Baseline

Edited by Bruce J. Richardson

The objective of BASELINE is to publish short communications on different aspects of pollution of the marine environment. Only those papers which clearly identify the quality of the data will be considered for publication. Contributors to Baseline should refer to 'Baseline—The New Format and Content' (*Mar. Pollut. Bull.* **42**, 703–704).

Alkylphenols in the core sediment of a waste dumpsite in the East Sea (Sea of Japan), Korea

Seongjin Hong [1], Kyung-Hoon Shin *

Department of Environmental and Marine Sciences, College of Science and Technology, Hanyang University, Ansan 426-791, Republic of Korea

Alkylphenols (APs) are degradation products of alkylphenol ethoxylates (APEOs) which have been used as detergents, wetting agents, dispersing agents and emulsifiers in various commercial, industrial and household surfactants (Giger et al., 1984; Renner, 1997). APEOs enter the natural environment mainly via direct urban or industrial inputs and sewage treatment plant (STP) effluents (Ahel et al., 1994; Ying et al., 2002; Li et al., 2008). Once AP and its ethoxylates have entered the aquatic environment, they are degraded by photo-oxidation and/or microbial activity in the water column and adsorb onto suspended particles, settle down and accumulate in the sediment and aquatic organisms according to their physico-chemical properties (Canadian Council of Ministers of the Environment (CCME), 2001; Ying et al., 2002; Correa-Reyes et al., 2007; Ferrara et al., 2008; Soares et al., 2008). The breakdown product, nonylphenol (NP), has more severe aquatic toxicity than its original surfactant and is a more persistent and lipophilic chemical (Servos, 1999). NP is also recognized as an endocrine-disrupting chemical which can cause estrogenic effects in fish and other aquatic organisms (Routledge and Sumpter, 1997). Therefore, some developed countries have banned the use of APEO products, but in many developing countries, they are still used because APEOs are inexpensive and have superior cleaning properties. In Korea, NP chemicals have been banned in kitchen cleaners since 2002, and all other domestic applications have been banned since 2007.

On the other hand, the Korean government has designated some areas in the waters off the coast of Gunsan, Ulsan and Pohang as maritime dumping zones since 1988. The dumpsite "Byung" in the East Sea (Sea of Japan) is located 125 km off the coast of Pohang (area: 3700 km^2; depth: 200–2000 m) (Fig. 1). Approximately 48 million tons of waste (excrements, livestock wastewater, domestic and industrial wastewater treatment sludge, etc.) have been discharged into the dumpsite "Byung" for 18 years. High concentrations of NP, nonylphenol monoethoxylate (NP1EO) and nonylphenol diethoxylate (NP2EO) have been detected in the effluents of many municipal STPs, and in industrial and domestic aerobically or anaerobically stabilized sludge samples (Giger et al., 1984; La Guardia et al., 2001; Nakada et al., 2006; Loyo-Rosales et al., 2007; Santos et al., 2007; Pothitou and Voutsa, 2008). Reportedly, sewage sludge included not only high concentrations of NP and NPEOs, but also heavy metals, polycyclic aromatic hydrocarbons (PAHs), polychlorinated biphenyls (PCBs) and polybrominated diphenyl ether (PBDE) (Wild et al., 1990; Knoth et al., 2007; Santos et al., 2007). Takada et al. (1994) also found sludge-derived PAHs in sediment from the DWDS 106, 185 km off the coast of New Jersey. Therefore, large amounts of waste dumping into the ocean can cause adverse effects to living organisms in the marine environment.

Carbon and nitrogen stable isotope ratios (δ^{13}C and δ^{15}N) are well known indicators of dumped waste-derived matter on seafloor sediment (Burnett and Schaeffer, 1980; Sweeney et al., 1980; Rogers, 2003). δ^{13}C values of sewage sludge samples were determined to have −25.7‰ and −26.0‰ from New York (Burnett and Schaeffer, 1980) and −23.5 ± 0.5‰ from Los Angeles (Myers, 1974) which were the values between terrestrial-derived (C3 plants: −26‰ to −28‰) and marine phytoplankton-derived (−19‰ to −22 ‰) organic matter (Fry and Sherr, 1984; Emerson and Hedges, 1988; Van Dover et al., 1992). Stable isotope ratios have been used to evaluate the influence of ocean dumping on sediments and suspended particles in the Deep Water Dump Site (DWDS) 106, 185 km off the coast of New Jersey and New York Bight dumpsite (Burnett and Schaeffer, 1980; Van Dover et al., 1992).

* Corresponding author. Tel.: +82 31 400 5536; fax: +82 31 416 6173.
  E-mail address: shinkh@hanyang.ac.kr (K.-H. Shin).
[1] Present address: Marine Environment and Pollution Prevention Research Department, Korea Ocean Research and Development Institute, Ansan 426-744, Republic of Korea.
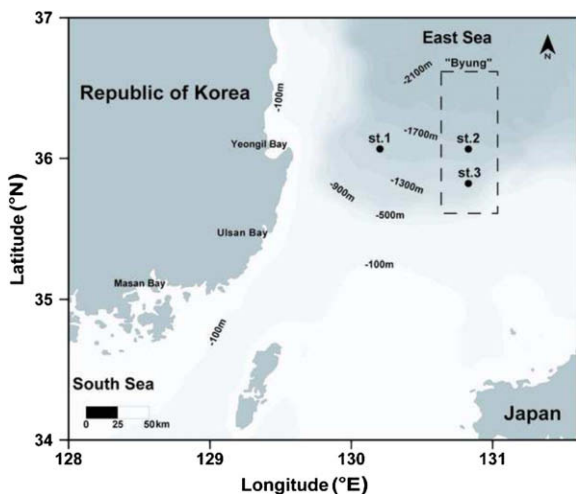
Fig. 1. Sampling sites of the non-dumpsite (st. 1) and dumpsite "Byung" (st. 2 and st. 3) in the East Sea (Sea of Japan), Korea.

