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Polyaromatic hydrocarbons (PAHs) levels from two industrial zones (Sihwa and Banwal) located in An-san city of the Korean Peninsula and their influence on lake

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ABSTRACT: The present research investigation was aimed at monitoring the levels of polyaromatic hydrocarbons (PAHs) in the Korean ambient air, pine needle, and soil. Samples were collected from two large industrial zones of An-san city namely Sihwa and Banwal, both these industrial zones were further divided into major and minor zones in order to compare the levels of PAHs between the two industrial zones. Furthermore, the quality of the lake water near these two industrial zones was also monitored by analyzing water (dissolved phase, suspended solids) and sediment samples for the detection of PAHs. In this study, a high volume sampling method (HVAS-Sibata) was employed to collect airborne PAHs in both the particulate and gas phases. Hewlett Packard gas chromatographs equipped with mass spectrometer detectors (GC/MS) were used to analyze the samples. The monitoring data revealed that Sihwa major industrial zone have lower levels of PAHs in comparison to Sihwa minor industrial zone where increase levels of PAHs were observed in both the ambient air and soil samples, whereas in case of pine needle sample the PAHs levels were higher in Sihwa industrial zone. The sum of PAHs levels in ambient air from Sihwa major industrial and minor zones were found to be ranging between 50.17 ng/m^3 and 96.46 ng/m^3 whereas the estimated levels of PAHs from Banwal major industrial and minor zones were found to be ranging between 149.64 ng/m^3 and 34.87 ng/m^3 respectively. Since Banwal major industrial zone includes many sources, higher levels of PAHs were observed in almost all the samples as compared to Banwal minor industrial zone. Similarly, the level of PAHs in water and sediment samples from lake near Sihwa industrial zone showed an increase trend in dissolved and suspended solids in comparison to samples collected near Banwal industrial zone. Phenanthrene, Indeno[1,2,3-c,d]pyrene and Benzo[g,h,i]perylene showed the highest levels in both the zones. However, the levels of PAHs in sediment samples were lower near Sihwa industrial zone and vice versa, however lowest concentration of Anthracene was observed in both the zones. A detailed and thorough environmental monitoring for the presence of these toxic compounds in the environment is currently needed to set a baseline for future research. The work is still in progress to estimate the levels of PAHs from both these sites within our laboratory. @JASEM

Polycyclic aromatic hydrocarbons (PAHs) form a ubiquitous class of environmental chemical pollutants. These are multi-ringed compounds and have received considerable attention in recent years because some of these compounds are potent carcinogenic or mutagenic in nature (Marr *et al.*, 1999). Their characteristic of lipophilicity, low water solubility and adsorption to marine particles and sediments makes them a potentially dangerous group of chemicals and a threat to the environment and its bioresources (Macias-Zamora *et al.*, 2002; Raoux *et al.*, 1999), as these compounds may undergo specific biotic and abiotic transformations reactions, thus causing harmful damaging effects on human health and its environment.

PAHs are derived mainly from anthropogenic inputs and are products of incomplete combustion. Although numerous researchers have measured PAHs concentration in ambient air, very few studies link their presence to a specific source. Anthropogenic sources contribute significantly to the concentration of PAHs in the environment, as well as natural combustion sources of PAHs. Each individual source is characterized by a specific molecular pattern, allowing the source of these compounds to be established (Savinov *et al.*, 2000; Guinan *et al.*, 2001). PAHs are often associated with small atmospheric particles that can be carried far from the point source (Preston *et al.*, 2000). The large amounts of fossil fuels burnt's for domestic heating could also contribute to a local atmospheric sources of PAHs along with urban run-off and automotive sources which have been shown to be a major source of PAHs (Dickhut *et al.*, 2000). Particle size and organic carbon have also been shown to influence the concentration and therefore distribution of PAHs in sediments (Yang, 2000). In addition, physical-chemical properties of some PAH, like chemical reactivity, can also contribute to modify the original distribution pattern of the emission sources (Soclo *et al.*, 2000). Industrial activities also constitute the

