Polynuclear Aromatic Hydrocarbon Concentration and Mutagenicity of Airborne Particles in Urban Air: Comparison of Tokyo Area and Santiago

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Five mutagenic and/or carcinogenic polynuclear aromatic hydrocarbons (PAHs), and Salmonella mutagenicity in airborne particles collected at three stations (industrial, commercial/residential, and agricultural areas) in Santiago, Chile were measured, and compared with the same measurements in the Tokyo metropolitan area. PAH concentrations showed daily variations in both cities. The concentrations of four-ring PAHs were higher in the Tokyo area than in Santiago, and the concentrations of five-or-more-ring PAHs were higher in Santiago than in the Tokyo area. Mutagenic activities also showed daily variations in both places, and were generally higher in Santiago. In the Tokyo area, the mutagenic activities were higher under conditions of TA98–S9 mix than under TA98+S9 mix while in Santiago, the activities were similar under the two mixes. There were good correlations between PAH concentrations and mutagenic activities in both areas. In Santiago, mutagenic activities and PAH concentrations were higher in the commercial/residential area and the industrial area than in the agricultural area.

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INTRODUCTION

Various pollutants exist in small quantities in a city atmosphere and are inhaled by human beings, and this may lead to cancer. This will also increase the ratio of lung cancer in people who are exposed to those harmful pollutants.[1)]

Santiago, the capital of the Republic of Chile on the South American continent, is positioned quite opposite to Japan, and the four seasons are reversed. Santiago lies in a basin at 520 m above sea level, and the precipitation amount is 267 mm per year.[2)] Although the air pollution problem has been intensifying with urbanization in recent years, understood, needed measurements have not been made of the emission of mutagenic /carcinogenic air pollutants in this area. The aim of the present study was to know the air pollution in Santiago and compare it with that in the Tokyo area. To understand the toxicity of the mutagenic /carcinogenic air pollutants, we analyzed 5 PAHs and also measured Salmonella mutagenicity in airborne particles.

MATERIALS AND METHODS

Reagents ——
Solvent: Pesticide-residue-analysis-grade dichloromethane (Kokusan Chemical Works, Ltd., Japan) and fluorometric-analysis-grade DMSO (Dojin Chemical Laboratory, Ltd., Japan) were used in mutagenic testing. For PAH analysis, pesticide-residue-analysis-grade acetonitrile (Kokusan Chemical Works, Ltd.) was used.
PAH Standard: Pyrene (Pyrene), benz[*a*]anthracene (BaA), benzo[*a*]pyrene (BaP) (Wako Pure Chemical Industries, Ltd., Japan), benzo[*k*]fluoranthene (BkF) (Koch-Light Laboratory, Ltd., U.K.), and benzo[*ghi*]perylene (BghiP) (Aldrich Chemical Co., Inc., U.S.A.) were used.
Mobile Phase: Liquid chromatograph-grade acetonitrile (Kokusan Chemical Works, Ltd.) and deionized distilled water were used.
Sampling of Airborne Particles ——
The Sampling Stations in Santiago: La Pintana (agricultural area), Nunoa (commercial and residential area), and Cerrillos (industrial area), are shown in

Fig. 1A. Airborne particles were collected on quartz fiber filters : QM-A (20 × 25 cm) (Whatman International, Ltd., Japan) by PM10 high-volume air samplers (Graseby Andersen 1200 VFC in La Pintana, Wedding & Associates in Nunoa and in Cerrillos), at a flow rate of about 1.1 m^3/min, for 24 hr at each sampling. The sampling term was from June 4 to July 22, 1996, during the Santiago winter.

The sampling stations in the Tokyo area are shown in Fig. 1B. Airborne particles were collected at three stations: in Shirokanedai, Minato-ku (a commercial and residential area, the roof of the National Institute of Public Health building); in Yoyogi, Shibuya-ku (a principal road, beside Yamate-doori street), and in Sagamihara city (a suburb of Tokyo, the roof of an Azabu University building), on quartz fiber filters: 2500QAT (20 × 25 cm) (Pallflex Products Co., U.S.A.), using a high-volume air sampler (Kimoto Electric Co., Japan), at a flow rate of about 1.3 m^3/min, for 24 hr at each sampling. As stated, sampling was done during the winter season in Santiago; in Tokyo also, sampling was conducted during the winter (November–January), as follows. In Shirokanedai, sampling was done at 5-day intervals from November 6 to November 24, 1996, from December 6, 1996 to January 17, 1997, and every day from November 26 to 30, 1996. In Yoyogi and Sagamihara city, sampling was done at 5-day intervals from November 2 to November 29, 1996, and from November 29 to December 5, 1996.

