

Temporal trend and long-range transport of particulate polycyclic aromatic hydrocarbons at Gosan in northeast Asia between 2001 and 2004

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[1] The temporal trend of the particulate polycyclic aromatic hydrocarbon (PAH) level was observed at Gosan, a background site in Korea, for 4 years between November 2001 and January 2004. The total average concentration of ambient particulate PAH compounds was $3.65 \pm 4.74 \text{ ng m}^{-3}$, which was mainly affected by a rather small number of very high PAH level samples. The PAH level at Gosan was 1 or 2 orders higher than those at other remote sites and 1 or 2 orders lower than those in urban areas in northeast Asia. The particulate PAH concentrations were high during cold periods mainly because of the seasonal variation of fossil fuel usage amount in northeast Asia. When the PAH levels were high, the ratio of BeP-to-BaP was also high, which is an indicator of particle residence time in the air. On the basis of the backward trajectory and upper wind direction analyses, it was observed that when air parcels were from China, the PAH levels were high. Also, the compositions of PAH compound ratios were similar to those in Beijing in winter. These indicate influence of emissions from China, especially from coal combustion and long-range transport. The relationship between the concentrations of PAHs and non-sea-salt-(nss)- SO_4^{2-} was generally good when the PAH levels were high. However, the periods of peaks were different, implying different emission patterns.

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1. Introduction

[2] The impact of air pollution in northeast Asia on the region itself and all over the world has increasingly been recognized. Thus several intensive and routine measurement studies have been performed at Gosan, Korea, to understand the characteristics of the long-range transport of various ambient trace species around the area [Arimoto *et al.*, 1996; Park *et al.*, 2004]. These studies, however, were mostly on inorganic species, ions, or/and elements. In a few studies, organic species were measured, but these were on the classification of organic carbon and elemental carbon [Kim *et al.*, 1999; Kaneyasu and Takada, 2004].

[3] Polycyclic aromatic hydrocarbons (PAHs) are ubiquitous organic pollutants, some of which are reported to be mutagenic and carcinogenic materials [Agency for Toxic Substances and Disease Registry, 1995]. PAHs are consid-

ered one of the persistent toxic substances (PTS) in central and northeast Asia (region VII) designated in the Stockholm convention [United Nations Environment Programme, 2002]. About 90–95 wt% of particulate PAHs are associated with fine particles [Baek *et al.*, 1991], and airborne particulate PAHs in this size range can be transported long distances. PAHs are mainly formed during incomplete combustion processes of organic matter and associated with black carbon (BC) or soot particles [Butler and Crossley, 1981]. BC is an important aerosol species because of its global and regional influence on radiative forcing [Streets *et al.*, 2001]. Thus understanding atmospheric processes of PAHs may help us to understand the behavior of anthropogenic BC particles.

[4] Northeast Asia, in particular China, is the world's largest coal consumption region (Energy Information Administration, International Energy Database, 2003, available at <http://www.eia.doe.gov/emeu/international/coal.html>). Thus it has been speculated that emissions and impacts of PAHs would be large. However, temporal trend and transport patterns of PAHs in this region have not been fully reported yet. In particular, long-term measurement of PAHs is needed to understand the atmospheric processes involved in temporal variation and transport.

[5] The site of this study, Gosan, is located at the western edge of Jeju Island (Figure 1). Jeju Island is located about 100 km south of the Korean Peninsula, about 500 km west

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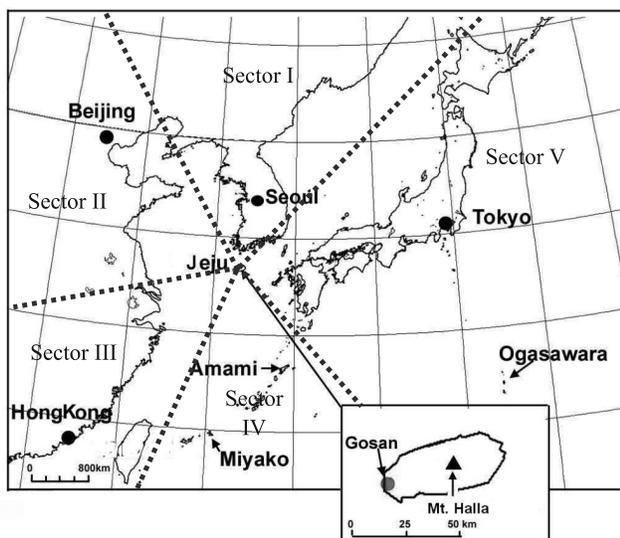


Figure 1. Map of this study site, Gosan, Jeju, Korea, and other remote and urban sites in northeast Asia and sector classification.

of China (Jiangsu province), and about 200 km east of the Japanese Islands (Kyushu) and is regarded as the intersection of pollutants' flow in this region. Because of its location, several intensive and routine measurement studies including Pacific Exploratory Mission (PEM)–West A and B, Aerosol Characterization Experiment (ACE)–Asia, and Atmospheric Brown Cloud (ABC) have been performed at this site since the 1990s.

[6] In this study, (1) the temporal trend of atmospheric particulate PAH levels at Gosan for 4 years is observed, (2) their level at Gosan is compared with the results at other areas in northeast Asia, and (3) characteristics of long-range transport of PAHs in northeast Asia are discussed.

2. Experiment

[7] Sampling occurred for 24 hours on every sixth day with no rain from November 2001 to January 2004. Mainly because of meteorological conditions, 103 samples out of about 130 possible samples were obtained. The sampling and analytical procedures used in this study are similar to the methods used in previous studies [Park *et al.*, 2002; Lee *et al.*, 2006]. A Greaseby high-volume total suspended particle (TSP) sampler was operated at a calibrated airflow rate of $\sim 1000 \text{ L min}^{-1}$. The particulate PAHs were collected on prefired quartz fiber filters (QFFs, Whatman, $20.3 \times 25.4 \text{ cm}$, QM-A). Sampling artifacts for particulate PAHs can occur because of gas/particle transport during the sampling. The sorbent system downstream of the filter can quantify negative artifacts due to evaporation of PAHs from particles but cannot quantify positive artifacts due to sorption of PAHs to the particles. The degree of sampling artifacts was not considered in this study because simultaneous sampling in a remote area was rather difficult to carry out. However, according to research by Simcik *et al.* [1999], who used a backup filter to quantify negative artifacts during

sampling, the negative artifacts were small, about 2~5% of the measured particulate PAH concentration.

