OCCURRENCE OF SYNTHETIC MUSK COMPOUNDS (SMCS) AS EMERGING CONTAMINANTS IN NAKDONG RIVER BASIN, KOREA

Seo C-D[1,2], Lee I-S[2] and Oh J-E[2]

[1] Water Quality Institute, Busan Water Authority, Republic of Korea; [2] Department of Civil and Environmental Engineering, Pusan National University, Busan 609-735, Republic of Korea

Abstract

The aims of this paper were to investigate and confirm the occurrence and distribution patterns of synthetic musk compounds(SMCs) in Nakdong river basin (i.e., mainstream and its tributaries), Korea. Four (i.e., HHCB, AHTN, AHDI and ADBI) out of six polycyclic musk compounds (PMCs) and one (i.e., Musk xylene) out of 5 nitro musk compounds (NMCs) were detected in 28 sampling sites and HHCB (>50%) was predominant compound followed by MK (16.7%) and AHTN (9.0%). The total concentration levels of SMCs in surface water samples ranged from N.D. to 2147 ng/L. The STPs along the river affect the SMCs levels in river and the SMCs levels decreased with downstream because of dilution effects. The HHCB/AHTN ratios can be used as in indicator of ongoing supply of HHCB and AHTN and the ratioof this study (mean HHCB/AHTN ratio 6.4) was higher than those of other countries (mean HHCB/AHTN ratio 1.7 - 4.3), indicating high usage of HHCB in Korea.

Introduction

Synthetic musk compounds (SMCs) are a group of organic compounds used commercially as fragrance ingredients. The SMCs are divided into two groups based on their chemical structures: nitro musk compounds (NMCs) and polycyclic musk compounds (PMCs)[1, 2]. SMCs are widely used as fragrance ingredients in many household products such as cosmetics, detergents, fabric softeners, shampoos, perfumes and other scented personal care products and HHCB and AHTN represent about 95% of fragrance market[3]. The use of SMCs caused their steady input into the environment via sewage treatment plant (STP) effluents[4] and STPs are regarded as a major source of SMCs in water environments[5, 6]. In the case of surface water, widespread and relatively high SMCs concentrations around urban areas were observed due to discharge of SMCs from point sources such as STP effluent as well as from non-point sources such as households as a result of the lack of sewage gathering systems [4, 7-10].However, there is no study that report the SMCs levels in surface water in Korea. Therefore, in this study, we intended (i) to investigate and confirm the occurrence and distribution pattern of SMCs in Nakdong river basin (i.e., mainstream and its tributaries), and (ii) to elucidate the effect of STP effluent on Nakdong river.

Materials and Methods

Sampling and Analytical procedures

Surface water samples were taken on February 2009 at 28 sampling sites in Nakdong river basin, Korea (Figure 1). The water samples were collected in amber glass sample bottles using grab sampling method and then preserved with 0.5% methanol (v/v) to prevent rancidity and kept at 4ºC prior to analysis. For liquid-liquid extraction, water samples (500 mL) were taken in a glass separatory funnel, and extracted with 100 mL of dichloromethane and hexane, respectively after spiking the internal standard, Musk xylene-d_{15}. The extract was passed through a glass funnel packed with anhydrous sodium sulfate for the removal of moisture and concentrated using a TurboVap II (Zymark, MA, USA) and a nitrogen-purge concentrator. The final volume of the extract was adjusted to 50 µL with DCM after spiking the recovery standard, phenanthrene-d_{10}. Each concentration of the 11 SMCs was determined by gas chromatograph interfaced with a mass spectrometric detector (GC/MSD, Agilent 6890 GC and 5973 series MSD; Agilent Technologies, CA, USA). GC separation was carried out using a 30 m DB-5MS fused silica column (0.25 mm i.d., 0.25 εm film thickness; J&W Scientific, CA, USA). Injection (2 µL) was performed in the splitless mode at 280 ęC with a constant helium gas flow of 1.0 mL/min. The GC oven temperature was programmed to increase from 50 ęC (1.5 min) to 150 ęC at a rate of 10 ęC/min, and subsequently to 190 ęC at a rate of 2 ęC/min, followed by a third ramp to 290 ęC at a rate of 25 ęC/min, and held for 10 min. The electron impact (EI)-MS was operated in the selective ion monitoring mode. Limit of quantifications (LOQs) ranged from 1 to 2 ng/L, which were tabulated in Table 1 and recoveries of Musk xylene-d_{15} were 83.2 ± 9.9% in all water samples.