We determined the distribution and characteristics of alkylphenolic chemicals in sediment cores collected from a dumpsite and a non-dumpsite in the East Sea, Korea. Sediment chronology in core samples were estimated by radioactive isotope techniques (^{210}Pb) and dumped waste-derived organic matter was distinguished using sewage tracers such as δ^{13}C and δ^{15}N. Also, contents of organic carbon (OC) and total nitrogen (TN) were determined for the influx pattern of organic matter over several decades. The present study is the first report on the comparison of APs and stable isotope ratios based on the sediment chronology to understand the dumpsite environment and anthropogenic disposals providing useful information for dumpsite management.

Sampling sites are shown in Fig. 1. Sediment samples were collected using a multiple corer (8 acrylic core liners, 8 cm i.d., 60 cm long, Marine Tech Inc., Korea) from two sites in the dumpsite "Byung" (st. 2 and st. 3) and non-dumpsite (st. 1) of the East Sea during a cruise of the R/V Tamyang in May 2007. Each sediment core was transferred into 100 mL amber glass bottles in slices of 2 cm intervals (total 20 cm) and immediately frozen at −20 °C until analysis. Sediment samples were freeze-dried, homogenized by grinding and stored in a vacuum desiccator before extraction.

The procedure of extraction for alkylphenolic chemicals analysis in sediment was followed from Li et al. (2003) and European Standard (2007). Briefly, about 5 g of sediment sample was weighed and transferred into a 50 mL Teflon tube, and then 100 μL of 1 mg L^{-1} of surrogate standards (bisphenol-A-*d16*, Isotec, Miamisburg, OH, USA and *n*-NP1EO ring-^{13}C$_6$, CIL, Andover, MA, USA) was added for quality control. Five milliliters of dilute water (Milli-Q system), acetone (J.T. Baker, Phillipsburg, NJ, USA) and hexane (J.T. Baker) were added, and then placed on a mechanical shaker. Tubes were shaken for 2 h at 250 strokes per min. The organic phase was transferred to a 100 mL flask and all extraction procedures were repeated twice. Residual water was removed from the extracting solvent through a funnel filled with anhyd sodium sulfate (fine powder, Fluka, Buchs, Switzerland) and concentrated to 1 mL under a gentle stream of nitrogen gas on a heating block at 30 °C. Extracts were derivatized with *N,O*-bis-(trimetylsilyl) trifluoroacetamide (BSTFA with 1% TMCS, Sigma–Aldrich, Saint Louis, MO, USA) using the silylation treatment kit and cleaned up with 1 g of activated Florisil (60–100 mesh, Sigma–Aldrich) with 7 mL of hexane (Li et al., 2001). GC internal standards were added and the sample was concentrated to 1 mL for GC–MS analysis. GC–MS analyses for NP, NP1EO, NP2EO, octylphenol (OP) and bisphenol-A (BPA) were performed using a gas chromatograph (Shimadzu GC-2010) coupled with a mass spectrometer (Shimadzu GCMS-QP2010 plus). A capillary column DB-5MS (30 m long x 0.25 mm i.d.; film thickness: 0.25 μm, J&W Scientific, Folsom, CA, USA) was utilized for the separation. The mass spectrometer was operated in electron impact ionization (EI) mode at 70 eV with the selected ion monitoring. Method detection limits for OP, BPA, NP, NP1EO and NP2EO were 1.07, 1.08, 2.11, 12.2 and 22.3 ng g^{-1}, respectively. For quality control, surrogate recoveries of bisphenol-A-*d16* and *n*-NP1EO ring-^{13}C$_6$ were 86.1–95.1% and 82.1–121%, respectively.

Freeze-dried sediment samples were treated for 24 h with 1 M HCl to remove inorganic carbon. Following neutralization with distilled water, sediments were again dried (Cifuentes et al., 1988). Four to eight milligrams of sediment was packed in tin foil capsules prior to analysis. The OC, TN (%), δ^{13}C and δ^{15}N in sediment samples were measured using an elemental analyzer (EA, Costech, ECS4010) – isotope ratio mass spectrometer (IRMS, Finnigan MAT, Delta plus). Stable isotope ratios were expressed in per-mil (‰) notation relative to the Pee Dee Belemnite (PDB) standard. The analytical precision of stable isotopic analyses of carbon and nitrogen are ± 0.15‰ and ± 0.21‰, respectively.

Sedimentation rates and sediment chronology in three sediment cores were estimated by ^{210}Pb (half-life: 22.3 y) dating techniques at the Korea Basic Science Institute (KSBI). Radioisotope activities of ^{210}Pb and ^{226}Ra were measured for three sediment cores at 2 cm intervals using a well-type HPGe gamma detector (GCW3523, Canberra Inc., USA) calibrated with IAEA certified reference materials (RGU-1, RGTh-1 and RGK-1), and determined following the method proposed by Kim and Burnett (1983). The average sediment accumulation rate based on excess ^{210}Pb was nearly uniform at 0.20 cm y^{-1} from a depth of 0 to 20 cm in the sediment core from the non-dumpsite, st. 1. At the dumpsite (st. 2), by contrast, the average sediment accumulation rates were 0.49 cm y^{-1} from 0 to 8 cm and 0.21 cm y^{-1} and from 8 to 20 cm in the sediment core. The average sedimentation rate values at st. 3 were 0.35 cm y^{-1} for 0–10 cm and 0.16 cm y^{-1} for 10–20 cm in the sediment core. Sedimentation rates observed at the dumpsites were more than two fold larger since the late 1980s and early 1990s. Increased sedimentation rates may be due to larger fluxes of sinking particles, which are related to direct waste disposal at sea. Sedimentation rates at deeper layers of the sediment cores in this study were similar to previously published data (Hong et al., 1997) from the same regions in the East Sea.