[8] Particulate PAH samples collected on the QFFs were extracted for 30 min in an ultrasonic bath with 25 mL of dichloromethane (DCM) solvent and then mechanically shaken for 5 min with a vortex mixer. The extracts were filtrated through a $0.45 \mu\text{m}$ pore size syringe filter. The above extraction procedure was repeated 3 times for the residual sample filters. These extracts were transferred to a vessel and concentrated at 20°C to a volume of 1 mL using an evaporator (Zymark, Turbovap 500), and then D_{10} -Phenanthrene was added to each concentrated sample solution as an internal standard for analysis.

[9] Seventeen PAH compounds were identified and quantified using a Hewlett Packard 5890 gas chromatograph (GC) equipped with a 5972 mass selective detector (MSD). The MSD was run in selected ion monitoring mode. Separation was achieved with splitless injection into a $25 \text{ m} \times 0.22 \text{ mm}$ inside diameter ultra-2 chromatographic column with a $0.33 \mu\text{m}$ film thickness. Helium was the carrier gas and operated at a 0.9 mL min^{-1} . The injector and detector were maintained at 270°C and 310°C , respectively. The GC temperature program was 50°C for 2 min, $17^\circ\text{C min}^{-1}$ to 260°C , 260°C for 1 min, $10^\circ\text{C min}^{-1}$ to 310°C and maintained for 15 min. The sample injection volume was $2 \mu\text{L}$. The names of the analyzed PAH compounds and their abbreviations are given in Table 1. The QFF field blanks were prepared and analyzed for each set of field samples with the same procedure.

[10] For quantification, response factors of 17 individual compounds in the standard solution with respect to D_{10} -Phenanthrene were calculated, and then calibration curves (response factors versus PAH concentrations) were drawn for each compound. The standard solution for calibration was prepared by diluting the Supelco stock solution (Supelco, EPA 610 polynuclear aromatic hydrocarbons mixture) containing 16 PAH compounds except BeP and the Aldrich BeP solution (Aldrich, B1010-2). Extraction recoveries were determined by spiking the PAH standard solution in the pre-extracted QFFs (real filter samples in which PAHs were extracted). The same pretreatment and analytical procedures had been repeated for the measurement of extraction recoveries. The reason of using the pre-extracted filter was to obtain extraction recoveries for the actual situation since particles on the filter might affect PAH extraction recovery. Method detection limits (MDL) were determined as the 3 standard deviations of the field blank analysis results, and the MDL values of individual PAH compounds were less than all the sample masses of individual compounds. The blank values were accounted for in the concentration calculation.

[11] The mean extraction recovery for particulate PAHs ranged from 82 to 96%, and these recoveries were accounted for in the concentration calculation. The accuracy of the analytical procedure was tested through the analysis of the National Institute of Standards and Technology (NIST) standard reference materials (SRM) 1649 urban dust sample. The extraction recoveries and analytical accuracy results for the SRM 1649 samples are presented in Table 1. The extraction and analysis methods adopted in this study gave reliable results.

Table 1. Particulate PAH Extraction Recovery Result and the National Institute of Standards and Technology Standard Reference Materials 1649 Urban Dust Sample Analysis Result in This Study^a

PAH Compound	Abbreviation	Recovery, %	Certified Value, ^a $\mu\text{g kg}^{-1}$	Measured Value, ^a $\mu\text{g kg}^{-1}$
Naphthalene	Naph	82	–	–
Acenaphthylene	Acy	86	–	–
Acenaphthene	Ace	85	–	–
Fluorene	Flu	85	–	–
Phenanthrene	Phen	86	4.14 ± 0.37	4.67 ± 0.49
Anthracene	Anthr	91	0.43 ± 0.08	0.46 ± 0.06
Fluoranthene	Flt	82	6.45 ± 0.18	5.50 ± 0.18
Pyrene	Pyr	82	5.29 ± 0.25	4.37 ± 0.22
Benz(a)anthracene	BaA	90	2.21 ± 0.07	1.84 ± 0.59
Chrysene	Chry	86	3.05 ± 0.06	3.67 ± 0.54
Benzo(b)fluoranthene	BbF	86	6.45 ± 0.64	5.43 ± 0.40
Benzo(k)fluoranthene	BkF	89	1.91 ± 0.03	2.27 ± 0.29
Benzo(e)pyrene	BeP	92	–	–
Benzo(a)pyrene	BaP	91	2.51 ± 0.09	2.92 ± 0.82
Indeno(1,2,3-c,d)pyrene	Ind	89	3.18 ± 0.72	2.87 ± 0.66
Dibenz(a,h)anthracene	DahA	96	0.29 ± 0.02	0.35 ± 0.04
Benzo(g,h,i)perylene	BghiP	89	4.01 ± 0.91	3.68 ± 0.69

^aAverage \pm standard deviation.

[12] In this study, 17 PAH compounds were identified. However, since Nap, Ace, Acy, and Flu exist predominantly in the gas phase in the atmosphere and because the major focus of this study is on the particulate PAH concentration, these compounds are excluded from further data analysis.

3. Results and Discussion

3.1. Temporal Trend of Particulate Total PAH Concentrations

[13] The temporal trend of the PAH concentrations is shown in Figure 2. The average concentration of ambient total particulate PAHs for the sampling period was $3.65 \pm 4.74 \text{ ng m}^{-3}$ with a range from 0.06 to 20.9 ng m^{-3} . The average annual PAH concentrations between 2001 and 2004 were not statistically different ($p < 0.01$). The average PAH concentration between October 2001 and December 2002 was $3.57 \pm 3.94 \text{ ng m}^{-3}$, and that between January 2003 and January 2004 was $3.75 \pm 5.59 \text{ ng m}^{-3}$. Also shown in Figure 2, the PAH concentrations increased from November to March, with the peaks in January. The PAH concentrations decreased from April to October.

[14] Since the concentration variation was quite large, the frequency distribution of the PAH concentrations is investigated to further identify the concentration variation. The number of samples for which the total PAH concentration was higher than the average was only 30 among 103 samples. The number of samples with concentrations over the average value plus 1 standard deviation σ (8.39 ng m^{-3}) was 13 (13%), and those over the average plus 2σ (13.1 ng m^{-3}) was 7 (7%). Thus it is evident that the PAH level at Gosan was mainly determined by a rather small number of episodic samples with high PAH levels.