Results and Discussion

The concentrations levels of SMCs

Four (HHCB, AHTN, AHDI and ADBI) out of six PMCs and one (MK) out of five NMCs were detected in 28 sampling sites (Table 1). HHCB (22/28), MK (20/28), and AHTN (15/28) were most frequently detected compounds. HHCB (>50%) was predominant compound followed by MK (16.7%) and AHTN (9.0%). HHCB, MK, AHTN, AHDI and ADBI were detected in river water samples at a concentration range from N.D. (i.e., not detected) to 1445.0 ng/L (mean, 158.1 ng/L), N.D. to 563.0 ng/L (mean, 58.2 ng/L), N.D. to 120.0 ng/L (mean, 24.7 ng/L), N.D. to 10.8 ng/L (mean, 5.4 ng/L) and N.D. to 8.2 ng/L(mean, 3.3 ng/L), respectively. The concentrations of DPMI, ATII, MX, MN, MM, and MA were below the LOQs in all samples. On the whole, the concentration levels of each synthetic musk compound were similar or a little higher than those of other countries except Ruhr, Germany where highly polluted river[10] (Table 2).

The relationship between SMCs levels in water and STPs

The mean SMCs concentration of main stream was 82.2 ng/L and the mean SMCs concentration of tributaries except Hot spots (S12, S13, S14, and S15) was 88.5 ng/L, which is similar with that of main stream. We considered S12, S13, S14 and S15 as hot spots because these sampling sites were located in big city, Daegu (250,000 inhabitants) and had large 8 STPs along these area. The capacity of A, B, C, D, E, F, G and H STPs is 10,000 m^3/day, 40,000 m^3/day, 47,000 m^3/day, 680,000 m^3/day, 45,000 m^3/day, 400,000 m^3/day, 170,000 m^3/day, and 520,000 m^3/day, respectively. The mean SMCs concentration in hot spots was 936.1 ng/L and it was conjectured that these STPs influenced on the SMCs levels in hot spots. Effluent discharges from A, B and C STPs seemed to affect the concentration of S12 point(Figure2). Discharge point of D STP is located in upstream of S13 point, therefore, S13 is affected from the effluent discharge D and E STPs. S15 showed the highest concentration of SMCs (2147 ng/L), because sampling site of S15 is located just besides by the discharge point of H STP. These results suggest the strong evidence of STPs effect on SMCs levels in river. Also, we can find the STPs effect on SMCs levels in mainstream river. No SMCs level was observed in upstream and the SMCs levels increased with midstream. The SMCs levels in S16 was the highest because of the influence of hot spot and these levels decreased with downstream because of dilution effects(Figure 1).

Distribution patterns of SMCs

SMCs were detected in 21 out of 28 sampling points. In principle component analysis, three groups are formed according to the distribution pattern of SMCs (Figure 3). HHCB is most dominant compounds in all samples and Group 1 has the highest proportion (87.6 ± 7.1%) of HHCB. Groups 2 and 3 have a little bit lower HHCB proportion (50~70%) compared to Group 1 and other PMCs like ADBI and AHDI are detected in Group 3 unlike Group 2. These distribution patterns indicate different usage pattern of SMCs in each sampling site. The production amount of HHCB and AHTN are high (>95%) among commercial fragrance compounds so the ratio of HHCB and AHTN can represent the usage pattern of fragrance in specific region. The median HHCB/AHTN ratio in Lippe River is close to 2.5[3]. In water samples from the Elbe River, the Mulde River, the Saale River and the Ruhr River, Germany, median HHCB/AHTN ratios were 1.7, 1.8, 1.7, and 2.8, respectively[10]. Zhang et al.[4] reported median concentrations of 60 ng/L HHCB and 14 ng/L AHTN (HHCB/AHTN ratio 4.3) were detected in surface waters of Suzhou Creek. However, median concentrations of HHCB and AHTN in this study were 158.1 ng/L and 24.7 ng/L, respectively (HHCB/AHTN ratio, 6.4) indicating high usage of HHCB in Korea compared to other countries.