The collected filters in Santiago were protected from light by aluminum foil, cooled on dry ice, and transported by air to Tokyo for analysis.

Extraction of Organic Components —— Two disks 20 mm diameter were cut from the collected filters with a belt punch for PAH analysis, and then 3.0 ml of acetonitrile was added and extracted by ultrasonication. The supernatant was used for HPLC analysis.

For mutagenic testing, half of the collected area of each filter was cut into small pieces and extracted with 100 ml of dichloromethane by ultrasonication. The residue was dissolved in 2.0 ml of DMSO and used for mutagenic testing.

PAH Analysis —— Using a multi-column HPLC/spectrofluorometer /computer[3] system, five PAHs (BaA, BkF, and BaP are carcinogens;[4] Pyrene and BghiP[5] are promoters of cancer) were determined in the atmosphere using previous wavelength conditions.[3]

Mutagenicity Testing —— The mutagenicity test was conducted by a pre-incubation method[6] using

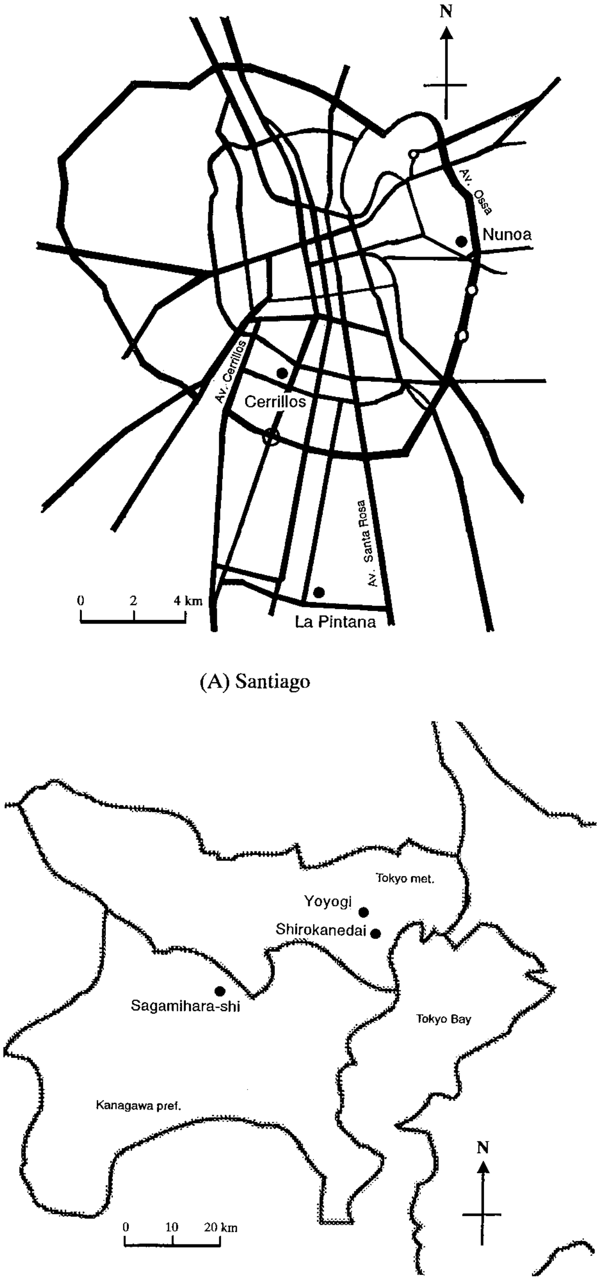

Fig. 1. Sampling station in (A) Santiago and (B) Tokyo Area

Salmonella typhimurium TA100 and TA98, each of them in the presence and absence of S9 mix. The specific mutagenic activity value of every sample in 1 m^3 air was calculated from the slope of the testing results.