Vertical profiles of alkylphenolic chemicals are shown in Fig. 2a. A small amount of NP was found at the non-dumpsite (st. 1), whereas high levels of NP were detected at the dumpsites (st. 2 and st. 3). NP was mostly detected at the depths above 10 cm. The highest NP concentrations were at 2–4 cm in the sediment core of the dumpsite. There were similar trends in the OP and BPA concentration profiles. According to the ^{210}Pb dating, APs increased gradually from the late 1980s and early 1990s, peaked after the year 2000, and subsequently decreased. This profile can be associated with the amount of waste disposal into the "Byung" since 1988, which increased from 1989 to 2005 and decreased since 2005 (Fig. 3). The relatively low concentrations of APs at the surface sediment (0–2 cm depth) of the dumpsite might be due to the ocean dumping management system, which has been based on the guidelines of discharge permits and on the reduction of ocean disposal in terms of recent regulations (since 2006) of the Korean government related to international regulations (London Convention 1972 and London Protocol 1996). Concentration levels of APs were higher in st. 2 than in st. 3, which could be explained by the different methods of waste disposal at sea. St. 2 is a centralized dumping area where wastes have been dumped while dumping vessels are stopped. St. 3 is a diffused dumping area where waste was dumped while sailing (>4 knots). The levels may also
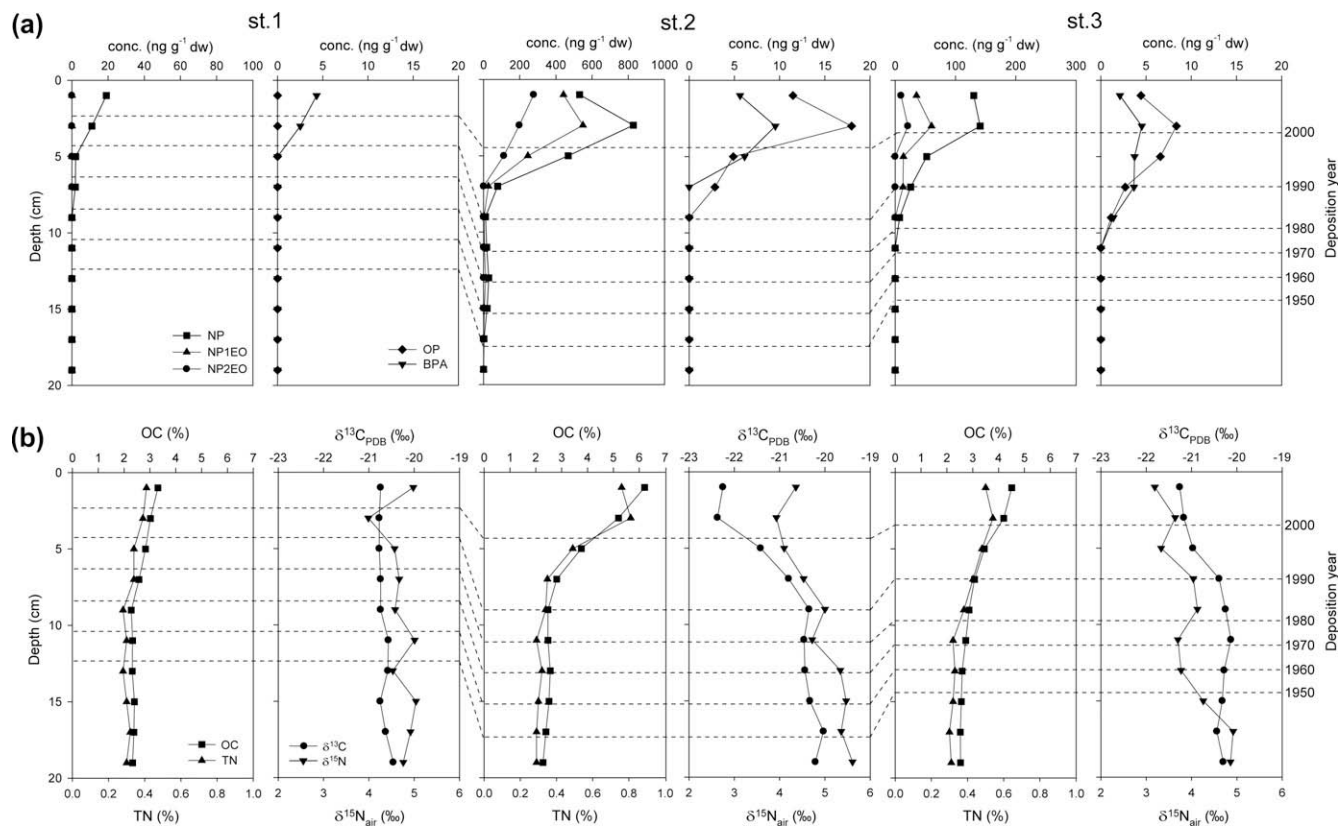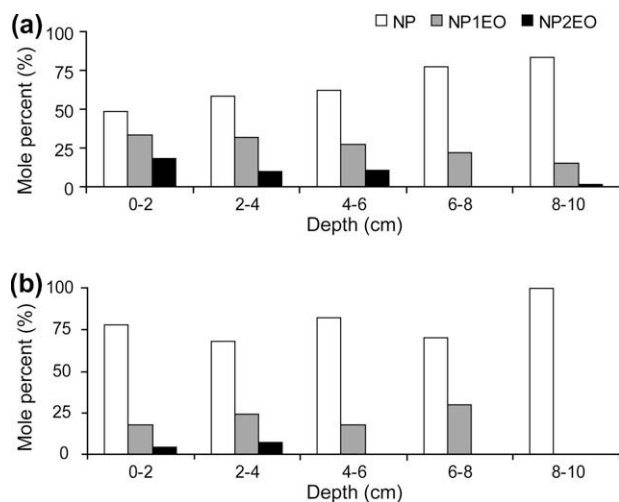
Fig. 2. Vertical profiles of (a) NP, NP1EO, NP2EO, OP and BPA, (b) OC, TN, $\delta^{13}C$ and $\delta^{15}N$ from non-dumpsite sediment (st. 1) and dumpsite sediment ("Byung", st. 2 and st. 3) in the East Sea (dotted lines: deposition year by ^{210}Pb dating).
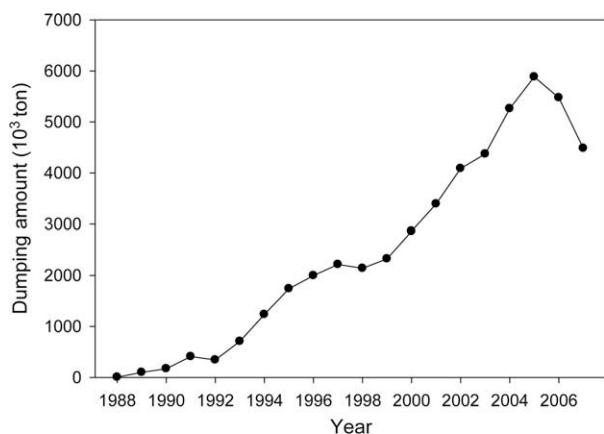
Fig. 3. Amount of waste disposal into the dumpsite "Byung" in the East Sea since 1988.

