Occurrence and fate of Synthetic Musk Compounds in Sewage Treatment Plants

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Introduction

About 2000 tonne/year polycyclic musk compounds (PMCs) like HHCB (marketed as galaxolides), AHTN (tonalides) and nitro musk compounds (NMCs) [e.g., musk ketone (MK) and musk xylene (MX)] are used in Europe as fragrances for personal care products such as cosmetics, detergents, fabric softeners, shampoos and perfumes etc[1]. Synthetic musk compounds (SMCs) including PMCs and NMCs are being now considered as emerging contaminants due to their persistence, bioaccumulation potential and their toxic effects on estrogen activity[2]. Recently, in the USA and Europe, a framework has been developed to prioritize toxic fragrance materials in aquatic environment[3]. Most of used SMCs in household are discharged directly into the sewage system and sewage treatment plants (STPs) treat these compounds. It is known that there are two main removal pathways of SMCs in STPs. One pathway is sorption of SMCs onto sludge and the other is degradation[4, 5]. Many studies were reported that sorption and degradation played a considerable role in removal of some SMCs and these removal efficiencies varied from 50% to 90% (in some cases, below 50%)[4-8]. In addition, it is reported that the size of the treatment plant, the population, the types of waste (domestic, industrial, and/or commercial) and the treatment methods employed could affect on removal efficiency of SMCs in STPs[9]. Most of these studies were done to investigate removal efficiency in primary physical treatment process (i.e., sorption and settling) and conventional activated sludge treatment process. However, there are many different types of activated sludge-based process and other treatment processes such as chemical and filtration treatment etc. Therefore, further research is needed to elucidate the effects of various treatment processes for the removal of SMCs in STPs.

In this study, we investigated the occurrence and distribution profiles of SMCs (i.e., HHCB, AHTN, MK and MX) which have been widely used and their removal efficiencies in various types of activated sludge-based treatment processes (i.e., AS, MLE, SBR and A2/O) and other processes such as chemical, filtration and disinfection treatment. This is the first study reports the levels of SMCs in Korean STPs and their fate and removal efficiencies in various types of sewage treatment processes.

Materials and Methods

Sampling. Ten onsite sewage treatment plants were selected for this study. Residential sewage flowed into 6 STPs and mixed sewage from industry and household ran into the other 4 STPs. All of 10 STPs had physical sorption and settling process as a primary treatment. And then, they applied biological or chemical treatment process as a secondary treatment and additional filtration and/or disinfection treatment processes to treat sewage. Grab sampling was performed for collecting sewage samples and sewage samples were taken at the outlet of each treatment process including influent and effluent. Detailed description about STPs and sampling positions were tabulated in Table 1. Acronyms and abbreviations of the treatment processes in this study were also presented in Table 1. Sewage samples were collected in clean 2 L amber bottles and stored below 4˚C prior to analysis.

Analytical procedures. Liquid-liquid extraction was performed on sewage water samples. Water samples (300 mL for sewage influent sample; 500 mL for other stage sewage samples) were taken in a glass separatory funnel, and then extracted with 100 mL of dichloromethane and subsequent hexane after spiking the internal standard, AHTN-d_3. Extracted organic layers were concentrated to 500 μL using a TurboVap (Zymark Corporation, USA) and a nitrogen-purge concentrator after removing moisture with anhydrous sodium sulfate. The concentration of each of the 4 SMCs was determined by use of a gas chromatograph interfaced with a mass spectrometric detector (Agilent 6890 GC and 5973 MSD; Agilent Technologies, USA). Gas chromatographic separation was carried out using a 60 m DB-5ms fused silica column (0.32 mm i.d., 0.25 μm film thickness; J&W Scientific, USA). Limit of quantification (LOQ) was 20 ng/L for sewage samples and recoveries of AHTN-d_3 in samples were 93.4±17.3%. Details of the analytical procedure and the instrumental conditions have been described in other studies[9, 10]. All multivariate statistical analyses including hierarchical cluster analysis and linear regression analysis were performed by SPSS 14.0K (SPSS inc., USA).