[15] This behavior is different from the concentration variation of another typical anthropogenic species, nss-SO_4^{2-} . Kaneyasu and Takada [2004] found that the concentrations of nss-SO_4^{2-} in TSP at Gosan were high with a small standard deviation. Also, the concentrations of most anthropogenic ionic species in TSP were highest in spring and lowest in summer [Park et al., 2004]. Thus these

observations suggest that PAHs and nss-SO_4^{2-} might have different emission/transport patterns.

3.2. Comparison With Other Sites' Results

[16] In Figure 3 the average concentrations of total PAHs in this study are compared with the results in remote and urban areas of northeast Asia [Kaneyasu and Takada, 2004; Park et al., 2002; Kumata et al., 2000; Zheng et al., 1997; J. Y. Lee et al., Particulate PAHs levels at Mt. Halla site in Jeju Island, Korea: Transport patterns of PAHs in northeast Asia, manuscript in preparation, 2006, hereinafter referred to as Lee et al., manuscript in preparation, 2006]. The average concentration of total particulate PAHs is the sum of the average concentrations of 7 common PAH compounds (Phen, Flt, Pyr, Chry, BaP, Ind, and BghiP) for the results.

[17] Mount Halla site is about 1100 m above sea level (asl) and 35 km east from Gosan and a representative remote site in Korea located at the center of Jeju Island. Amami and Miyako islands are Japanese remote sites in the East China Sea far south of Gosan. Seoul (Korea), Tokyo (Japan), and Hong Kong and Beijing (China) are representative urban sites in northeast Asia (Figure 1).

[18] The level of total PAH concentrations at Gosan was about 1 or 2 orders lower than those at the urban sites in northeast Asia. The average concentration of PAHs at Seoul was similar to that at Tokyo and Hong Kong in winter and in Beijing in summer. The seasonal variation of particulate PAH concentrations in Beijing was large. Also, the average PAH concentration in Beijing measured in winter was about 1 order higher than those at other urban sites in northeast Asia. In Beijing, coal has been used for residential heating in winter season during the sampling period (1998), while coal was not a major energy source for residential heating in Seoul or Tokyo.

[19] However, when compared to the PAH concentrations at Mount Halla site in Jeju, or Amami and Miyako in Japan, the average concentration of PAHs at Gosan was 1 or 2 orders higher. The reason for this was because either Mount Halla site was usually above the mixing height (Lee et al., manuscript in preparation, 2006) or Japanese sites were far from the Asian continent [Kaneyasu and Takada, 2004].

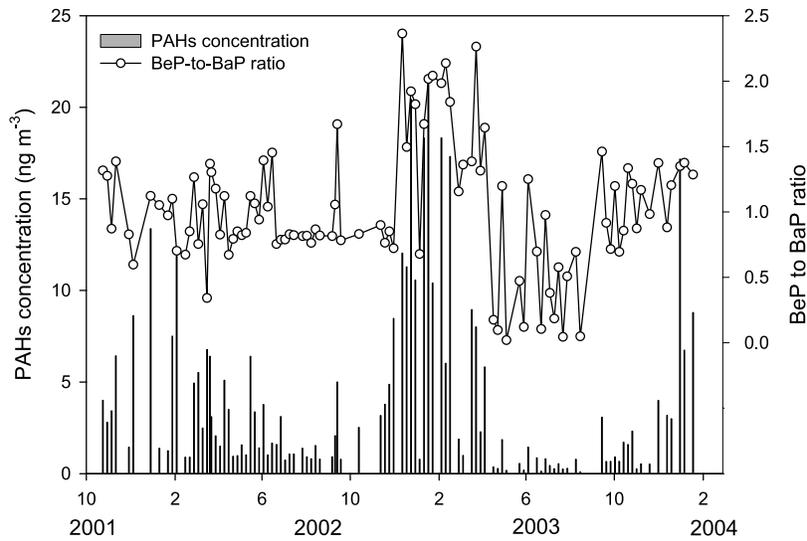


Figure 2. Temporal trend of the particulate total PAH concentrations and BeP-to-BaP ratio between 2001 and 2004 at Gosan.

[20] Worldwide, the particulate PAH concentrations at Gosan were comparable to those found at other urban or suburban sites in the world such as Baltimore (0.33–6.52 ng m^{-3} [Dachs et al., 2002]). Also, the particulate PAH

concentrations at Gosan were 3–15 times higher than in other remote sites such as Lake Superior, United States (0.12 ng m^{-3} [Baker and Eisenreich, 1990]), and high-mountain regions in Europe (Ovre Neadalsvatn, Gossen-

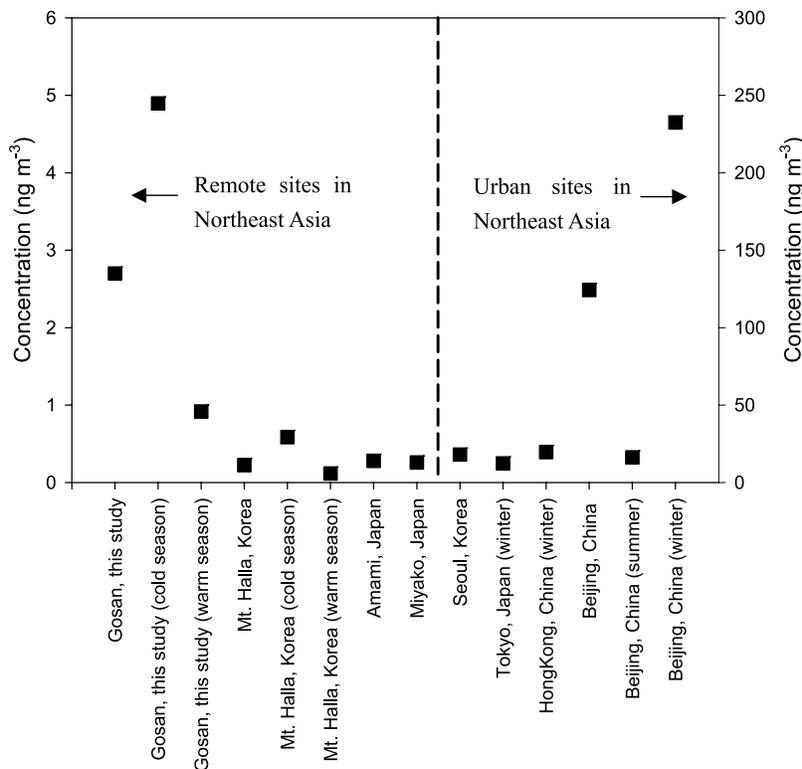


Figure 3. Comparison of the average concentrations of total particulate PAHs (sum of seven PAH compounds (Phen, Flt, Pyr, Chry, BaP, Ind, and BghiP)) measured at Gosan (this study) and other sites in northeast Asia. The sampling data at Mount Halla in Korea are from Lee et al. (manuscript in preparation, 2006), those from Amami and Miyako in Japan are from Kaneyasu and Takada [2004], those from Seoul in Korea are from Park et al. [2002], those from Hong Kong in China are from Zheng et al. [1997], and those from Tokyo in Japan and Beijing in China are from Kumata et al. [2000].