Fig. 4. Relative mole percent (%) of NP, NP1EO and NP2EO in core sediment (0–10 cm) samples from the dumpsite "Byung" ((a) st. 2, (b) st. 3) in the East Sea.

be influenced by the inhomogeneous deposition of dumped wastes.

The relative mole percent of nonylphenolic chemicals in the dumpsite is shown in Fig. 4. NP was the most abundant chemical in sediment core samples, followed by NP1EO and NP2EO. The depth distribution of nonylphenolic chemicals showed a peak at the 2–4 cm depth, except for NP2EO at st. 2 (Fig. 2a). The relative mole percent of NP indicated increases with deeper core depths at st. 2 and st. 3, possibly due to the results of *in situ* biotransformation from NP1EO and/or NP2EO to NP by microbial activity. The observed relative mole percentage of NP at st. 3 was higher than that at st. 2, suggesting that st. 3 received less fresh nonylphenolic chemicals influx than st. 2 (Li et al., 2008). Ferguson

et al. (2003) investigated *in situ* transformation from NP1EO to NP in the upper portion of the sediment core of Jamaica Bay, NY, which was impacted by sewage inflow. They discussed that NPEOs would degrade more easily via cleavage or oxidation than NP because of the significant difference in their chemical structures.

Vertical profiles of NP showed a peak at a depth of 2–4 cm in the dumpsite "Byung" (Fig. 2a), followed by a decrease with depth that may be reflective of both the amount of waste disposal at sea (Fig. 3) and the persistence of the dumpsite sediment. Shang et al. (1999) determined the persistence of NPEOs (ethoxy

Table 1
Total TEQ values (ng g^{-1} TEQ) of alkylphenolic chemicals in the surface sediment (0–6 cm) from the non-dumpsite (st. 1) and dumpsite "Byung" (st. 2 and st. 3) in the East Sea.

Site	Depth (cm)	Chemical concentration[a] (ng g^{-1} dw) × TEF[b]				Total TEQ[c]
		NP	NP1EO	NP2EO	OP	
St. 1	0–2	5.7	0.0	0.0	0.0	5.7
	2–4	3.7	0.0	0.0	0.0	3.7
	4–6	0.7	0.0	0.0	0.0	0.7
St. 2	0–2	85.5	71.1	44.6	0.9	202.1
	2–4	159.3	105.7	38.1	1.8	304.9
	4–6	124.5	65.2	29.8	1.6	221.1
St. 3	0–2	28.9	7.8	2.2	0.5	39.4
	2–4	33.5	14.4	5.0	1.1	54.0
	4–6	15.2	4.0	0.0	1.1	20.3

[a] Chemical concentration: mean values (n = 3, RSD < 9%) and normalized to 1% TOC.
[b] TEF (toxic equivalency factors relative to NP): NP = 1; NP1EO, NP2EO = 0.5; OP = 1, from CCME, 2001.
[c] Total TEQ (alkylphenolic chemicals expressed as toxic equivalent of NP): sum of the chemical concentration × TEF, from CCME, 2001.

chain = 0–20) in core sediments near a municipal outfall exhibiting little degradation in the sediment (estimated half-life > 60 y). Previous studies on NPEOs decay kinetics show a wide range of half-lives for NPEOs, from shorter than a day to several decades in the environment (Ferguson and Brownawell, 2003). Additionally, NPEO degradation rates are strongly influenced by oxygen concentrations, temperature, organic carbon contents, electron acceptors (such as sulfate, nitrate and iron (III)) and microbial community activity (Ferguson et al., 2003; Ferguson and Brownawell, 2003; Lu et al., 2008a,b). Therefore, persistence of nonylphenolic chemicals in the sediment of the dumpsite "Byung" should be different according to various environmental factors. Further investigation is needed to establish such a correlation.