Results and Discussion:

The concentrations of 4 SMCs in influent and effluent

HHCB, AHTN and musk ketone were detected in all sewage samples but musk xylene was only detected in influent samples. The total concentrations of 4 SMCs in influents and effluents ranged from 3.693 to 7.325 μg/L and from 0.960 to 2.689 μg/L, respectively (Figure 1). These concentration levels were similar with or a little bit lower than those of previous reports in European countries and United States[6, 9]. HHCB was predominant compound in all influent and effluent samples and its concentration ranged from 2.764 to 4.516 μg/L for influents and 0.508-1.924 μg/L for effluents. The average concentrations of AHTN and MK were over 4 times lower than those of HHCB in influent and effluent samples. These results coincide with the greater production and usage of HHCB compared with AHTN, MK and MX. Hierarchical cluster analysis was performed with the total SMCs concentrations in influent to investigate their occurrence pattern according to input sources and capacity of sewage in STPs and two main groups were observed according to the total concentration. Group I-2 was clustered with sewage samples that had low concentration levels of SMCs while Group I-1 showed relatively higher concentration levels than Group I-2. The influent sewage samples in Group I-1 were 100% residential sewage while those of Group I-2 were industrial sewage mixed with treated wastewater from industrial complex except GD STP, indicating sewage from household might be the main source of SMCs. The capacity of GD for sewage treatment was the lowest among 10 STPs and this low burden of sewage caused relatively low SMCs level compared to other STPs which treated residential sewage.

The fate of the 4 SMCs

The ratios of each SMC in water samples have been normally used for identifying their fates in water system[11]. The relative distribution profiles of the 3 SMCs (MX was excluded because this compound was only detected in 5 influent samples) were quite similar in all influent and effluent sewage samples (68.3±5.3% and 67.9±2.8% for HHCB; 15.0±1.1% and 15.1±2.4% for AHTN; 15.6±5.3% and 17.0±2.4% for MK), indicating the fates of these compounds in sewage treatment processes were similar. Therefore, we performed linear regression analysis using each concentration level of 3 SMCs in sewage samples (i.e., influents, treatment process effluents and final effluents) in this study. Then, we obtained very significant linear regression equations among the concentrations of HHCB, AHTN and MK, indicating the close relationship among these compounds (Eq. 1 and Eq. 2 are presented in Figure 2). This result also presents that it is able to predict AHTN and MK concentrations if a HHCB concentration in any processes is given. Figure 2 shows the comparison results between measured concentration of AHTN (Figure 2A) and MK (Figure 2B) and those of estimated concentrations with Eq. 1 and Eq. 2. The slope lines are estimated values of AHTN and MK based on measured HHCB concentrations. As Figure 2 is shown, the measured values of AHTN and MK fit very well with those of estimated values based on HHCB concentration except the case of MK in influent samples, indicating the similar fate of these compounds in STPs. The discrepancy between measured MK and estimated MK in influent samples may be due to the different sources of MK compared to HHCB but the fate of MK in other treatment stages seems to be similar to that of HHCB. The similar fate of these compounds in STP can be explained by their similar K_{ow} values of 5.9, 5.7 and 4.3[6], respectively. These results indicates that these 3 SMCs have similar removal mechanism (generally, sorption) in sewage treatment processes. Until now, the researches regarding the fate of HHCB and AHTN in sewage treatment have mainly been performed and the similar fate of these two compounds is reported[8, 9, 11] however there is no report about describing the fate of another SMC like musk ketone. This is the first study that reports the significant relationship between HHCB and MK and their similar fate in STP in our knowledge.

The removal efficiencies of the 4 SMCs

The removal efficiencies of 4 SMCs with various types of sewage treatment processes were investigated and their removal efficiencies in each treatment process are shown in Figure 3. It was not available to obtain MX removal efficiency in each treatment process because MX concentration was too low and detected only in 5 influent samples. Four different biological treatment processes (MLE, SBR, A2O and AS) were investigated in this study and MLE, SBR and A2/O were the modified processes of conventional AS process to increase biological removal efficiency for nutrient (i.e., nitrogen and phosphorus) and decrease solid retention time. Many researchers were examined the removal efficiency of SMCs in conventional AS process and reported good removal efficiency[3, 6]. 5 out of 10 STPs in this study had AS process as a secondary treatment. The average