Table 2. Seasonal Difference of the Concentrations of Individual PAH Compounds Measured at Gosan Between 2001 and 2004^a

PAH Compound	Warm Season (April–October)	Cold Season (November–March)	Whole Period
Phen	0.10 ± 0.11	0.99 ± 1.01	0.51 ± 0.81
Anthr	0.04 ± 0.03	0.05 ± 0.04	0.04 ± 0.03
Flt	0.18 ± 0.25	1.14 ± 1.12	0.62 ± 0.91
Pyr	0.16 ± 0.20	0.82 ± 0.76	0.46 ± 0.63
BaA	0.04 ± 0.04	0.20 ± 0.19	0.11 ± 0.15
Chry	0.12 ± 0.14	0.64 ± 0.62	0.36 ± 0.50
BbF	0.13 ± 0.14	0.56 ± 0.63	0.33 ± 0.49
BkF	0.09 ± 0.08	0.32 ± 0.31	0.19 ± 0.25
BeP	0.10 ± 0.11	0.35 ± 0.36	0.21 ± 0.29
BaP	0.09 ± 0.09	0.25 ± 0.21	0.16 ± 0.17
Ind	0.11 ± 0.16	0.52 ± 0.52	0.30 ± 0.42
DahA	0.05 ± 0.04	0.11 ± 0.08	0.08 ± 0.07
BghiP	0.11 ± 0.17	0.51 ± 0.53	0.29 ± 0.43
Total PAHs	1.32 ± 1.40	6.43 ± 5.74	3.65 ± 4.74

^aValues are average ± standard deviation. Units are in ng m⁻³.

kolle, and Estany Redo, 0.07–1.1 ng m⁻³ [Fernandez *et al.*, 2002]) or rural sites (Chesapeake Bay, United States, 0.11–3.65 ng m⁻³ [Dachs *et al.*, 2002]).

[21] As pointed out in section 3.1, no year-by-year trend for the particulate PAH level was observed at Gosan. This is mainly due to short study period. A long-term trend (a decade or longer) is an important indicator for the regional PAH emission trend. In the United States, sediment core data for a longer time span (typically 5 decades or more) were used to find out the long-term PAH emission trend [Lima *et al.*, 2003; Schneider *et al.*, 2001; Van Metre *et al.*, 2000]. Generally, it was observed that the total PAH fluxes to water bodies have leveled off or increased recently.

3.3. Seasonal Variation of the PAH Compound Concentrations

[22] To further identify the seasonal trend, we define the period from November to March as the cold season and the other period from April to October as the warm season. The concentrations of PAH compounds showed a clear seasonal pattern, displaying higher concentrations in the cold season than in the warm season as shown in Table 2. Among 13 PAH compounds quantified, the concentrations of 11 PAH compounds in the cold season were from 3 times to 1 order higher than those in the warm season. The Phen concentration showed the largest difference followed by Flt, Pyr, and Chry.

[23] In the previous studies on the seasonal variations of PAHs [Fernandez *et al.*, 2002; Park *et al.*, 2002; Gigliotti *et al.*, 2000; Halsall *et al.*, 1997], it was suggested that two factors might cause this seasonal pattern: One is the increased fossil fuel usage for heating, and the other is preferential particle phase partitioning of PAHs due to lower temperature during the cold season.

[24] Streets *et al.* [2003] estimated the seasonal variation of fuel-combustion-based emissions in Asia, especially in China. They showed strong seasonal dependence for BC and CO emissions due to the amount of fossil fuel usage. The fraction of the estimated annual emission for BC increased from November to March with a peak in January that coincides with the temporal trend of PAH concentrations observed at Gosan. Thus it is probable that the high concentration of PAHs in the cold season, especially in

January, observed at Gosan is related to the increased fossil fuel usage in China due to lower temperature. This possibility is further discussed in this section and following sections.

[25] Several previous studies have suggested that seasonal variation in PAH concentrations might also be caused by higher preferential particle phase partitioning due to lower temperature during the cold period [Halsall *et al.*, 1997; Gigliotti *et al.*, 2000; Fernandez *et al.*, 2002; Park *et al.*, 2002]. Gas-to-particle partitioning of PAHs is determined by both temperature and TSP concentration. In this study, because only the particulate PAH concentrations were measured, the effect of temperature on the partitioning of PAH compounds between the gas and particle phases was estimated indirectly. The correlations between the temperature and the concentrations of individual PAH compounds did not vary widely (the range of correlation coefficient (r) was from -0.31 to -0.59). If the particulate PAH concentrations increased because of preferential particle phase partitioning, the correlations with temperature and individual PAH compounds should be different since individual PAH compounds have unique vapor pressures.

[26] Since most PAHs are in fine particles [Baek *et al.*, 1991], PM₁₀ can be a substitute for TSP. PM₁₀ was measured at Gosan by Ministry of Environment, Korea. The PM₁₀ concentration for the same sampling day showed no apparent variation between the cold ($37.7 \pm 19.9 \mu\text{g m}^{-3}$) and warm ($39.5 \pm 20.2 \mu\text{g m}^{-3}$) season.

[27] Thus it is likely that the effect of temperature or TSP concentrations on the partitioning of PAH compounds between the gas and particle phases was not a major contributor to the high concentrations of PAHs in the cold season observed at Gosan. To sum it up, the effect of temperature to the fossil fuel usage was more important than the preferential particle phase partitioning to the high concentrations of particulate PAHs at Gosan.