RESULTS

PAH Concentration

The geometric mean values of concentrations of

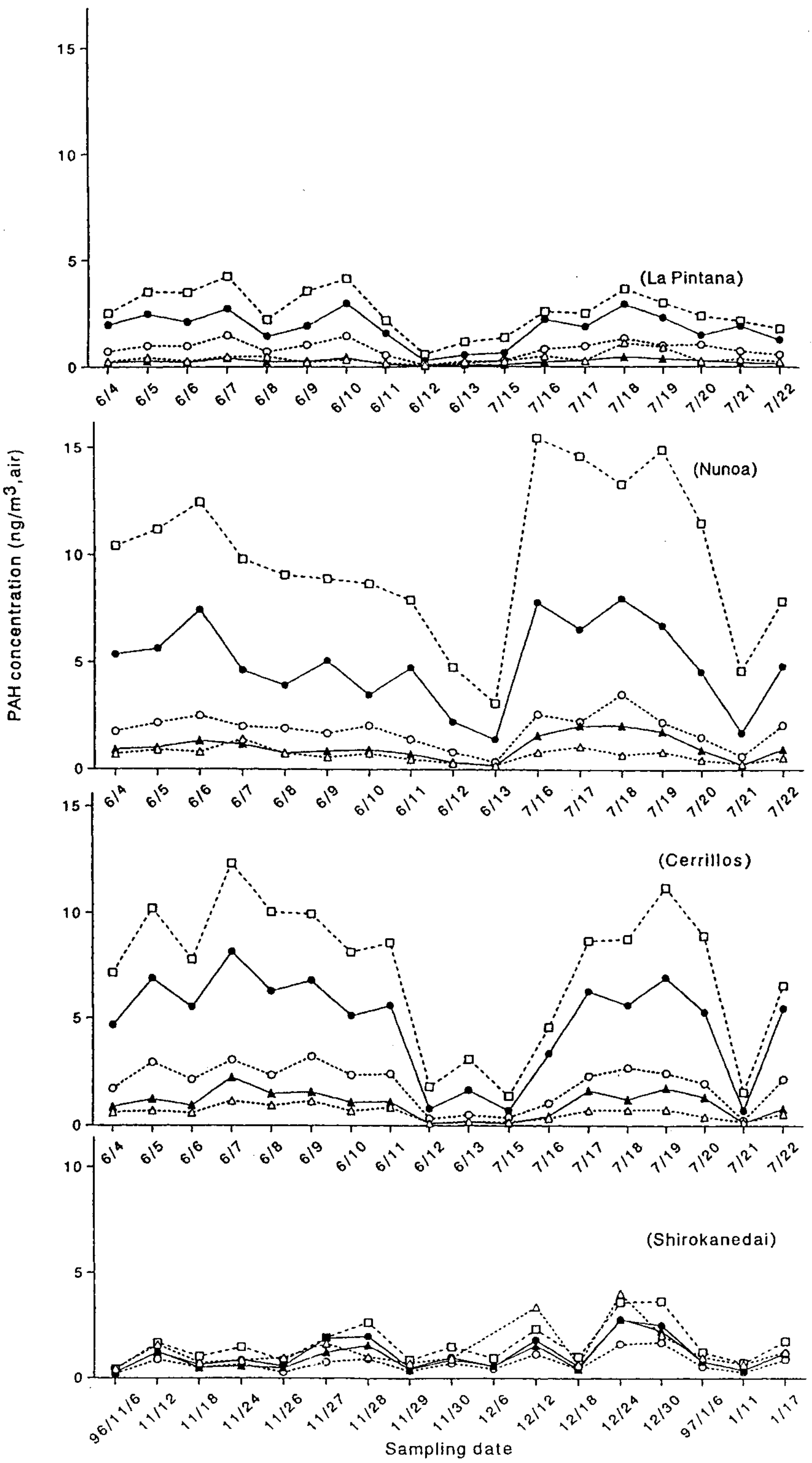

Fig. 2. Daily Variations of PAH Concentrations in Airborne Particulate Extracts
--△--, Pyrene. —●—, Benzo[*a*]pyrene. —▲—, Benz[*a*]anthracene. ---□---, Benzo[*ghi*]perylene. ---○---, Benzo[*k*]fluoranthene.

atmospheric suspended particles were 137 μg/m^3 (maximum, 267 μg/m^3; minimum, 15 μg/m^3) in Santiago, and 73 μg/m^3 (maximum, 248 μg/m^3; minimum, 26 μg/m^3) in the Tokyo area.

The results of PAH concentrations in the atmospheric suspended particles in Santiago and in Shirokanedai are shown in Fig. 2. These results indicated that the concentrations of PAHs varied daily.