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** Corresponding Author: Phone 92-(051)9271598 Ext: 114; Fax 92-(051)9271597; E-mail: hashmi71@gmail.com* main source of PAHs, but it is difficult to identify which PAHs have been introduced from pyrogenic or petrogenic origin. Studies have shown that PAHs from these sources exhibited different chemical behaviors and distributions. PAHs from pyrogenic sources tend to be more strongly associated with sediment and soot particles and more resistant to microbial degradation than PAHs from petrogenic sources (Benlahcen *et al.*, 1997). It is generally accepted that pyrogenic PAHs are characterized by the dominance of high molecular mass 4-6 ring PAHs over the low molecular mass 2-3 ring compounds (Guinan *et al.*, 2001). Ratios between individual PAHs compounds are used to identify the processes from which PAHs originate (Wang *et al.*, 1999; Woodhead *et al.*, 1999), however they are not conclusive in the analysis of petrogenic and pyrolytic origin. Baumard *et al.*, (1999) reported that PAHs ratios between compounds suggested that a mass petrogenic signature existed closer to land than in offshore sediments (fig 1).

The objectives of the current study were to monitor and compare the levels of PAHs from two major and minor industrial zones of An-san city namely Sihwa and Banwal, and also to observe the quality of the lake water near these two industrial zones. In general, an attempt was also made to identify the possible contribution from long-range transport.

MATERIALS AND METHODS

Two sampling sites were identified for detecting the levels of PAHs these includes Sihwa and Banwal industrial zones for sample collection. The information related to each sampling site is described in Fig 1.

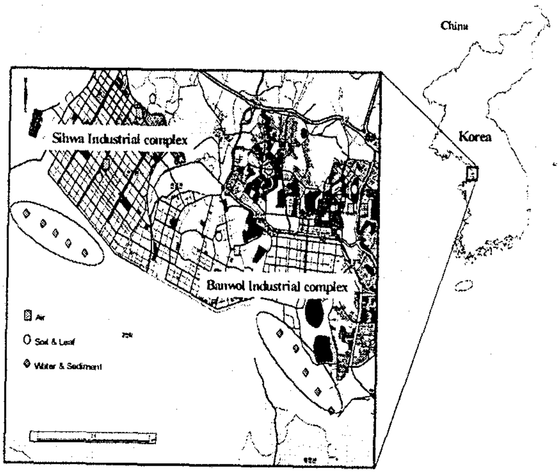

Fig 1: Geographical location of sample collection from Korean

Sample collection: Ambient air samples were collected using glass fiber filter (GFF) and polyurethane foam plugs (PUF) were used to collect the particulate and gaseous phases for the PAHs. The GFFs were pre-cleaned by baking at 450 °C for 24 hours followed by storage in an aluminum package within a dessicator prior to use. The PUF plugs were pre-extracted in acetone for 18h. Ambient air samples were collected between January 2002 and February 2002 using a high volume air sampler. Similarly, soil samples were collected from superficial surface from each zone at 10-different points and then mixed in equal proportion so as to represent a single sample. The pine needle samples were also collected in the similar manner approximately 2-2.5 meters high above the ground level. However for water and sediments composite samples were prepared by selecting five sampling points at individual site from each zone at a distance of approximately 100 cm from each other. The samples after collection were transported to the laboratory and stored at 4 °C prior to analysis.

Analytical method: The sample analysis was performed according to modified US EPA method TO13A. The GFFs and PUF plugs were extracted for 24 hours in ASE-Dionex-2000, respectively. The resulting solutions were then spiked with a mixture of PAH surrogate standards (50 ng), then cleaned up by refluxing in n-hexane, followed by fractionation on a 200 ml DCM 10% in n-hexane. The final elutes were concentrated to 100 $\mu\ell$ with N_2 gas before being spiked with PAH internal standards (50 ng). The final elutes were specifically analyzed using highresolution gas chromatography (HP6890) and mass spectrometry (HP-5893) with a DB5 column (J & W Scientific, DB-5 crosslinked 5 % phenylmethyl silicone; 80m x 0.32 mm, 1.0 µm film thickness) or equivalent, by injecting 1 µL of the sample (injection temperature; 280 °C) using Helium as an carrier gas with a flow rate of 1.2ml/min. The mass spectrometer was operated in the EI mode on the analyzer mode SIR. The GC was operated with a splitless 1 µl injection at a temperature of 280 °C. The instrument was programmed as follows; the temperature was altered in three steps, initially it was maintained at 90 °C (4min), then it was slightly increased to 300 °C at 10 °C /min, and finally it was increased to 300 °C where it was held isothermally for 15min. At least 5 scans per peak were obtained, not to exceed 1 second per scan.

