Estimation of polycyclic aromatic hydrocarbons emission from sewage sludge of sewerage treatment plants in Korea

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Polycyclic aromatic hydrocarbons (PAHs) are an important group of organic contaminants present in sewage sludge, due to their persistence, toxic, bioaccumulative and long range transfer. These characters make themselves as Persistent Organic Pollutants(POPs)[1] in Long Range Transboundary Air Pollutions convention(LRTAP) of Europe. A method of the gas chromatographic–mass spectrometric (GC–MS) determination of PAHs present in sewage sludge was developed and applied to analyzed samples from five sewerage treatment plants (SWTPs), having different treatment types.

PAHs were extracted from freeze-dried samples by toluene 16 hours in a soxhlet extraction system. The sludge extracts were cleaned-up by an activated silica gel column chromatography. The sum of the 16 US Environmental Protection Agency PAHs sewage sludge samples varied from 2.44 to 4.82 µg/ g. Concentration of emission carcinogen PAHs(PAHcarc), such as Benzo(a)anthracene, Benzo(b)fluoranthene, Benzo(k)fluoranthene, Benzo(a)pyrene, Dibenzo(a,h)anthracene and Indeno(1,2,3-cd)pyrene ranged from 0.62 to 1.03 µg/g. The total amount of PAHs emission from sewage sludge in Korea was calculated as a top-down approach. PAHs and ∑PAHcarc from sewage treatment plants had several pathway each by-products. In the ocean dumping, PAHs and ∑PAHcarc emissions were 1155.95 kg/year and 5040.32 kg/year. In recycle, PAHs and ∑PAHcarc emissions were 98.36 kg/year and 428.87 kg/year. In the landfill, PAHs and ∑PAHcarc emissions were 190.40 kg/year and 830.21 kg/year. In the incineration, PAHs and ∑PAHcarc emission were 33.10 kg/year and 830.21 kg/year. (In case of incineration, the whole provisions of PAHs and ∑PAHcarc contained to flowed in sludge was supposed to be exhausted to environment through exhaust after incineration.)

Key words: PAHs, ∑PAHcarc, Sludge, Sewerage treatment plant, Emission Factor.

1. Introduction

A typical and important source of PAHs emission into the environment is the incomplete combustion of fossil fuel and organic materials, caused from incinerators, residential heating, power generator and industrial facility [2),3)].

Another PAHs are derived from industrial waste as well as from domestic sludge, atmospheric rainfall, airborne pollutants and runoff on road surfaces. They are also produced by forest fires and microbiological synthesis[4)]. A number of PAHs have been identified to be potent mammalian carcinogens and designated as priority pollutants with respect to the public health risk[5]. Some of PAHs, including Benzo[a]pyrene (BaP), are also indicated mutagen and carcinogen, namely Endocrine Disruptors (EDs) in view of the environmental toxicology [3)].

A new draft directive of the Council of the European Community has been released, to control of the amount nonylphenol ethoxylates, AOXs, linear alkylbenzene sulfonates (LASs), di(2-ethylhexyl)phthalate, PCDDs/ Fs, PCBs, and PAHs used in agriculture[6)]. The limitation for PAHs included in sewage sludge was set at 6 mg/ kg. The interest for PAHs in sewage sludge is because of their persistence in the soil, their low biodegradability, high lipophilicity, their ultimate fate in agricultural systems, food chain

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biomagnification and possible harmful effects on biota and carcinogenicity on humans.

Sewage sludge is what is left behind after water is cleaned in sewerage treatment plants. Sewerage catchments receive organic pollutants from different sources: human excretion products, household disposals, fossil fuel spillages, and urban runoff inputs flushing organics deposited on the ground surface from vehicles or heating systems[7].

The final products of the sewage sludge are the mixture of organic and inorganic pollutants and have been disposed of in different ways such as ocean dumping, landfills, incineration and recycle. In Korea, the application of sewage sludge to ocean is a major route for disposal (about 73% of total treatment). In these days, many international convention prohibited the ocean dumping, which represents an economic but environmentally doubtful method for the treatment of sludge produced by the SWTPs.

The objectives of this study were to determine the amount of 16 EPA PAHs in the sewage sludge and to estimate the total amount of PAHs from sewage sludge originated from sewerage treatment plants in Korea.

2. Experimental Methods

2.1 Sampling and sample preparation

The collection and analysis of samples were performed to investigate the contamination characteristics of PAH compounds in sewage sludge for 5 sewerage treatment plants in March and April, 2003.

Sample bags were stored in the dark, and firmly closed to avoid contamination or losses.

Samples of filter-pressed sewage sludge obtained from treatment plants were homogenized prior to analysis. Each samples of compost were stored at -20□, then freeze-dried and powdered to analysis

10 g of each sewage samples were extracted with 200 mℓ toluene for 16 hours in a soxhlet extraction system for PAHs analysis. After extracted, samples were filtered and concentrated to 10 mℓ by rotary evaporator.