[28] BaP and BeP are isomers with five rings, and the ratio of BeP to BaP is commonly used for distinguishing specific sources of PAHs [Lima *et al.*, 2005]. Since ozonolysis and photodegradation of BaP are faster than BeP [Lima *et al.*, 2005; Katz *et al.*, 1979], the ratio of BeP to BaP contains information on the relative residence time of the PAHs in the atmosphere [Kaneyasu and Takada, 2004;

Table 3. Comparison of the BeP-to-BaP Ratios in This Study With Other Study Results

Site	Period	BeP-to-BaP Ratio	Reference
Gosan, Korea	cold season between 2001 and 2004	0.34~2.36	this study
Gosan, Korea	warm season between 2001 and 2004	0.02~1.67	this study
Gosan, Korea	seven samples when very high PAH concentrations between 2001 and 2004	1.35~2.04	this study
Amami and Miyako island, Japan	June 1993 to Aug. 1994	0.83~5.00	<i>Kaneyasu and Takada</i> [2004]
Amami and Miyako island, Japan	midwinter (period when the concentrations of nss-SO_4^{2-} were high)	2.44~3.13	<i>Kaneyasu and Takada</i> [2004]
Chicago, United States	1994–1995	1.1	<i>Simcik et al.</i> [1999]
Lake Michigan, United States	1994–1995	0.62	<i>Simcik et al.</i> [1999]
Canadian and Russian Arctic	Oct. 1993 to April 1994	2.14~3.59	<i>Halsall et al.</i> [1997]
Canadian and Russian Arctic	May–Sept. 1994	0.67~4.44	<i>Halsall et al.</i> [1997]

Lee et al., 2001; *Simo et al.*, 1991; *Daisey et al.*, 1986]. As shown in Figure 2, the BeP-to-BaP ratio value was distributed from 0.02 to 2.36. Generally, the BeP-to-BaP ratio values were higher (from 0.34 to 2.36) in the cold season than the warm season (from 0.02 to 1.67) at Gosan. In particular, the ratio values between November 2002 and March 2003 (0.73~2.36) and, especially, in the seven samples with high PAH concentrations (1.35~2.04) were high. This indicates that the air parcels arriving at Gosan for the high PAH levels are aged, presumably transported over long distance. Evidently, in this analysis, it is assumed that both BeP and BaP are emitted and transported simultaneously. As *Lima et al.* [2005] have suggested, the diagnostic ratio such as BeP to BaP should be used carefully because the diversity of fuels and combustion conditions was likely to produce variations in ratios from a source.

[29] The BeP-to-BaP ratios from this study are compared with those from other studies in Table 3. The range of BeP-to-BaP ratios in the warm season at Gosan was lower than that at Amami and Miyako island, Japan, and the Canadian and Russian Arctic. This range is similar to those at Chicago and Lake Michigan, United States, indicating the possibility of emission from local emission sources in addition to a small influence of long-range transport. The BeP-to-BaP ratios in the cold season and, particularly, for the seven samples with very high PAH concentrations were similar to those at Amami and Miyako island, Japan, and the Canadian and Russian Arctic. Thus the higher ratios of BeP to BaP in the cold season and, especially, for the seven samples with high PAH concentrations suggest that the air parcels arriving at Gosan are aged.

3.4. Characteristics of Air Parcel Movements

[30] Since it is likely that the PAH levels observed at Gosan and air parcel movement are related, we further studied the variation of the PAH compound concentrations by wind direction at 850 hPa height as shown in Figure 4. The wind direction at 850 hPa has been measured twice per day at Gosan by the Korean Meteorological Administration. We used the data at 0900 local time (LT, sampling start time). The concentrations of PAH compounds were high when the wind came from the northwest and west. *Park et al.* [2004] showed similar trend for nss-Ca^{2+} and NO_3^- at Gosan from the TSP measurement data between 1992 and 2002. *Kaneyasu and Takada* [2004] also demonstrated that the northwesterly and westerly prevailing winds from winter through spring have a significant influence on the high

concentrations of nss-SO_4^{2-} and BC around the Asia-Pacific rim.

[31] To further understand the correlation between the PAH concentrations and air parcel movement arriving at Gosan, backward trajectory analysis was performed for 0900 LT (sampling starting time) on the sampling days using the Hybrid Single-Particle Lagrangian Integrated Trajectory (HYSPLIT4) model (<http://www.arl.noaa.gov/ready/hysplit4.html>, NOAA Air Resources Laboratory, Silver Spring, Maryland, United States). Backward trajectories were calculated for 96 hours using the vertical velocity method at the three starting heights of 500, 1500, and 3000 m, respectively. On the basis of the starting height of 1500 m, the trajectories were classified into five sectors based on the sectors proposed by *Kim et al.* [1998] as shown in Figure 1. An air parcel trajectory was assigned to the sector in which the trajectory stayed most time. The reason the trajectory at 1500 m was used is that it was the lowest height with a minimal topographic effect [*Park et al.*, 2004].

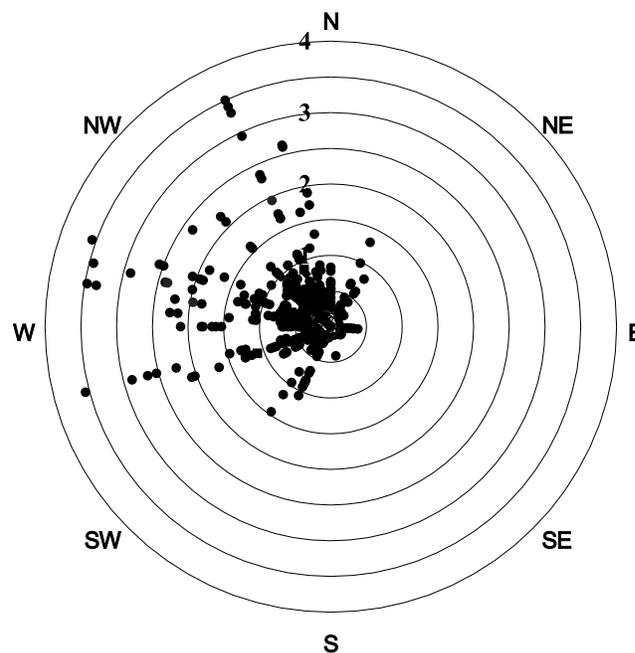


Figure 4. Variation of the particulate total PAH concentrations between 2001 and 2004 at Gosan according to wind direction at 850 hPa level (concentration scale 0.5 ng m^{-3}).