Total toxic equivalent (total TEQ) values were calculated to assess pollution levels using the concentrations of alkylphenolic chemicals and their toxic equivalency factors (TEF) at the surface sediment (0–2, 2–4 cm depth) in the dumpsite "Byung" (Table 1). Although the obtained total TEQ values at the dumpsite were not higher than the Interim Sediment Quality Guidelines (1 μg g^{-1}, normalized to 1% TOC; assumed that the Koc (partition coefficient) values of each chemical are the same) (CCME, 2001) expressed on a TEQ basis, the benthic environment could be affected by adverse effects such as endocrine disruption, bioaccumulation and toxicity to living organisms on a long-term basis. Dumped sewage comprises not only APs but also pollutants such as PCBs, PAHs, polychlorinated dibenzo-*p*-dioxins and dibenzofurans (PCDD/Fs) and trace metals (Wild et al., 1990; Santos et al., 2007; Ju et al., 2009). Ju et al. (2009) investigated the concentration of organic pollutants from WWTP and STP sludge samples, which have been disposed by ocean dumping in Korea. The concentrations of organic pollutants (PCDD/Fs, PCBs, OCPs, PAHs and chlorophenols) in sludge samples showed various levels, depending on their different sources. The dumping area "Byung" is located near habitats for red crabs and snails. Therefore, it is necessary to investigate the potential risks of organic pollutants, including APs, to benthic organisms near the dumpsite "Byung".

Vertical profiles of OC, TN, δ^{13}C and δ^{15}N in sediment from the dumpsite and non-dumpsite are presented in Fig. 2b. Maximum amounts of OC and TN were measured in the surface slice (0–2 cm depth) of the sediment cores at each site. OC and TN contents showed decreasing trends with increasing core depth. The maximum contents of OC and TN in the surface sediment might be affected by the initial rapid degradation of labile organic matter during early diagenesis at the sediment–water interface. OC and TN contents in the upper layers from the dumpsite (st. 2 and st. 3) were about 2–3 times higher compared with the non-dumpsite (st. 1). Deposition fluxes of OC and TN showed rapid increases with nonylphenolic chemicals from the late 1980s and early 1990s,
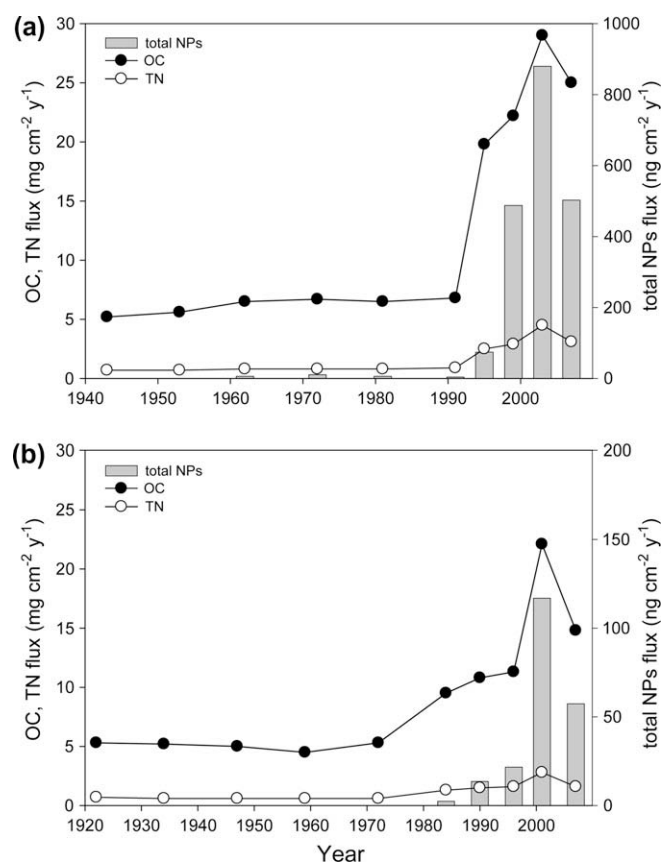
Fig. 5. Deposition fluxes of OC, TN and total NPs (NP + NP1EO + NP2EO) of the dumpsite "Byung" ((a) st. 2, (b) st. 3) in the East Sea (Flux = $C_i \rho_i \gamma_i$; where C_i is the measured concentration of total NP and the content of OC and TN in the sediment layer i. ρ_i (g cm^{-3}) and γ_i (cm y^{-1}) are the dry mass and sedimentation rate, respectively).

which was profoundly linked to the amount of waste disposal into the dumpsite "Byung" (Fig. 5). The benthic environment in dumpsite "Byung" has been affected by an excess of ocean dumping.

The vertical distribution of δ^{13}C showed constant values for all depths (0–20 cm) at st. 1, whereas lighter values in st. 2 and st. 3 were present at 0–10 cm depth, with the lightest value at 2–4 cm depth and relatively heavier values at 0–2 cm depth. The δ^{15}N values of the bulk sediment core in dumpsite "Byung" were not significantly different from that in the non-dumpsite (Fig. 2b). δ^{13}C values are well known land waste-derived organic matter indicators (Burnett and Schaeffer, 1980; Sweeney et al., 1980; Rogers,

