-ammonia-water (10:2:88, v/v) solution. The cartridges were then eluted with 7 mL of methanol-methyl t-butyl ether (10:90, v/v). After evaporating the methanol-methyl t-butyl ether solution, the extract was derivatized with the addition of N,O-bis [trimethylsilyl]trifluoroacetamide (BSTFA).

The detailed extraction procedure for the target compounds in the filters followed the method of Li et al. (2004a, b). The filters containing trapped particulate matter were cut into fine pieces and acidified with 5 mL of 0.1 N HCl. The samples were then extracted with 5 mL of dichloromethane using a vortex mixer, and the organic layer was transferred to a 20-mL glass tube. This procedure was repeated two more times. The extract was concentrated under a gentle flow of nitrogen. After derivatization, the samples were cleaned using Florisil and eluted with hexane. The eluted sample was concentrated again to below 0.5 mL. The solution was then analyzed using

gas chromatography-mass spectroscopy (GC-MS; Agilent 6890N-5973N).

A DB-5MS (J&W Scientific) fused silica capillary column (30 m, 0.25 mm internal diameter, and 0.25 μm film thickness) was used with helium as the carrier gas at 1.2 mL. The GC-MS operating conditions were 70 eV ionization potential with the MS interface at 280°C and the electron multiplier voltage at -1800 eV. The injection port was maintained at 280°C, and the sample was injected in splitless mode followed by a purge 1 min after injection. The column oven temperature for analysis was initially 50°C for 2 min, and was then raised to 200°C at 30°C/min, to 230°C at 2°C/min, to 310°C at 30°C/min, and held for 10 min. A selected ion-monitoring method was used after an initial solvent delay time of 4 min.

Recovery of the target compounds was based on five replicate analyses of ultrapure water and filters spiked with OP, NP, BPA, and $NP_{1-2}EO$ standard solutions. The recoveries of OP, NP, BPA, and NP_{1-2} EO for dissolved water were 70±5, 82±7, 97±8, and 65±12%, respectively. The recoveries in the filters were 87±8, 92±11, 94±7, and 117±7%, respectively. The reproducibility of the target compounds for dissolved samples was examined in a duplicate analysis of all samples. The relative standard deviations (RSD) for OP, NP, BPA, and $NP_{1-2}EO$ were 9, 10, 5, and 7%, respectively. The recoveries of $^{13}C_6$-NP and BPA-d_{16} surrogate standards in real samples using this method were 55 and 72% for dissolved water samples and 73 and 66% for filter samples, respectively. The method detection limits were 0.001 μg/L for OP and BPA, 0.01 μg/L for NP, and 0.02 μg/L for $NP_{1-2}EO$.

Results and Discussions
Levels of phenolic compounds

The concentrations of NP, OP, BPA and $NP_{1-2}EO$ in six rivers flowing into Masan Bay are listed in Table 1. All of the target compounds were detected in all samples. Even in water samples from the rivers that receive only municipal wastewater, these compounds were found at concentrations much higher than the detection limit. This concurs with the considerable use of APEOs for household applications in Korea. Their concentrations also did not show as much variability over the sampling period as in other studies, suggesting that these compounds are introduced into the rivers continuously in large amounts and originate primarily from constant sources, such as industrial and domestic effluents, rather than from incidental sources, like runoff from areas contaminated with pesticide applications.

The phenolic compounds were dominated by NP_{1-2} EO (86.0%), followed by NP (10.1%), BPA (3.6%) and OP (0.3%). The concentrations of nonylphenolic compounds were much higher than those of OP, similar to the results found in other countries. This is consistent with the report that NPEOs account for about 82% of the APEO world market, followed by octylphenol polyethoxylates (15%) and small amounts of dodecylphenol and dinonylphenol polyethoxylates (1-2%; Naylor et al., 1992). The fact that the $NP_{1-2}EO$ concentrations were much higher than those of NP suggests that incompletely treated wastewater was discharged to the rivers. The concentrations of $NP_{1-2}EO$ were similar to or lower than those of NP in effluents from sewage and industrial treatment plants that use a secondary biological treatment process, because NPEOs are degraded