Table 4. Number of Samples, Particulate PAH Concentration, and BeP-to-BaP Ratio by Air Parcel Trajectory^a

Sector	All Seasons				Cold Season				Warm Season			
	Number of Samples (Percent of Total)	Average Concentration, ng m ⁻³	Average BeP-to-BaP Ratio	Number of Samples (Percent of Total)	Average Concentration, ng m ⁻³	Average BeP-to-BaP Ratio	Number of Samples (Percent of Total)	Average Concentration, ng m ⁻³	Average BeP-to-BaP Ratio	Number of Samples (Percent of Total)	Average Concentration, ng m ⁻³	Average BeP-to-BaP Ratio
I	17 (17)	1.56 ± 1.80	0.91 ± 0.36	3 (6)	2.31 ± 3.29	1.04 ± 0.36	14 (26)	1.40 ± 1.47	0.88 ± 0.37	11 (20)	1.78 ± 1.47	1.10 ± 0.32
II	36 (35)	4.85 ± 5.13	1.17 ± 0.43	25 (51)	6.21 ± 5.59	1.20 ± 0.47	11 (20)	1.84 ± 2.11	0.76 ± 0.42	8 (15)	1.84 ± 2.11	0.76 ± 0.42
III	26 (25)	5.96 ± 5.80	1.19 ± 0.55	18 (37)	7.79 ± 6.01	1.39 ± 0.50	8 (15)	0.69 ± 0.64	0.59 ± 0.37	10 (19)	0.69 ± 0.64	0.59 ± 0.37
IV	11 (10)	1.07 ± 1.40	0.61 ± 0.35	1 (2)	4.87	0.75	10 (19)	0.62 ± 0.58	0.67 ± 0.40	11 (20)	0.62 ± 0.58	0.67 ± 0.40
V	13 (13)	0.63 ± 0.36	0.74 ± 0.42	2 (4)	0.68 ± 0.38	1.17 ± 0.27	11 (20)					
Total	103 (100)			49 (100)			54 (100)					

^aThe values shown for concentration and ratio indicate average value ± 1 standard deviation.

[32] The number of samples, the PAH concentrations, and the BeP-to-BaP ratio for each sector during the whole period and in the cold and warm seasons are shown in Table 4. In the whole period about one third of air parcels came from sector II, northern China, and about a quarter came from sector III, southern China. The air parcels from sector I, Korea, were next, with 17% of the total samples. In the cold season, about 90% of air parcels came from either sectors II or III. However, the air parcels observed in the warm season were evenly distributed. Thus it is evident that the air masses observed at Gosan were mainly from China, especially in the cold season.

[33] For the whole period, the total PAH concentrations at sectors II and III were about 5 times higher than those at other sectors ($p < 0.01$), but there was no statistical difference ($p > 0.05$) in the PAH concentrations between sectors II and III. When air parcels were from sector V, the concentrations of total PAHs, though the lowest, were not statistically different ($p < 0.05$) from the concentrations of PAHs from sector IV.

[34] In the cold season, higher PAH concentrations were observed when air parcels came from sector III, and lower ones were observed when air parcels came from sector V. In the cold season, the total PAH concentrations were higher in all sectors than in the warm season except sector V, indicating that the PAH concentrations increased regardless of air parcel trajectories at Gosan in the cold season. In the warm season the concentrations of PAHs in sectors II and III were high although the frequencies of the air parcels from sectors II and III were similar to those from other sectors. Thus it is clear that the PAH concentrations at Gosan were influenced when air parcels moved from northern and southern China irrespective of the season, but it is more evident in the cold season.

[35] The distribution of the BeP-to-BaP ratios by sector was similar to that of the PAH concentrations. The BeP-to-BaP ratios in sectors II and III were higher than those in other sectors during the whole period, indicating that the particulate PAHs from sectors II and III were relatively aged compared to other sectors. All of the BeP-to-BaP ratios from the five sectors in the cold season were higher than those in the warm season. This result means that the particulate PAH concentrations at Gosan in the cold season were more aged. Thus the influence of long-range transport seems to be high in the cold season.

[36] Figure 5 shows the variation of the mean concentrations of each PAH compound by sector. The concentrations of most PAH compounds were higher when air parcels were from sectors II or III than those from other sectors. This trend is most evident for the compounds with high concentrations such as Flt, Pyr, and Phen at Gosan.

[37] The ratios of the concentration of individual PAH compounds to the total PAHs (individual PAH/ \sum PAHs) were also different according to sector as shown in Figure 6a. This indicates that the major emission sources and/or transport patterns of particulate PAH compounds were different depending on the sectors. The ratios were similar both in sectors II and III. The sum of the ratios of Phen, Flt, and Pyr in sectors II and III were up to 40% and were higher than other sectors. However, the ratios at sectors I, IV, and V were different from each other and from the values in sectors II and III.

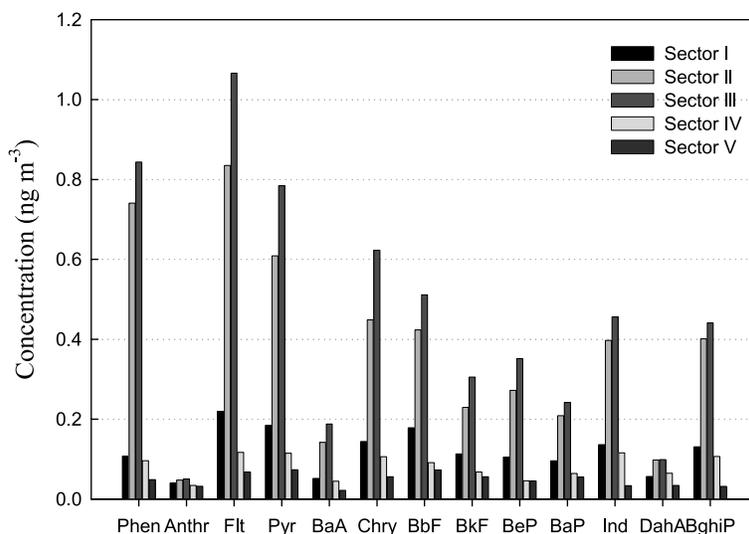


Figure 5. Variation of the average concentrations of individual PAH compounds by sector classification. The sector classification is shown in Figure 1.