Extracts were transferred to n-hexane and an internal standard (ES 2055 ; Deuterated PAHs solution, Cambridge Isotope Laboratories, Inc) was spiked. Extracts were clean up on an activated silica gel column and with successively eluted of n-hexane and 15% methylene dichloride in n-hexane. The second fraction was concentrated to less than 1 mℓ, and left at a room temperature for one or two days (evaporate to 200 μℓ). The residue was dissolved with 200 μℓ of n-nonane and determined for PAHs .

2.2 Analysis

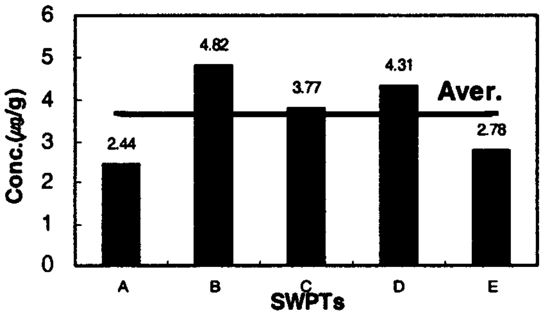
The GC/MS-SIM (Selected Ion Monitoring) anaiysis were carried out using HP6890 plus chromatography coupled with a HP5973 mass spectrometer and equaled with HP-5MS capillary column.

3. Results and Discussion

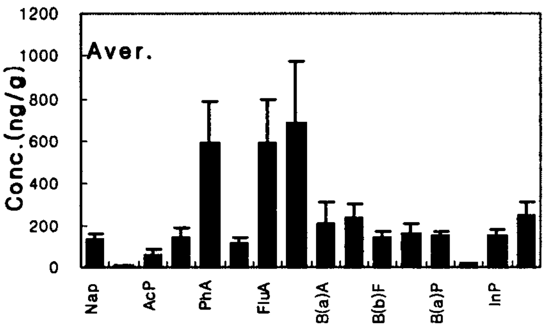
3.1 Emission level of PAHs

Concentration of 16 PAHs (sum of two- to six-ring PAHs) at 5 SWTPs are shown in Fig. 1.

Total PAHs concentrations ranged from 2.44 to 4.82 μg/g, which were very related with environmental characteristics of treatment sampling areas.



(a)



(b)

Fig. 1. Total concentration of 16 PAHs for each SWPTs (a) and concentration of 16 PAHs in sludgesamples (b).

The highest concentration of 16 PAHs occurred at B SWTP sites with 4.82 $\mu g/g$, and A SWTP site presented the lowest concentration of 2.44 $\mu g/g$.

Relative ratios among compound having different ring number in each sludge sample are shown in Fig. 2. PAH compounds of 3, 4, 5 -rings show high concentration.

By comparing this result with those of another study[8], PAHs compound ratio of sewage sludge was similar to those of soils at factory and resident area. The portion of PAH compounds having six rings in sewage sludge samples were lower than those of soils at traffic areas.

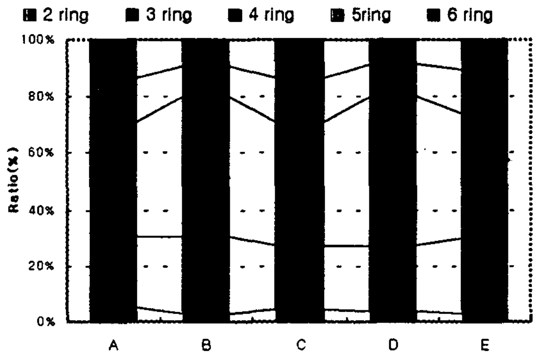
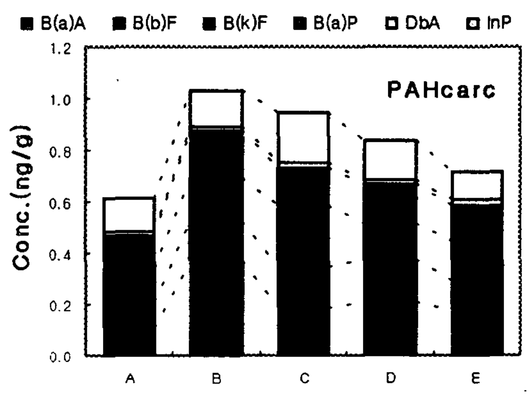
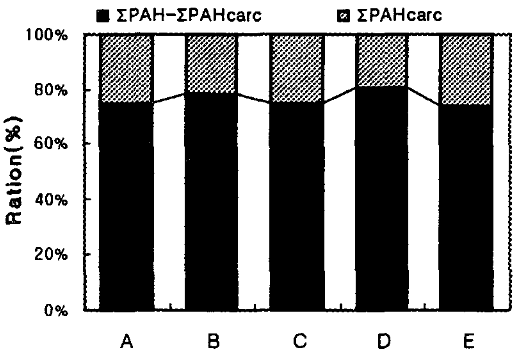


Fig. 2. Relative ratio of each compound within ring in sludge

PAHcarc concentration at sludge of SWPTs [Benzo(a)anthracene (B(a)A), Benzo(b)fluoranthene (B(b)F), Benzo (k)fluoranthene (B(k)F), Benzo(a)pyrene (B(a)P), Dibenzo(a,h)anthracene (DbA) and Indeno(1,2,3cd)pyrene (InP)] ranged 0.62 – 1.03 $\mu g/g$. (Fig. 3).