RESULTS AND DISCUSSION

PAHs levels in ambient air from two industrial zones: The PAHs levels in ambient air from both the major and minor industrial zones of the Sihwa and Banwal is reported in Table 1. The levels of PAHs' compounds in samples collected from Sihwa major and minor industrial zones for ambient air revealed that the sum of PAHs is lower in Sihwa major industrial zone as compared to Sihwa minor industrial zone, however the levels of Phenanthrene. Indeno[1,2,3-c,d]pyrene and Benzo[g,h,i]perylene were higher in both the zones, whereas the lowest levels of Benz[a]anthracene was observed in both the zones. These compounds have been found in the ambient air (Pyysalo *et al.*, 1987), and some of them have been identified as potential tracers of PAHs emissions (Ramdahl *et al.*, 1982).

Similarly, the levels of PAHs in Banwal major and minor industrial zones were found to be highest for Indeno[1,2,3-c,d]pyrene and Benzo[g,h,i]perylene in Banwal major industrial zone, whereas the lowest levels of Benz[a]anthracene and Chrysene was observed. However, in Banwal minor industrial zone, no significant values were observed, indicating that the level of PAHs is low. Besides, it is important to note that PAHs distribution in atmospheric particles were mainly low-molecular-weight components (Benlahcen *et al.*, 1997). The pre dominance of high-molecular-weight PAHs is less often observed (Muel and Saguem, 1985).

PAHs levels in pine needle and soil from two industrial zones: The samples collected from pine needle showed the highest values of Phenanthrene, Fluoranthene and Pyrene in almost all the industrial zones, whereas lower levels of Dibenzo[a,h]anthracene and Benzo[a]pyrene was observed in almost all the samples. The soil samples also showed the highest levels of Indeno[1,2,3-c,d]pyrene and Benzo[g,h,i]perylene in almost all the samples, whereas the lower levels of Anthracene was observed in all the samples collected.

PAHs levels in water (dissolved phase and suspended solids) and sediment from lake near two industrial zones: In dissolved phase higher levels of Phenanthrene was observed in both the zones, whereas lower levels of Benz[a]anthracene and Benzo[a]pyrene was observed in samples collected from lake near Sihwa industrial zone, Dibenzo[a]anthracene was below detection limit in both the zones, however 0.494 ng/L PAHs levels were observed in the dissolved phase as reported in the Table 2.

The most contaminated samples were localized near the lake and higher levels of Indeno[1,2,3-c,d]pyrene and Benzo[g,h,i]perylene was observed in both the suspended solids and sediments samples collected from lake near these two industrial zones. Indeed, this zone is considered as the possible seat of major industrial activities, whereas the lower levels of Anthracene was observed as also reported in the Table 2.

The distribution of PAHs in the multimedia: The cumulative results of ambient air were further categorized according to the distribution of the ring structure and are presented in Figure 2. It can be observed that the 6-membered ring occupy the highest % (42.1%) among all the compounds, whereas the 3 and 4-membered ring accounts for the lowest % ranging between 21.2-21.9 %. However, in case of soil samples the 6-membered ring occupy the highest % (46.8%) followed by the 4-membered ring (23.6%). In sediment samples 4-membered ring occupy for highest %, whereas the 3-membered ring occupy the lowest % as shown in the Figure 1. Similarly water samples showed the highest % of 3-membered ring followed by the 4-membered ring, however 5 and 6-membered ring does not contribute significant levels. Finally, the pine needle samples showed the 4-membered ring to account for the highest % (53.3%) subsequently followed by 3-membered ring structure.