[38] When compared to the ratios at several urban sites in northeast Asia (Figure 6b), the composition ratios from sectors II and III were similar to that in Beijing in winter. In Beijing, the sum of the ratios of Phen, Flt, and Pyr was also up to 40% in winter and decreased to about 20% in summer. The ratios of Ind and BghiP in Beijing in summer were higher, indicating the seasonal change of PAH emission sources. Phen, Flt, and Pyr are mainly emitted from coal combustion and used as fingerprints of coal combustion [Simcik *et al.*, 1999; Larsen and Baker, 2003]. Thus the difference in the ratios to the total PAHs between winter and summer indirectly indicates the increase of fossil fuel usage, in particular, coal usage in Beijing in winter. This result agrees well with the result of Streets *et al.* [2003], who showed strong seasonal variability of BC according to the amount of fossil fuel usage in China. The composition ratio in Tokyo in winter was different from that in Beijing in winter although the sampling period was the same, indicating that the main fossil fuel for heating was different between Tokyo and Beijing in winter.

[39] Ind and BghiP are representative compounds to be emitted from vehicles [Simcik *et al.*, 1999; Rogge *et al.*, 1993]. In Figure 6b the values of ratios for Ind and BghiP in Beijing in summer were about twice as high as those in winter and similar to those in Seoul and Tokyo in winter. Thus the contribution of vehicular emissions to the PAHs seems to be high during summer in Beijing, Seoul, and Tokyo in winter.

[40] Among the fingerprint species for coal combustion and vehicle emission, some compounds are mostly in the particle phase (Ind and BghiP), and others exist both in the gas and particle phases (Phen, Flt, and Pyr). Since we have measured only particulate PAHs, direct use of these compounds as fingerprints might give limited results. Still, this approach can give useful information since high concentration of Phen, Flt, and Pyr indirectly implies higher emissions of both the gas and particle phases.

3.5. Relationship Between the Particulate PAHs and Non-sea-salt-(nss)-SO₄²⁻

[41] The correlations among ambient trace species become higher when their emission source or/and transport patterns in the atmosphere are similar. In order to understand the long-range transport pattern for particulate PAHs, the relationship between the concentration of particulate PAHs and nss-SO₄²⁻ measured on the same sampling days of PAHs is investigated. Among inorganic ions in aerosol, nss-SO₄²⁻ observed at Gosan is thought to be mainly derived from fossil fuel combustion and transported from China except in summer [Arimoto *et al.*, 1996; Park *et al.*, 2004]. As discussed in section 3.1, nss-SO₄²⁻ has different characteristics compared to PAHs: small concentration variation and different concentration peaks, in spring instead of winter.

[42] In Figure 7a the total particulate PAH concentrations were correlated with nss-SO₄²⁻. In the warm season, even when the concentrations of nss-SO₄²⁻ were high, the PAH concentrations remained relatively low. In the warm season, wind directions were mainly from the east and southeast. Thus the high concentrations of nss-SO₄²⁻ in this season were due to local emission sources from Jeju Island and/or transport from Japan. Kaneyasu and Takada [2004] stated that relatively high concentration of nss-SO₄²⁻ at Gosan in summer was caused by pollution sources or volcanic emissions from Japan. The low concentrations of PAHs seem to be related with the low level of PAH concentration in Japan (for example, Tokyo, shown in Figure 3).

[43] In the cold season, the high concentrations of particulate PAHs were correlated with the high concentrations of nss-SO₄²⁻. At the same time, BeP-to-BaP ratios were high when nss-SO₄²⁻ concentrations were high (Figure 7b). In the cold season the northwestern monsoon prevails at Gosan. Thus high concentrations of nss-SO₄²⁻ and PAHs during the cold season were apparently due to transport from the northeast Asian continent outflow rather than the influence

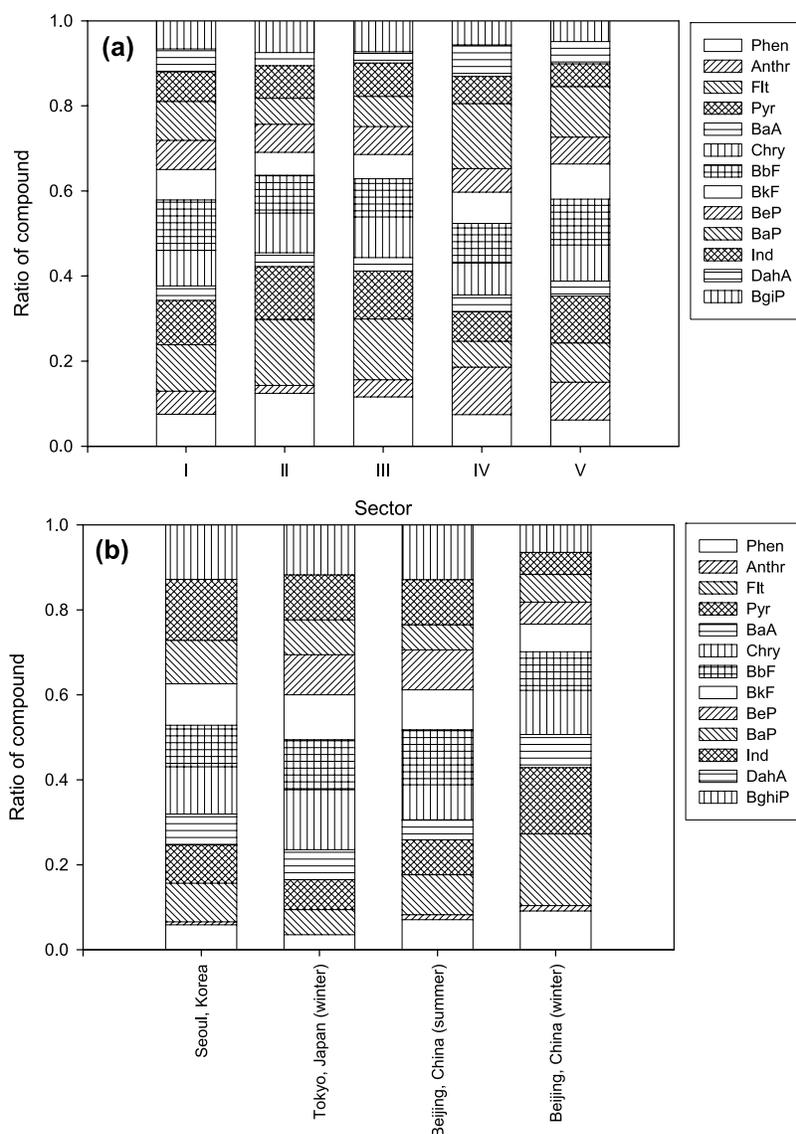


Figure 6. Compositions of PAH compounds (individual PAH/ Σ PAHs) (a) at Gosan according to sector classification given in Figure 1 and (b) at several urban sites in northeast Asia (the data from Seoul are from *Park et al.* [2002], and those from Tokyo and Beijing are from *Kumata et al.* [2000]).

of local emission sources, though they showed different concentration characteristics.