Table 1. Concentrations (μg/L) of phenolic compounds in 6 rivers flowing into Masan Bay

	Characteristics	NP	$NP_{1-2}EO$	OP	BPA
Hoewon River	Residential	0.15-0.55[a]	1.69-7.83	0.005-0.013	0.041-0.154
		(0.32)[b]	(4.90)	(0.008)	(0.102)
Sanho River	Industrial &	0.52-0.68	3.59-5.48	0.011-0.017	0.031-0.330
	Residential	(0.59)	(4.69)	(0.013)	(0.149)
Changwon River	Industrial &	0.61-1.14	3.28-7.45	0.014-0.041	0.059-0.467
	Residential	(0.82)	(5.88)	(0.025)	(0.195)
Nam River	Industrial	0.36-1.68	2.15-22.70	0.008-0.067	0.080-0.299
		(0.85)	(8.06)	(0.028)	(0.166)
Guidong River	Residential	0.30-0.50	3.19-5.38	0.006-0.019	0.076-0.610
		(0.39)	(4.17)	(0.011)	(0.227)
Sini River	Residential	0.20-0.38	1.42-5.00	0.003-0.016	0.024-0.138
		(0.27)	(2.76)	(0.007)	(0.086)
Total		0.15-1.68	1.42-22.70	0.003-0.067	0.024-0.610
		(0.54)	(4.90)	(0.015)	(0.154)

[a]concentration range, [b]concentration mean.

and then transformed into NP during anaerobic digestion in such treatment plants. These results have been reported in studies of surface waters collected near sewage and industrial treatment plants (Ferguson et al., 2001; Isobe et al., 2001, Tsuda et al., 2001).

NP, which is the most toxic of the analytes and has the greatest potential to bioaccumulate, ranged from 0.15 to 1.68 μg/L, with a mean of 0.54 μg/L. The highest concentrations of NP were recorded in the Nam (1.68 μg/L) and Changwon (1.14 μg/L) Rivers, which receive discharges from industrial complexes. There are many machine industry plants around these rivers, which use large quantities of NPEOs as cleaning agents, emulsifiers, and lube oils. This is in agreement with Li et al. (2004b), who reported that the major sources of NP pollution in Lake Shihwa were the effluents from the industrial area, rather than the municipal area.

Domestic sewage effluents can contain NP at up to hundreds of μg/L (Ahel et al., 1994; Naylor et al., 1995). By contrast, some industrial effluents, such as those originating from pulp mills and textile industries, can contain up to mg/L levels. In the UK, industrial effluents contain concentrations of NP that may exceed 100 μg/L (Tyler et al., 1998). Comparisons of NP concentrations in river from different locations of Korea and foreign countries are summarized in Table 2. The concentrations in European rivers have decreased over the last decade and are now generally below 1 μg/L for NP (Petrovic et al., 2003). This decrease has resulted from restrictions in the use of NPEOs in laundry detergents and the voluntary elimination of NPEO surfactants from industrial cleaning products. Most reported NP concentrations in rivers are lower than 10 μg/L, although Asian countries had higher concentrations than countries in Europe and North America (Table 2). NP concentrations in the present study fell within the

range reported for other areas. These comparable concentrations of NP may result from the fact that there are no major sources, such as pulp and textile industries and industrial or municipal wastewater treatment plants, in the area studied. In addition, the greatest concentration of NP reported in Korean sediments until now, 57 μg/g dry weight, was observed near an industrial dye complex (Kim et al., 2003).