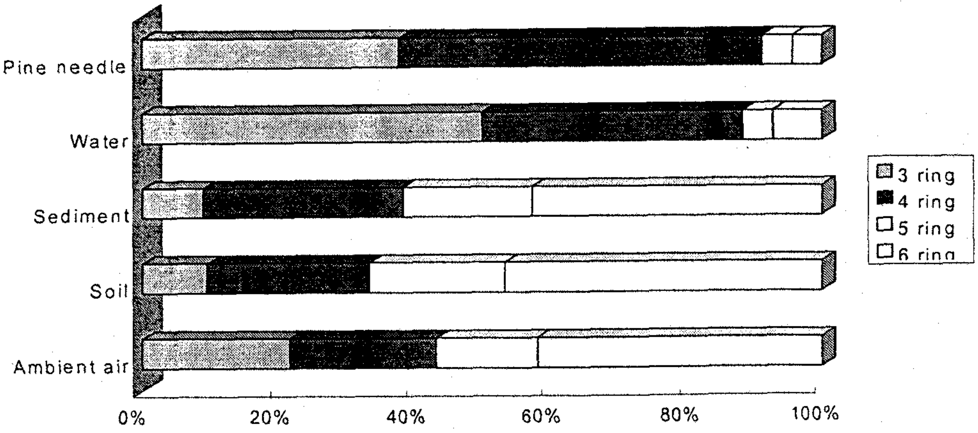

Fig 2 : Distribution of PAHs in multimedia with sample types

Similarly the cumulative results of PUFs and GFFs (air) and particulate and dissolved phase (water) were categorized according to the distribution of the ring structure and are presented in Figure 2. It can be observed that the 3-membered ring occupy the highest % (59.7 %) among all the compounds, whereas the 5 and 6-membered ring does not contribute significant levels and accounts for the lowest 0.3 %. However, in case of dissolved phase samples (water) the 3-membered ring occupy the highest % (55.0 %) subsequently followed by the 4-membered ring structure (38.8 %). In particulate phase samples (water) 6-membered ring occupy for highest % (35.0 %), whereas the 5-membered ring occupy the lowest % (15.2 %) as shown in the Figure 2. Similarly GFF (air) samples showed the highest % of 6-membered ring (61.5 %) followed by the 5-membered ring (21.7 %), however 3 and 4-membered ring does not contribute significant levels (3.0 – 13.7 % respectively).

Table 1. Polyaromatic hydrocarbons (PAHs) levels in ambient air, pine needle and soil samples from two industrial zones

Compounds	Sihwa major industrial zone			Sihwa minor industrial zone		
	Ambient air ng/m^3	Pine needle (ng/g)	Soil (ng/g)	Ambient air ng/m^3	Pine needle (ng/g)	Soil (ng/g)
Anthracene	0.615	3.800	0.747	3.693	7.963	1.170
Fluorene	4.849	7.188	1.693	5.339	9.403	2.090
Phenanthrene	8.434	41.433	12.913	11.795	44.679	14.061
Fluoranthene	5.723	58.060	13.358	10.369	37.596	12.443
Pyrene	4.890	53.606	8.531	9.191	25.654	18.565
Benz[a]anthracene	0.517	3.539	1.019	1.572	1.931	2.383
Chrysene	0.971	18.081	4.124	1.43	8.669	4.936
Dibenzo[a,h]anthracene	2.458	1.119	5.090	6.115	0.149	22.327
Benzo[b]fluoranthene	1.368	5.284	3.541	2.354	1.372	4.864
Benzo[k]fluoranthene	1.508	4.904	5.113	3.245	1.385	1.774
Benzo[a]pyrene	0.850	1.303	1.531	2.711	0.266	6.602
Indeno[1,2,3-c,d]pyrene	9.408	5.149	24.516	20.421	0.902	63.232
Benzo[g,h,i]perylene	8.586	4.613	27.757	18.225	0.793	37.025
Σ PAHs	50.17	208.08	109.93	96.46	140.76	191.47
Compounds	*Banwal major industrial zone*			*Banwal minor industrial zone*		
Anthracene	5.111	1.944	1.199	1.708	1.318	0.881
Fluorene	6.895	14.267	1.635	3.577	15.004	1.204
Phenanthrene	12.583	50.919	13.727	5.679	14.753	9.898
Fluoranthene	12.426	25.632	23.109	4.650	15.772	15.224
Pyrene	11.002	21.928	13.250	4.422	11.431	9.027
Benz[a]anthracene	2.071	2.063	4.708	0.593	1.107	1.611
Chrysene	1.666	11.100	11.587	0.86	5.145	5.272
Dibenzo[a,h]anthracene	13.147	0.197	10.510	1.381	1.723	17.314
Benzo[b]fluoranthene	3.881	2.054	11.635	0.882	1.935	5.852
Benzo[k]fluoranthene	4.095	1.862	11.464	1.144	1.737	4.699
Benzo[a]pyrene	3.35	0.847	11.915	0.716	0.499	1.810
Indeno[1,2,3-c,d]pyrene	39.119	1.260	34.672	4.971	6.244	44.243
Benzo[g,h,i]perylene	34.294	0.988	29.509	4.286	4.903	35.534
Σ PAHs	149.64	135.06	178.92	34.87	80.67	152.57