removal efficiencies of HHCB, AHTN and MK in AS process were 53.2±6.0%, 56.0±4.7% and 53.2±12.1%, respectively. Previous studies reported that approximately, 50 to more than 90% of HHCB and AHTN mainly were removed by sorption onto sludge particles[4, 6, 12] and their efficiencies were similar with or higher than the result of this study. MLE, modified process of AS treatment, was applied in 2 STPs and the average removal efficiencies were somewhat higher than AS process (64.8±2.0% for HHCB, 64.3±1.3% for AHTN and 41.2±11.5% for MK). 3 STPs adopted SBR, A2/O and DE process as a secondary treatment, respectively. Modified versions of AS (i.e., SBR and A2/O) had a similar or higher removal efficiencies of SMCs compared to MLE and AS processes. However, DE process as chemical treatment had lower removal efficiency (37.2% for HHCB and AHTN and 36.4% for MK) than biological treatment. Generally, the removal efficiencies of modified biological treatment processes (i.e., MLE, SBR and A2/O) for HHCB and AHTN were slightly higher than conventional AS process and that of DE process as chemical treatment in this study was lower than biological treatment processes. In filtration treatment processes followed by secondary treatment, the removal efficiency in BF (Biofilter) was 3-8 times higher than that of SF (Sand filtration). This result indicates that biological filtration has better efficiency for SMCs removal compared to physical filtration treatment process even though this were obtained from one case study. Cl and UV treatment as additional disinfection process showed low removal effect (below 10%). Cl and UV disinfection treatments prior to discharging the effluent into surface water have been normally used to remove viruses and bacteria in wastewater and reported good removal efficiency[10]. However, in this study, disinfection processes were not so effective to remove SMCs.

References

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Table 1. The description of surveyed 10 STPs

STP	Capacity (m^3/day)	Source	Treatment processes and Sampling points* (n)
GD	15,000	100% RS[1]	Influent(1)→SBR(2)→SF(3)→UV→Effluent→(4)
HUD	65,000	100% RS	Influent(1)→AS(2)→SF(3) →UV→Effluent→(4)
DB	135,000	100% RS	Influent(1)→DE(2)→BF→Effluent→(3)
SY-1	286,000	100% RS	Influent(1)→AS(2)→Cl→Effluent→(3)
SY-2	264,000	100% RS	Influent(1)→AS(2)→UV→Effluent→(3)
NB	340,000	100% RS	Influent(1)→AS(2)→Cl→Effluent→(3)
SH	24,000	40% IS[2] + 60% TW[3]	Influent(1)→MLE(2)→SF→Effluent→(3)
NS	160,000	30% IS + 70% TW	Influent(1)→MLE(2)→UV→Effluent→(3)
JR-1	330,000	50% RS + 50% TW	Influent(1)→AS(2)→Cl→Effluent→(3)
JR-2	285,000	50% RS + 50% TW	Influent(1)→A2O(2)→UV→Effluent→(3)

- [1]RS: Residential sewage; [2]IS: Industrial sewage; [3]TW: Treated wastewater

*Acronyms and abbreviations of the treatment processes in this study: Secondary treatment [Activated sludge, AS; Modified Ludzack-Ettinger, MLE; A2/O; Sequencing batch reactor, SBR; DENSADEG, DE], Disinfection [Chlorination, Cl; UV disinfection, UV], Filtration [Biofilter, BF; Sand filtration, SF]

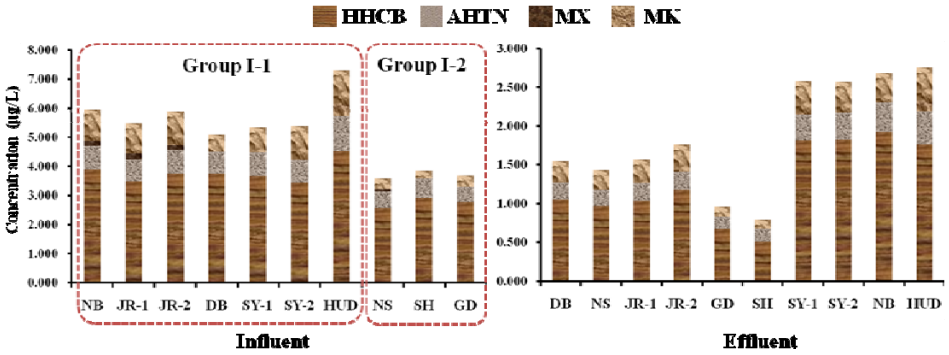

Figure 1: The concentrations of SMCs in sewage influent and effluent samples and clusters in influent samples