$NP_{1-2}EO$ was found at concentrations ranging from 1.42 to 22.70 μg/L with a mean of 4.90 μg/L. The highest concentration for $NP_{1-2}EO$, 22.70 μg/L, was found in the Nam River, similar to NP. The concentrations of $NP_{1-2}EO$ increased with industrial activity (Table 1). Higher $NP_{1-2}EO$ levels were found in the rivers passing through industrial areas, such as the Nam and Changwon Rivers, while lower levels were found in rivers in municipal areas, such as the Guidong and Sini Rivers (Table 1). NP also showed a pattern similar to that of $NP_{1-2}EO$ (r=0.833, p< 0.0001). This indicates that the $NP_{1-2}EO$ and NP in the area studied had similar sources and that they were primarily industrial wastewater. The concentrations of $NP_{1-2}EO$ measured in this study were comparable to those reported in Canada (ND-11.8 μg/L for $NP_{1-2}EO$), the Netherlands (<0.18-8.70 μg/L for NPEOs), the UK (<0.6-46 μg/L for $NP_{1-2}EO$), China (1.0-97.6 μg/L for NPEOs), and Taiwan (2.8-25.7 μg/L for $NP_{1-3}EO$; Bennie et al., 1997; Blackburn et al., 1999; Ding et al., 1999; Shao et al., 2005; Vethaak et al., 2005).

The OP concentrations ranged from 0.003 to 0.067 μg/L with a mean of 0.015 μg/L. The highest concentration of OP, 0.067 μg/L, was found in the Nam River and the next highest concentration, 0.041 μg/L, was found in the Changwon River. The spatial distribution of the OP concentrations matched those for NP (r=0.903, p<0.0001) and $NP_{1-2}EO$ (r=0.802, p<0.0001). This suggests that applications of OPEOs resemble those of NPEOs, although they are not used widely in the area studied. The OP levels we measured were comparable to those in water samples from Japan (0.01-0.18 μg/L), Germany (0.0008-0.054 μg/L), and Canada (ND-0.47 μg/L; Bennie et al., 1997; Isobe et al., 2001; Kuch and Ballchmiter, 2001).

BPA was detected at concentrations of 0.024-0.610 μg/L and the mean was 0.154 μg/L. The highest concentration of BPA, 0.610 μg/L, was recorded in the Guidong River, which mainly receives municipal discharge. Relatively high BPA concentrations were also found in the Changwon, Nam, and Sanho Rivers, which are influenced by industrial activities. However the mean BPA concentrations in all of the rivers did

Table 2. Comparison of nonylphenol concentrations (μg/L) in river water with other areas

Location	NP	Reference
The present study	0.15 – 1.68	
Shihwa Lake, Korea	0.16 – 26.0	Li et al. (2004b)
Lake Biwa, Japan	0.11 – 3.08	Tsuda et al. (2000)
Yangtze River, China	0.1 – 7.3	Ding et al. (1999)
Lao-Jie River, Taiwan	1.8 – 10.0	Shao et al. (2005)
U.S.A. 30 Rivers	<0.11 – 0.64	Naylor et al. (1992)
St. Lawrence River, Canada	<0.01 – 0.92	Bennie et al. (1997)
Baden-Württemberg, Germany	<0.01 – 0.49	Bolz et al. (2001)
Switzerland	<LOD – 0.48	Ahel et al. (2000)

not differ significantly. The spatial distribution of BPA differed from those of the other compounds studied (r=-0.244-0.199, p>0.01), perhaps because of its source and properties. BPA, an important industrial compound, is widely used as a monomer in the production of polycarbonates, epoxy resins, and coatings. Likely sources of BPA in the environment are where it leaches from plastics and other epoxy products. Therefore, BPA levels higher than 1 μg/L would be very difficult to detect, except at sampling stations near point sources, such as BPA and epoxy manufacturing facilities. Moreover, BPA is readily diluted in and removed from surface water because it is very water soluble (120-300 mg/L at pH 7) and has a relatively short environmental half-life in water, i.e., 2.5-4 days (Staples et al., 1998). In comparison with reported BPA levels, the concentrations in our study area were comparable to the range reported for Japan (0.017-0.150 μg/L), Germany (ND-0.272 μg/L), and the Netherlands (<0.009-1.0 μg/L; Stachel et al., 2003; Furaichi et al., 2004; Vethaak et al., 2005).