References

1. Peck A.M. *Anal Bioanal. Chem.* 2006; 386: 907.
2. Gatermann R., Biselli S., Hühnerfuss H., Rimkus G.G., Hecker M. and Karbe L. *Arch. Environ. Contam. Toxicol.* 2002; 42: 437.
3. Balk F. and Ford R.A. *Toxicol. Lett.* 1999; 111: 57.
4. Zhang X., Yao Y., Zeng X., Qian G., Guo Y., Wu M., Sheng G. and Fu J. *Chemosphere* 2008; 72:1553.
5. Bester K. *Chemosphere* 2004; 57: 863.
6. Zeng X., Sheng G., Gui H., Chen D., Shao W. and Fu J. *Chemosphere* 2007; 69: 1305.
7. Bester K. *J Environ. Monit.* 2005; 7: 43.
8. Dsikowitzky L., Schwarzbauer J. and Littke R. *Org. Geochem.* 2002; 33: 1747.

9. Quendnow K. and PŤttmann W. *Clean* 2008; 36: 70.
10. Rimkus G.G. *Toxicol. Lett.* 1999; 111: 37

Table 1. Concentration levels of SMCs (ng/L)

	HHCB	AHTN	AHDI	ADBI	PMCs[a]	MK	NMCs[b]	total
Avg.	158.1	24.7	5.4	3.3	184.7	58.2	58.2	244.1
SD	314.2	30.3	4.7	6.6	351.3	127.1	127.1	474.9
Min	ND[c]	ND	ND	ND	ND	ND	ND	ND
Max	1445.0	120.0	10.8	8.2	1584.0	563.0	563.0	2147.0
DF	22/28	15/28	3/28	4/28		20/28		
LOQ	2.0	2.0	1.0	1.0		1.0		

[a]PMCs: polycyclic musk compounds; [b]NMCs: nitro musk compounds; [c]ND: not detected, DF; detection frequency

Table 2. Comparison of SMCs levels with other countries (ng/L)

	HHCB	AHTN	MK
This study	158(1445)	25(120)	58(563)
[1]Germany (Ruhr)	400(11200)	200(11200)	-
[1]Germany (Elbe)	90(100)	50(100)	-
[2]Germany (Hessen)	150(460)	50(170)	
[2]Netherlands (Rhine)	60(160)	50(100)	-
[2]Switzerland	61(97)	25(45)	-
[3]Japan	80-100	-	-
[3]UK	-	-	17-24