2003). The end-member value of non-affected by ocean dumping in this study can be −20.29‰ which was the average value from the 10 to 20 cm depth at st. 2 and st. 3. The $\delta^{13}C$ values in the upper depths from the dumpsite sediment cores (st. 2 and st. 3), which were affected by ocean dumping, had lighter $\delta^{13}C$ values (maximum ∼2‰) than the end-member value. Results showed a good correlation ($r^2 > 0.9$) between $\delta^{13}C$ values and total NP (NP + NP1EO + NP2EO) concentrations in two core sediments from the dumpsite "Byung". This relationship indicates that most of the nonylphenolic chemicals originated from dumped wastes. The $\delta^{13}C$ value in bulk sediment is relatively easy and quick to measure, and reflects the consequences of waste disposal at sea. Accordingly, we suggest that spatial and vertical distributions of $\delta^{13}C$ values can be valuable indicators of dumped waste-derived organic matter in sediment from the dumpsite "Byung". $\delta^{15}N$ values have been used for tracers of sewage-derived organic matter in sediment, biota, sewage sludge and effluent from the inner bay, coastal regions, continental shelf and near the effluent outfall (Sweeney and Kaplan, 1980; Tucker et al., 1999; Rogers, 2003). However, the observed $\delta^{15}N$ values in this study can presumably be reflected by interactions of various processes in the water column such as microbial degradation of organic matter, primary production (new production and/or regenerative production), food chain, etc. Therefore, we suggest that $\delta^{15}N$ values are not suitable as dumped waste-derived organic matter tracers in sediment from the dumpsite "Byung" compared to $\delta^{13}C$ values.

In conclusion, high concentrations of alkylphenolic chemicals in the dumpsite sediment are a result of waste disposal into the sea, exhibiting high sedimentation rates. Deposition fluxes of OC, TN and nonylphenolic chemicals showed rapid increases from the late 1980s and early 1990s, which were profoundly correlated to the amount of waste disposal into the dumpsite. The $\delta^{13}C$ values in the dumpsite sediment had lighter values which were affected by ocean dumping, so spatial and vertical distributions of $\delta^{13}C$ values can be valuable indicators of dumped waste-derived organic matter. These results provide historical pollution records for alkylphenolic compounds, as well as useful information about the benthic environment in the dumpsite "Byung", East Sea.

References

Ahel, M., Giger, W., Koch, M., 1994. Behaviour of alkylphenol polyethoxylate surfactants in the aquatic environment I. Occurrence and transformation in sewage treatment. Water. Res. 28, 1131–1142.

Burnett, W.C., Schaeffer, O.A., 1980. Effect of ocean dumping on $^{13}C/^{12}C$ ratios in marine sediments from the New York Bight. Estuar. Coast. Mar. Sci. 11, 605–611.

Canadian Council of Ministers of the Environment (CCME). 2001. Canadian sediment quality guidelines for the protection of aquatic life: nonylphenol and its ethoxylates. In: Canadian Environmental Quality Guidelines 1999. Canadian Council of Ministers of the Environment, Winnipeg.

Cifuentes, L.A., Sharp, J.H., Fogel, M.L., 1988. Stable carbon and nitrogen isotope biogeochemistry in the Delaware estuary. Limnol. Oceanogr. 33, 1102–1115.

Correa-Reyes, G., Viana, M.T., Marquez-Rocha, F.J., Licea, A.F., Ponce, E., Vazquez-Duhalt, R., 2007. Nonylphenol algal bioaccumulation and its effect through the trophic chain. Chemosphere 68, 662–670.

Emerson, S., Hedges, J.I., 1988. Processes controlling the organic carbon content of open ocean sediments. Paleoceanography 3, 621–634.

European Standard, 2007. Solids, sludged and treated bio-waste – Determination of nonylphenols (NP) and nonylphenol-mono- and diethoxylates – Method by gas chromatography with mass selective detection (GC–MS). TC BT WI. CSS99040.

Ferguson, P.L., Bopp, R.F., Chillrud, S.N., Aller, R.C., Brownawell, B.J., 2003. Biogeochemistry of nonylphenol ethoxylates in urban estuarine sediments. Environ. Sci. Technol. 37, 3499–3506.

Ferguson, P.L., Brownawell, B.J., 2003. Degradation of nonylphenol ethoxylates in estuarine sediment under aerobic and anaerobic conditions. Environ. Toxicol. Chem. 22, 1189–1199.

Ferrara, F., Ademollo, N., Delise, M., Fabietti, F., Funari, E., 2008. Alkylphenols and their ethoxylates in seafood from the Tyrrhenian Sea. Chemosphere 72, 1279–1285.

Fry, B., Sherr, E.B., 1984. $\delta^{13}C$ measurements as indicators of carbon flow in marine and freshwater ecosystem. Contrib. Mar. Sci. 27, 13–47.

Giger, W., Brunner, P.H., Schaffner, C., 1984. 4-Nonylphenol in sewage sludge: accumulation of toxic metabolites from nonionic surfactants. Science 225, 623–625.

Hong, G.H., Kim, S.H., Chung, C.S., Kang, D.-J., Shin, D.-H., Lee, H.J., Han, S.-J., 1997. 210Pb-derived sediment accumulation rates in southwestern East Sea (Sea of Japan). Geo-Mar. Lett. 17, 126–132.

Ju, J.-H., Lee, I.-S., Sim, W.-J., Eun, H., Oh, J.-E., 2009. Analysis and evaluation of chlorinated persistent organic compounds and PAHs in sludge in Korea. Chemosphere 74, 441–447.

Kim, K.H., Burnett, W.C., 1983. γ-Ray spectrometric determination of uranium-series nuclides in marine phosphorites. Anal. Chem. 55, 1796–1800.

Knoth, W., Mann, W., Meyer, R., Nebhuth, J., 2007. Polybrominated diphenyl ether in sewage sludge in Germany. Chemosphere 67, 1831–1837.