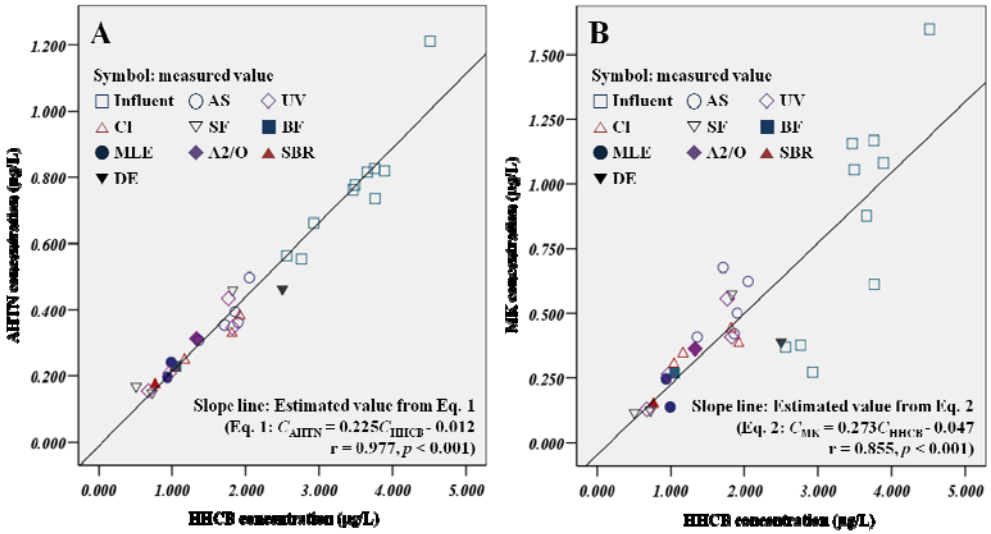

Figure 2: Comparison of measured concentration in all sewage samples with estimated concentration from Eq. 1 and Eq. 2 for (A) AHTN and (B) MK [inset: linear regression equation between HHCB and AHTN (Eq. 1), HHCB and MK (Eq. 2)]

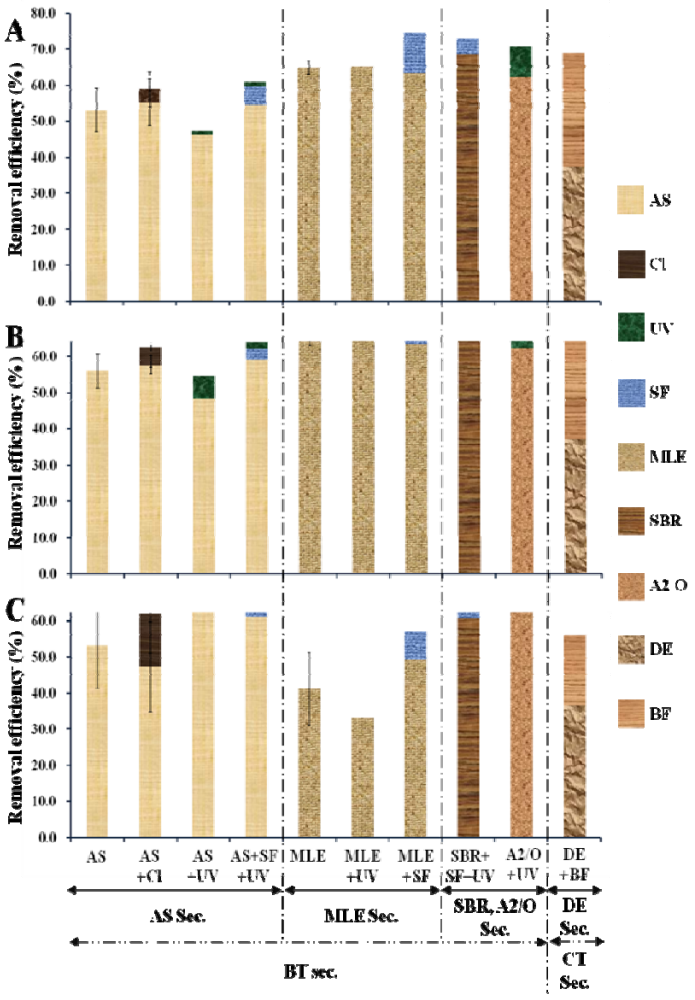

Figure 3: The removal efficiencies of (A) HHCB, (B) AHTN and (C) MK in sewage treatment processes (Sec., Secondary treatment; BT, Biological secondary treatment; CT, Chemical secondary treatment)