[1] median (maximum); [2] median (90th-percentile of the data); [3] range

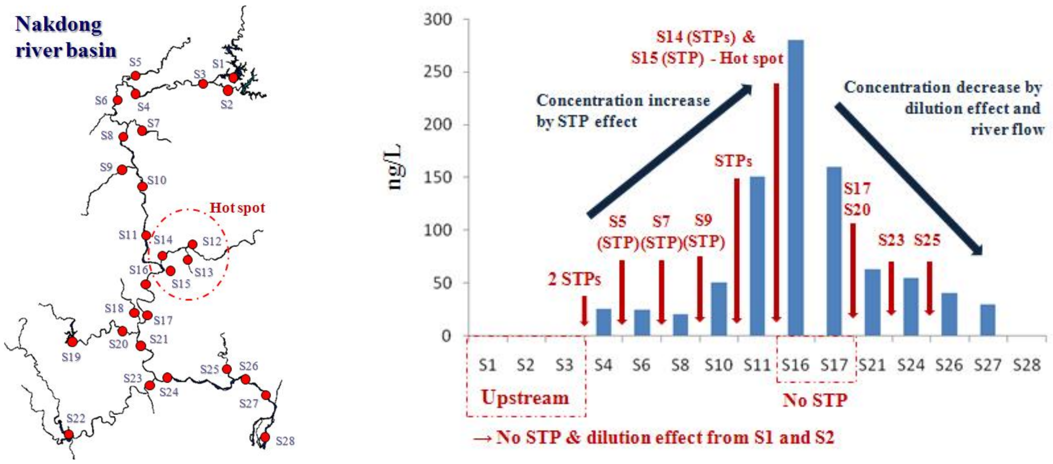

Figure 1. Sampling sites (left) and variation of total SMCs concentration (right) in main stream

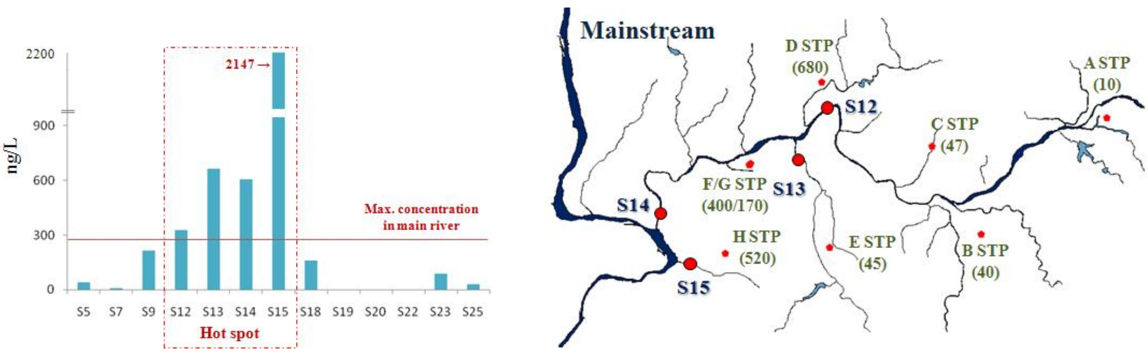

Figure 2. Total concentrations in tributaries (left) and STP locations and their capacities (unit: x 10^3 m^3/day) around Hot spots (right)

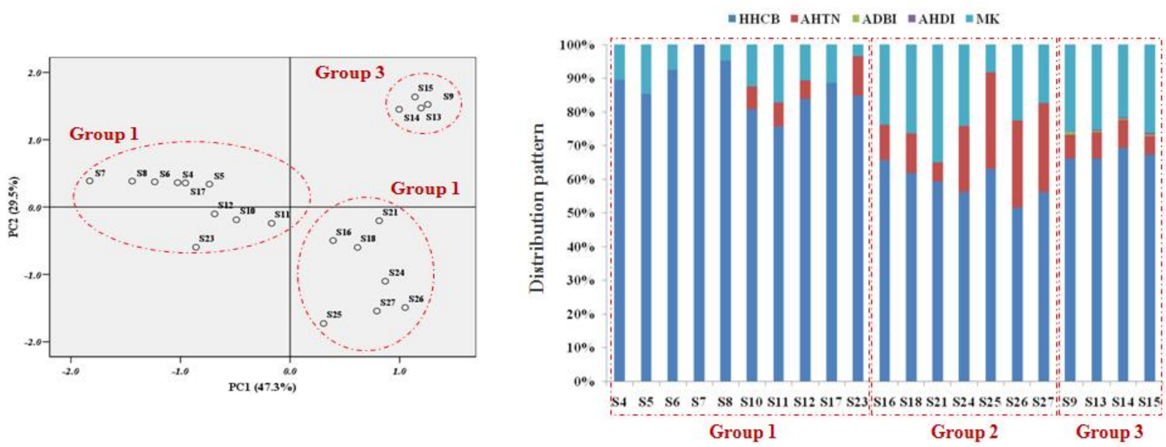

Figure 3. Distribution patterns of SMCs according to sampling sites