La Guardia, M.J., Hale, R.C., Harvey, E., Mainor, T.M., 2001. Alkylphenol ethoxylates degradation products in land-applied sewage sludge (biosolids). Nature 35, 4798–4804.

Li, D., Dong, M., Shim, W.J., Yim, U.H., Hong, S.H., Kannan, N., 2008. Distribution characteristics of nonylphenolic chemicals in Masan Bay environments, Korea. Chemosphere 71, 1162–1172.

Li, D., Oh, J.-R., Park, J., 2003. Direct extraction of alkylphenols, chlorophenols and bisphenol A from acid-digested sediment suspension for simultaneous gas chromatographic mass spectrometric analysis. J. Chromatogr. A 1012, 207–214.

Li, D., Park, J., Oh, J.-R., 2001. Silyl derivatization of alkylphenols, chlorophenols, and bisphenol A for simultaneous GC/MS determination. Anal. Chem. 73, 3089–3095.

Loyo-Rosales, J., Rice, C., Torrents, A., 2007. Fate of octyl- and nonylphenol ethoxylates and some carboxylated derivatives in three American wastewater treatment plants. Environ. Sci. Technol. 41, 6815–6821.

Lu, J., He, Y., Wu, J., Jin, Q., 2008a. Aerobic and anaerobic biodegradation of nonylphenol ethoxylates in estuary sediment of Yangtze River, China. Environ. Geol.. doi:10.1007/s00254-008-1276-2.

Lu, J., Jin, Q., He, Y., Wu, J., Zhang, W., Zhao, J., 2008b. Anaerobic degradation behavior of nonylphenol polyethoxylates in sludge. Chemosphere 71, 345–351.

Myers, E.P., 1974. The Concentration and Isotopic Composition of Carbon in Marine Sediments Affected by Sewage Discharge. Ph D. Dissertation, California Institute of Technology, Pasadena.

Nakada, N., Tanishima, T., Shinohara, H., Kiri, K., Takada, H., 2006. Pharmaceutical chemicals and endocrine disrupters in municipal wastewater in Tokyo and their removal during activated sludge treatment. Water. Res. 40, 3297–3303.

Pothitou, P., Voutsa, D., 2008. Endocrine disrupting compounds in municipal and industrial wastewater treatment plants in Northern Greece. Chemosphere 73, 1716–1723.

Renner, R., 1997. European bans on surfactant trigger transatlantic debate. Environ. Sci. Technol. 31, 316A–320A.

Rogers, K.M., 2003. Stable carbon and nitrogen isotope signatures indicate recovery of marine biota from sewage pollution at Moa Point, New Zealand. Mar. Pollut. Bull. 46, 821–827.

Routledge, E.J., Sumpter, J.P., 1997. Structure features of alkylphenolic chemical associated with estrogenic activity. J. Biol. Chem. 272, 3280–3288.

Santos, J.L., Gonzalez, M.D.M., Aparcio, I., Alonso, E., 2007. Monitoring of di-(2-ethylhexyl) phthalate, nonylphenol, nonylphenol ethoxylates, and polychlorinated biphenyls in anaerobic and aerobic sewage sludge by gas chromatography–mass spectrometry. Int. J. Environ. Anal. Chem. 87, 1033–1042.

Servos, M.R., 1999. Review of the aquatic toxicity, estrogenic responses and bioaccumulation of alkylphenols and alkylphenol polyethoxylates. Water Qual. Res. J. Can. 34, 123–177.

Shang, D.Y., Macdonald, R.W., Ikonomou, M.G., 1999. Can. Environ. Sci. Technol. 33, 1366–1372.

Soares, A., Guieysse, B., Jefferson, B., Cartmell, E., Lester, J.N., 2008. Nonylphenol in the environment: a critical review on occurrence, fate, toxicity and treatment in wastewaters. Environ. Int. 34, 1033–1049.

Sweeney, R.E., Kalil, E.K., Kaplan, I.R., 1980. Characterisation of domestic and industrial sewage in southern California coastal sediments using nitrogen carbon, sulphur and uranium tracers. Mar. Environ. Res. 3, 225–243.

Sweeney, R.E., Kaplan, I.R., 1980. Tracing flocculant industrial and domestic sewage transport on San Pedro Shelf, southern California, by nitrogen and sulfur isotope ratios. Mar. Environ. Res. 3, 215–224.

Takada, H., Farrington, J.W., Bothner, M.H., Johnson, C.G., Tripp, B.W., 1994. Transport of sludge-derived organic pollutants to deep-sea sediments at deep water dump site 106. Environ. Sci. Technol. 28, 1062–1072.

Tucker, J., Sheats, N., Giblin, A.E., Hopkinson, C.S., Montoya, J.P., 1999. Using stable isotopes to trace sewage-derived material through Boston Harbor and Massachusetts Bay. Mar. Environ. Res. 48, 353–375.

Van Dover, C.L., Grassle, J.F., Fry, B., Garritt, R.H., Starczak, V.R., 1992. Stable isotope evidence for entry of sewage-derived organic material into a deep-sea food web. Nature 360, 153–156.

Wild, S.R., Waterhouse, K.S., McGrath, S.P., Jones, K.C., 1990. Organic contaminants in an agricultural soil with a known history of sewage sludge amendments: polynuclear aromatic hydrocarbons. Environ. Sci. Technol. 24, 1706–1711.

Ying, G.-G., Williams, B., Kookana, R., 2002. Environmental fate of alkylphenols and alkylphenol ethoxylates – a review. Environ. Int. 28, 215–226.