(a)



(b)

Fig. 3. Concentration(a) and ratio(b) of PAHs and PAHcarc compounds.

$\sum$PAHcarc concentration levels at B, C, D SWPTs were higher than at A and E SWPTs, suggesting that B SWPTs located in factory area were input leachate from waste landfill facility and C, D SWPTs were influenced from the density of residence.

B(a)A recorded 24.5% (as an average) and it was the highest amount in the homologue pattern of PAHs. Although the magnitude of PAHs was not uniform, for five sludge samples, the homologue patterns of PAHs were identical. B(a)P and B(k)F occupied the highest proportion among sewage sludge from A and C SWTPs, respectively.

3.3 Estimation of emission of PAHs from STWPs

The released amount R_{eni} of PAHs in sewage sludge from sewerage treatment plants can be calculated as below;

$$R_{eni} = EF_{aver} \times A \qquad (1)$$

, where EF_{aver} represents an average emission factor (g/ton) and A indicates an activity rate (ton/year)

The emission factor (EF) was derived from the calculation below ;

$$EF_{aver} = [EF_1 + EF_2 + EF_3 + \cdots + EF_n]/n \qquad (2)$$

, where EF_1, EF_2, EF_3 and EFn means an emission factor (g/ton) of each plant and n indicates number of measured plant.

$$EF = C \times M \qquad (3)$$

, where C is the concentration (ng/g) of target contaminant, and M represents the disposal sewage amount.

From equations of (1), (2) and (3), the estimated amount of target compounds is summarized in table 1.

Table 1. Summary of the released amount of PAHs and ∑PAHcarc, emitted from sewage of sewerage treatment plants in Korea (2001)

Target compounds	EF (μg/g)	R_{env} (kg/year)
PAHs	2.44 – 4.82 (3.62)	6801.12
∑PAHcarc	0.62 – 1.03 (0.83)	1559.77

The annual emission amount of PAHs and Benzo(a)pyrene (BaP), the main substance of mutagenicity and carcinogen amount of PAHs compounds, from 1997 to 2001 were estimated by using the emission factor. The result is illustrated in Fig. 4.

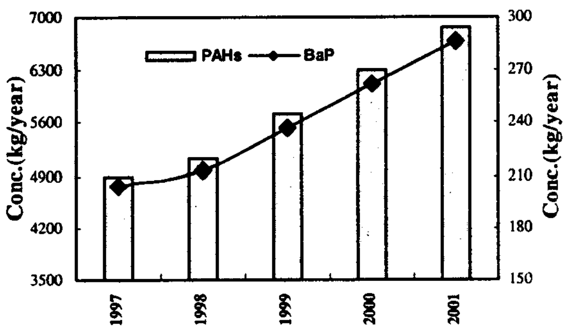


Fig. 4. Trend of PAHs and BaP amount from sludge of SWTPs in Korea.

PAHs and BaP emission amounts have continuously increased and thus emission amount of PAHs from SWTPs depends on disposal amount of sewage sludge.

4. Conclusions

Characteristics of PAHs concentrations in sewage sludge were investigated according to different SWTPs in Korea. For further study, research about PAHs and POPs for wastewater and sludge as the whole process in sewage treatment plants should be performed.

References

1) UNEP, 2001, Resolutions adopted by the conference of plenipotentiaries on the stockholm convention on persistent organic pollutants.
2) ATSDR, 1996, Top 20 Hazardous Substances.
3) D. Golomb, D. Ryan, J. Underhill, T. Wade and S. Zemba, 1997, Atmospheric deposition of toxics onto Massachusetts bay-I. Metals, Atomospheric Environment 31(9), 1349-1359.
4) J.D. Berset, R. Holzer, 1999, Quantitative determination of polycyclic aromatic hydrocarbons, polychlorinated biphenyls and organochlorine pesticides in sewage sludges using supercritical fluid extraction and mass spectrometric detection, J. Chromatogr. A 852, 545.
5) M. Casellas, P. Fernandez, J.M. Bayona, A.M. Solanas, 1995, Bioassay-directed chemi-cal analysis of genotoxic components in urban airborne particulate matter from Barcelona (Spain), Chemosphere 30, 725.
6) Council of the European Community, 2000, Working Document on Sludge, 3rd Draft, Brussels.
7) Sandra Perez, Miriam Guillamon, Damia Barcelo, H.R. Rogers, 1996, Quantitative analysis of polycyclic aromatic hydrocarbons in sewage sludge from wastewater treatment plants, Sci. Total Environ. 185, 3.
8) Dong-Hwan Kim[a], Gon Ok[a], , Young-Kyo Kim[a], Sang-Jo Kim[a], Jee-Hoon Kim[a], Sung-Ho Kong[b], 2001, Survey on contamination characteristics of PAHs in soil in Seoul Korea, 21st International symposium on halogenated environmenttal organic pollutants and POPs, 51, 150-153.