Potential effects of nonylphenolic compounds on aquatic life

The measured concentrations of phenolic compounds were 1-2 orders of magnitude lower than the reported acute toxicity levels (hundreds of micrograms per liter, Comber et al., 1993). However, it was reported recently that much lower concentrations of phenolic compounds disrupt the endocrine systems of aquatic organisms (Jobling et al., 1996).

Nice et al. (2000) demonstrated the effects of NP on oyster embryos. The lowest concentration used in this experiment was 0.10 μg/L, which still produced significant malformations. Billinghurst et al. (1998) found effects on barnacle settlement starting with concentrations of 0.10 μg/L. They also published data on the effects on barnacles at 0.01 μg/L concentrations (Billinghurst et al., 2000). The lowest concentrations of NP and OP required to induce the production of vitellogenin, which is a sensitive biomarker of exposure to estrogenic chemicals, in the plasma of a male rainbow trout, *Oncorhynchus mykiss*, were 20.3 and 4.8 μg/L, respectively (Jobling et al., 1996). Naylor et al. (1992) reported that the no-observed-effect concentration (NOEC) of NP for length of *Mysidopsis bahia* at 28 days was 3.9 μg/L. Based on these toxicity reports, the US and European regulatory standards have been set at 1 μg/L. Based on a medaka partial life cycle, the Ministry of the Environment of Japan also proposed that the predicted no effect concentration of NP be 0.608 μg/L (Furaichi et al., 2004).

Jobling et al. (1996) stated that 30 μg/L for NP_2EO produced a significant increase in the plasma vitellogenin concentration and a decrease in the gonadosomatic index in maturing male rainbow trout during a 3-week exposure. The lowest-observed-effect concentration (LOEC), NOEC, and effective concentration at 10% inhibition (EC10) values reported in an exposure experiment with BPA on prosobranch snails were 0.0483, 0.0079, and 0.0139 μg/L, respectively (Stachel et al., 2003). The Netherlands recently proposed maximum permissible concentrations (MPC) in water of 0.33 μg/L for NP and 0.12 μg/L for $NP_{1-2}EO$ (Jonkers et al., 2005b). These results provide strong hints concerning the possible effects on wildlife.

Phenolic compounds, including NP and NPEOs, typically occur together as mixtures in the aquatic environment. Therefore, to assess risk more exactly and to reduce underestimates of the overall toxicity of the mixture, their toxic effects should not be considered separately. The Canadian Council of the Ministers of the Environment (Environment Canada, 2002) proposed the toxic equivalency (TEQ) approach, using toxic equivalency factors (TEFs), like dioxins and furans, to consider the additive effects of nonylphenolic compounds. NP TEFs for various nonylphenolic compounds were calculated for the Canadian Environmental Protection Agency (CEPA) assessment of NP (Environment Canada, 2002) and are listed in Table 3. The degradation products of NPEOs (e.g., NP, NP_1EO, and NP_2EO) are more toxic than the parent compounds. In the application of a TEQ approach to these compounds, potency is expressed relative to NP, the most toxic compound. The total concentration of NP and NP-equivalents in a sample can be calculated by multiplying all the levels in surface waters by the TEQs. The four equivalent NP concentrations of each sample are summed and the result is compared with

Table 3. Summary of relative toxicity of nonylphenolic and related compounds

Chemicals	Toxic equivalency factors (TEFs) relative to NP
Nonylphenol	1
NPnEO (1≤n≤8)	0.5
NPnEO (n≥9)	0.005
NP$_1$EC	0.005
NP$_2$EC	0.005
Octylphenol	1
OPnEO (1≤n≤8)	0.5
OPnEO (n≥9)	0.005
OP$_1$EC	0.005
OP$_2$EC	0.005