Metal accumulation in sea urchins and their kelp diet in an Arctic fjord (Kongsfjorden, Svalbard)

In-Young Ahn *, Jungyoun Ji, Hyun Park

Korea Polar Research Institute of Korea Ocean Research and Development Institute (KORDI), Songdo Technopark, 7-50 Songdo-dong, Yeonsu-gu, Incheon 406-840, Republic of Korea

The Arctic marine environment is a significant repository of anthropogenic pollutants, including heavy metals (Bard, 1999; Muir et al., 1999; AMAP, 2002, 2005). Elevated concentrations of some toxic metals such as Hg, Pb, Se, and Cd have been reported from several marine birds and mammals (Ronald et al., 1984; Wagemann et al., 1996; Bard, 1999; Muir et al., 1999; Fant et al., 2001; AMAP, 2002, 2005; Dehn et al., 2006). Studies on metal accumulation in prey organisms in Arctic waters have been limited to some major pelagic species such as zooplankton and fish (Ritterhoff and Zauke, 1997; Dehn et al., 2006), despite the fact that a variety of prey organisms, including benthic invertebrates, constitute a major part of the diet for many Arctic marine mammals (Bustamante et al., 2004; Dehn et al., 2006, 2007). Several studies have already reported higher concentrations of Cd in Arctic seals that prey on benthic invertebrates rather than fish (Bustamante et al., 2004; Dehn et al., 2005).

Sea urchins are an important prey item of predatory organisms at higher trophic levels, such as fish, seals, and whales (Muir et al., 1999), and are thus considered to contribute significantly to the transfer of metals and other pollutants to higher trophic levels. Apparently, by virtue of their commercial importance, most studies on sea urchins related to metals have focused on metal toxicity to sea urchin embryos or larval development (Radenac et al., 2001; Kobayashi and Okamura, 2005; Gopalakrishnan et al., 2008), effects on adult reproduction (Au et al., 2001), and development of molecular biomarkers to detect metal exposure (Aspholm and Hylland, 1998; Riek et al., 1999; Geraci et al., 2004). Few studies have examined metal accumulation in natural sea urchin populations (Bohn, 1979; Sadiq et al., 1996; Aspholm and Hylland, 1998; Strorelli et al., 2001; Deheyn et al., 2005), despite their abundance and wide distribution. Therefore, further study to elucidate metal accumulation through the food web is warranted.

Sea urchins of the genus *Strongylocentrotus* have a wide geographic distribution, occurring in the North Atlantic, North Pacific, and Arctic Oceans (Bohn, 1979; Bazhin, 2002; Gagnon et al., 2004; Addison and Hart, 2004, 2005), including the Svalbard Islands, a key area in the Arctic Monitoring and Assessment Programme (AMAP, 1996). The green sea urchin *S. droebachiensis* is reportedly a key species on shallow rocky subtidal substrata in Kongsfjorden on West Spitsbergen, Svalbard (Hop et al., 2002; Kaczmarek et al., 2005; Beuchel and Gulliksen, 2008). Hop et al. (2002) reported that the coverage of laminarian kelps fluctuated widely in this location, and heavily grazed areas devoid of kelps were commonly associated with high densities of *S. droebachiensis*. The morphologically similar species *S. pallidus* occurs concomitantly in such areas, but is less abundant (Hop et al., 2002).

This study aimed to assess the metal accumulation of the sea urchins *Strongylocentrotus* spp., and further to improve the understanding of metal transfer at lower trophic levels in Arctic marine ecosystems. Sea urchins (*S. droebachiensis, S. pallidus*) were collected from shallow subtidal waters (5–15 m) of Kongsfjorden in two consecutive summers, late July to early August 2003 and late June 2004, from three stations (A, B, and C) along the shoreline (Fig. 1). Kongsfjorden (79°N, 12°E) is a glacial fjord that is influenced by both Atlantic and Arctic water masses, and contains a mixture of boreal and Arctic flora and fauna (Hop et al., 2002). As an important feeding ground for marine mammals and seabirds, Kongsfjorden has received extensive research interest, and is currently regarded as a suitable site for investigating impacts of global climate change. Hydrographic and oceanographic features of the fjord are described in detail in Svendsen et al. (2002). The sampling stations were chosen to represent varying degrees of glacial runoff influence, as reflected in surface water temperature and salinity regime (Svendsen et al., 2002; Kang et al., 2003). Station A was adjacent to the pier, had a medium degree of melt-water influence, and was likely to be the most polluted. Station B, near the inlet of the fjord, was least influenced by melt-water, and was likely to be least influenced by anthropogenic activities. Station C was closest to melt-water runoff sources and submerged glaciers and was most influenced by melt-water.

Laminarian kelps (*Laminaria saccharina, L. digitata*, and *Alaria esculenta*) and seawater samples were also collected from the sea urchin habitats to elucidate metal accumulation through a food web. Laminarian kelps are preferred foods of sea urchins in shallow rocky subtidal habitats (Miller and Mann, 1973; Vadas, 1977; Keats et al., 1984; Lemire and Himmelman, 1996; Minor and Scheibling, 1997; Gagnon et al., 2004; Wessels et al., 2006), and are also reported to have high rates of growth and reproduction (Vadas, 1977; Keats et al., 1984; Lemire and Himmelman, 1996; Minor and Scheibling, 1997; Lyons and Scheibling, 2007). Wessels et al. (2006) found that *S. droebachiensis* in Kongsfjorden have a significant preference for leathery seaweeds like *Laminaria* and *Alaria*.

Collected sea urchins were dissected and freeze-dried in the lab at Ny-Ålesund. Test diameter of each individual sea urchin was determined to the nearest 0.01 mm with vernier calipers. The soft

* Corresponding author. Tel.: +82 (0)32 260 6150; fax: +82 (0)32 260 6109.
E-mail address: iahn@kopri.re.kr (I.-Y. Ahn).