Σ PAHs = sum PAHs

* Based on mean of two results (n=2)

Table 2. Polyaromatic hydrocarbons (PAHs) levels in water (dissolved phase and suspended solids) and sediment from lake near two industrial zones

Compounds	Lake samples near Sihwa industrial zone			Lake samples near Banwal industrial zone		
	Water (ng/L)		Sediment	Water (ng/L)		Sediment
	Dissolved phase	Suspended solids	(ng/g)	Dissolved phase	Suspended solids	(ng/g)
Anthracene	1.710	0.070	0.442	0.799	0.027	1.817
Fluorene	8.140	0.231	0.988	4.756	0.120	2.085
Phenanthrene	24.966	1.232	3.434	12.278	0.654	9.131
Fluoranthene	9.104	1.475	4.005	7.024	0.917	21.152
Pyrene	14.308	0.995	3.044	3.728	0.577	17.636
Benz[a]anthracene	0.267	0.127	0.650	0.393	0.085	2.761
Chrysene	0.543	0.396	1.274	1.729	0.548	6.610
Dibenzo[a,h]anthracene	0.494	BDL	1.810	BDL	BDL	10.361
Benzo[b]fluoranthene	0.320	0.620	1.987	0.661	0.426	7.436
Benzo[k]fluoranthene	0.363	0.638	2.126	0.742	0.536	9.052
Benzo[a]pyrene	0.219	0.053	1.942	0.191	BDL	2.863
Indeno[1,2,3-c,d]pyrene	1.257	1.755	7.979	0.311	0.943	36.634
Benzo[g,h,i]perylene	1.166	1.874	6.392	0.235	0.662	32.982
Σ PAHs	62.85	9.46	36.07	32.85	5.49	160.52

BDL = Below detection limit; Σ PAHs = sum PAHs

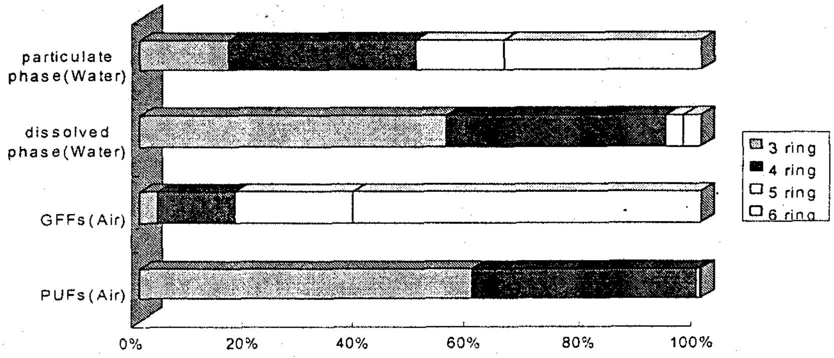

Fig 3: Distribution of PAHs in water (particulate and dissolved phase) and air (GFFs and PUFs) from two industrial zones

Conclusion: Comparison of data collected from Sihwa and Banwal major and minor industrial zones and their individual effect on lake water will help in providing a baseline for future research and at present will serve as a useful tool in assessing PAHs contamination levels and possible sources responsible. It is also suggested that atmospheric deposition may be the major source of PAHs to the water bodies. The comparison of Sihwa industrial zones (major and minor) revealed that Sihwa major industrial zone is contributing some effect on the Sihwa minor industrial zone as higher levels of PAHs were observed in Sihwa minor industrial zone in both the ambient air and soil samples except for pine needle samples. Banwal major industrial zone has no significant effect on Banwal minor industrial zone as can be observed from the Table 1.

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