Table 4. Concentrations of nonylphenolic compounds (nonylphenol, octylphenol and $NP_{1-2}EO$) in sediments in nonylphenol equivalents and exceeding frequency of the guidelines for the protection of aquatic life

Stations	Concentrations in NP equivalents (µg/L)			Exceeding frequency of the guideline (1.0 µg/L)
	Minimum	Maximum	Mean	
Hoewon River	1.1	5.5	2.8	4
Sanho River	2.3	3.4	2.9	4
Changwon River	2.3	4.9	3.8	4
Nam River	1.8	13.1	4.9	4
Guidong River	1.9	3.2	2.5	4
Sini River	0.9	2.9	1.7	3

the freshwater quality guidelines for the protection of aquatic life, expressed as a concentration of NP (Table 4).

The frequency given in the guidelines was exceeded in 23 out of our 24 surface water samples and the total concentrations of NP-TEQs in all of the rivers ranged from 0.9 to 13.1 µg NP-TEQ/L (Table 4). These concentrations would be increased if compounds such as longer-chain NPEOs, OPEOs, and nonylphenoxy carboxylic acids (NPECs) were analyzed. In Canadian rivers, the reported concentrations were 0.00-8.62 µg NP-TEQ/L for $NP_{1-17}EOs+NP_{1-2}ECs$ (Berryman et al., 2004). A study of river waters in Taiwan reported 3.3-24.3 µg NP-TEQ/L using the compounds NP, $NP_{1-3}EOs$, and $NP_{1-3}ECs$ (Ding et al. 1999). According to Li et al. (2004b), the NP concentrations alone varied from 0.156 to 26.0 µg/L in the rivers flowing into Shihwa Lake. Based on these results, they asserted that the concentrations of phenolic compounds should be monitored until they fall below those known to induce biological effects. These results suggest that nonylphenolic compounds must be considered priority substances.

Estimated load of phenolic compounds entering the bay

Phenolic compounds can be transported at least several hundred kilometers out to sea (Bester et al., 2001; Vethaak et al., 2005). If these substances flow continuously into Masan Bay, a semi-enclosed bay, the wildlife inhabiting this area may be considerably affected given that little dilution occurs and organisms would remain in contact with contaminants for a relatively long time.

We measured the flow rates in each river, along with levels of the compounds, to estimate the load of nonylphenolic compounds entering Masan Bay and to identify which rivers are potential sources. The flow rates ranged from 2532 to 59,868 tons/day and the greatest mean rate was measured for the Sanho River (40,345 tons/day), followed by the Nam (39,793 tons/day), Changwon (20,607 tons/day), Hoewon

(10,476 tons/day), Guidong (5275 tons/day), and Sini (4497 tons/day) Rivers.

The loads of phenolic compounds were calculated by multiplying the concentrations of phenolic compounds in the river waters by the flow rates. The greatest mean load, 137 kg/year, was observed for the Nam River, followed by the Sanho (83 kg/year), Changwon (54 kg/year), Hoewon (18 kg/year), Guidong (9 kg/year), and Sini (5 kg/year) Rivers. The mean load in the Nam River was significantly higher than those observed for the Hoewon, Guidong, and Sini Rivers, which flow through municipal areas (ANOVA, $p<0.05$). This indicates that the pollution of rivers by phenolic compounds is associated with industrial effluents and that considerable amounts of these compounds are discharged through the Nam River into Masan Bay. To efficiently manage terrestrial pollutants such as phenolic compounds in the study area, it would be best to improve the connection rate of the sewage system in industrial complexes.

In conclusion, phenolic compounds such as NP and NPEOs are present in the six rivers studied, especially in industrial areas, at concentrations near those for which effects have been described, indicating that the rivers around Masan Bay are contaminated by phenolic compounds because of the widespread use of APEOs in households and factories. Therefore, it may be necessary to extend the monitoring program to other Special Management Coastal Areas, such as Ulsan, Busan, and Gwangyang Bay, which are highly urbanized, sewage-affected estuaries, and to take action to reduce these concentrations to safer levels.

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