4. Summary

[44] To characterize the temporal trend and to understand long-range transport characteristics of particulate PAHs in northeast Asia, particulate PAHs were measured for 4 years between November 2001 and January 2004 at Gosan, a background site in Korea. The total average concentration of PAHs ($3.65 \pm 4.74 \text{ ng m}^{-3}$) was about 1 or 2 orders lower than those in Seoul, Tokyo, Hong Kong, and Beijing, representative urban areas in northeast Asia. However, when compared to the PAH concentrations in remote areas such as Mount Halla in Korea and Amami and Miyako in Japan, the average concentrations of PAHs at Gosan were 1 or 2 orders higher, indicating the strong influence of

continental outflow. The PAH concentrations increased from November to March and decreased from April to October mainly because of the seasonal variations in fossil fuel usage amount. Preferential partitioning to the particulate phase due to low temperature in the cold season was not a dominant factor.

[45] The PAH concentrations at Gosan increased when air parcels moved from northern and southern China irrespective of the season. In the distribution of PAH compounds by sector, the concentrations of Flt, Pyr, and Phen and their ratios over the total PAH concentrations were higher when air parcels were from China than when they were from other areas. Compared to the ratios at several urban sites in northeast Asia, the ratios were similar to those in Beijing, China, in winter, indicating the influence of emissions from coal combustion in China.

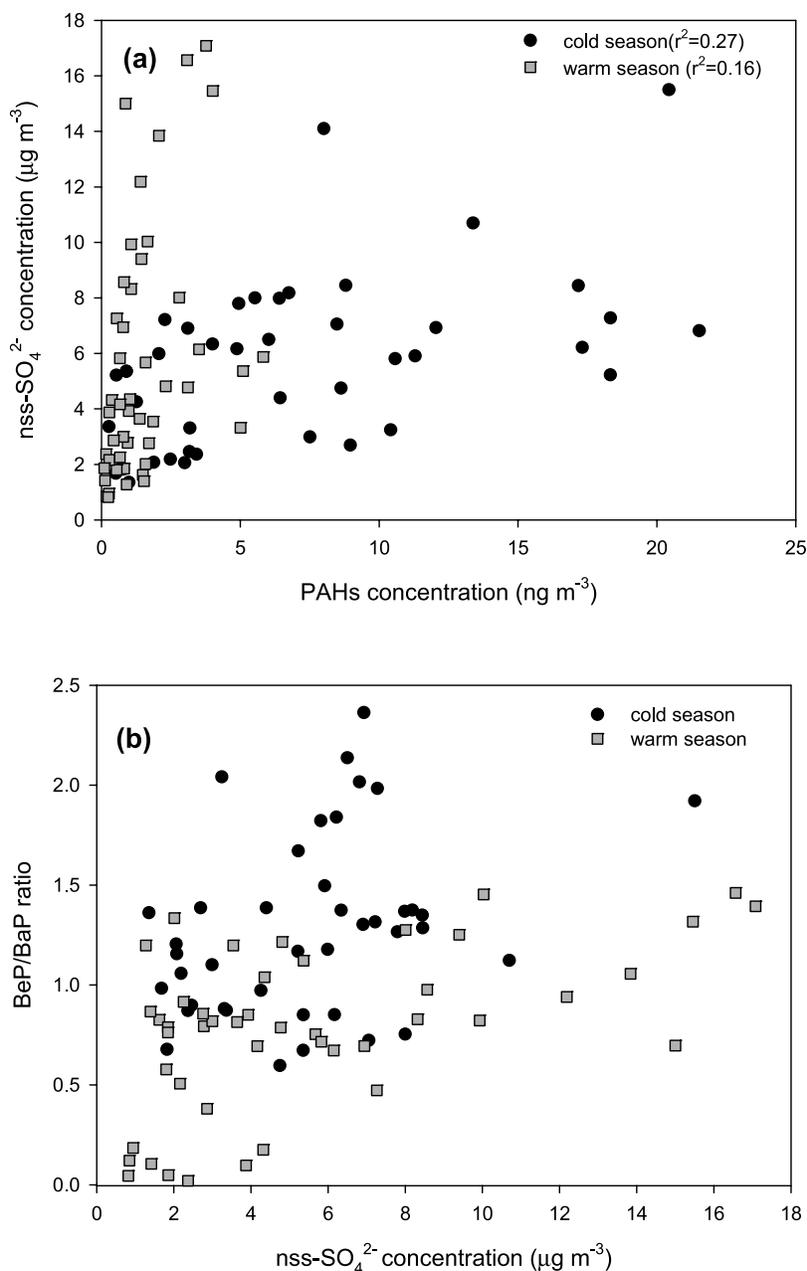


Figure 7. Relationship between the concentrations of nss-SO₄²⁻ concentrations and (a) particulate PAHs concentrations and (b) BeP-to-BaP ratios measured between 2001 and 2004 at Gosan.

[46] The correlation between the high concentrations of PAHs and nss-SO₄²⁻ during the cold season was good apparently because of transport from the northeast Asian continent outflow, by the northwestern monsoon that prevails over the region. However, the period of the maximum concentrations of PAHs and nss-SO₄²⁻ was different, winter for PAHs, and spring for nss-SO₄²⁻, implying different emission patterns.

[47] To monitor the long-term trend of PAH emissions, it is important to identify major emission sources in northeast Asia and to estimate their effects on human health, the ecosystem, and the global environment. Evidently, this study result alone is not sufficient to suggest a

long-term trend. Thus further continuous measurement is warranted.

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