Table 1. PAH Concentrations in Airborne Particulate Extracts

Sampling station	n	PAH concentrations (ng/m^3)														
		Pyrene			BaA			BkF			BaP			BghiP		
		G.m.	Max	Min	G.m.	Max	Min	G.m.	Max	Min	G.m.	Max	Min	G.m.	Max	Min
La Pintana	18	0.34	1.14	0.09	0.22	0.47	0.05	0.70	1.50	0.10	1.60	2.98	0.30	2.39	4.26	0.60
Nunoa	17	0.62	1.43	0.20	0.89	2.08	0.20	1.65	3.53	0.36	4.48	8.05	1.43	9.16	15.48	3.09
Cerrillos	18	0.51	1.16	0.12	0.74	2.25	0.11	1.51	3.21	0.26	3.81	8.17	0.71	6.10	12.31	1.38
Santiago	53	0.47	1.43	0.09	0.52	2.25	0.05	1.20	3.53	0.10	2.99	8.17	0.30	5.05	15.48	0.60
Shirokanedai	17	1.14	4.05	0.45	0.81	2.83	0.26	0.61	1.70	0.20	0.93	2.79	0.26	1.40	3.67	0.43
Yoyogi	4	3.85	4.78	2.84	2.16	3.86	1.39	1.02	2.26	0.53	2.15	4.23	1.22	3.14	5.43	2.05
Sagamihara	4	1.73	2.60	1.20	1.57	1.94	1.27	0.70	0.93	0.58	1.67	2.01	1.43	1.98	2.28	1.79
Tokyo area	25	1.50	4.78	0.45	1.06	3.86	0.26	0.68	2.26	0.20	1.17	4.23	0.26	1.68	5.43	0.43

G.m.: geometric mean. BaA: benz[*a*]anthracene, BkF; benzo[*k*]fluoranthene, BaP; benzo[*a*]pyrene, BghiP; benzo[*ghi*]perylene.

The range of PAH concentrations, for example, BaP (a carcinogen generally measured) in Cerrillos in Santiago was greater than in the other stations. The geometric mean and the maximum and minimum values for each area of the PAH concentrations, including Yoyogi and Sagamihara city, are summarized in Table 1. The atmospheric PAH concentration decreased in the order of Nunoa ≥ Cerrillos > La Pintana in Santiago, and Yoyogi > Sagamihara city ≥ Shirokanedai in the Tokyo area. The atmospheric PAH concentrations of the four-ring PAHs pyrene and BaA in the Tokyo area were higher than or equal to those in Santiago. PAHs having more than four rings in Santiago, BkF, BaP, and BghiP, were higher than those in the Tokyo area. Statistically, the geometric mean value of BaA in La Pintana was significantly lower ($p = 1\%$) than in Shirokanedai, although there were no significant differences between Shirokanedai and Nunoa/Cerrillos. The values of BaP in Nunoa, and Cerrillos in Santiago were significantly higher ($p = 1\%$) than in Shirokanedai. There was not much difference in any of the PAH concentrations in the Tokyo area, and in Santiago the PAH concentration decreased in the order of BghiP > BaP > BkF > Pyrene ≒ BaA.

Mutagenic Activities

The results of specific mutagenic activity of the atmospheric suspended particles in Santiago and in Shirokanedai are shown in Fig. 3. The activity varied from day to day, as those of PAH concentrations. In the air particles, the difference of specific mutagenic activity value in Cerrillos showed the greatest day-to-day range under the condition of TA100–S9 mix. The geometric mean and maximum and minimum values for each area of the activity are summarized in Table 2, where the mean value of this activity in the atmosphere decreased in the order of Nunoa ≒ Cerrillos > La Pintana in Santiago, under the conditions of TA100 ± S9 mix and TA98 ± S9 mix.

In the Tokyo area, mutagenic activity decreased in the order of Yoyogi > Sagamihara city ≥ Shirokanedai, under the same respective conditions. Under the conditions of TA100–S9 mix, the specific mutagenic activity decreased in the order of Yoyogi > Sagamihara city ≥ Shirokanedai. Overall, mutagenic specific activity values in Santiago were higher than in the Tokyo area.

DISCUSSION

First, we looked at the correlations between airborne particle concentrations, PAH concentrations, and also specific mutagenic activity values. The correlation coefficient for Santiago is shown in Table 3, and for the Tokyo area in Table 4. The values were significant ($p < 1\%$), and there was no remarkable difference between the correlations of the two cities.

The collected airborne particles in Santiago were PM10, and those in the Tokyo area were total suspended particles (TSP). Fine particles under 10 μm, which are said to strongly influence artificial contaminations, contain about 90% or more PAHs[7,8] and mutagenic materials of those in TSP.[9–12] Therefore, PAH concentrations and mutagenic activities in Santiago may be comparable to the measurements in the Tokyo area, even though sampling methods were different.

In Santiago, PAH concentrations in urban dis-

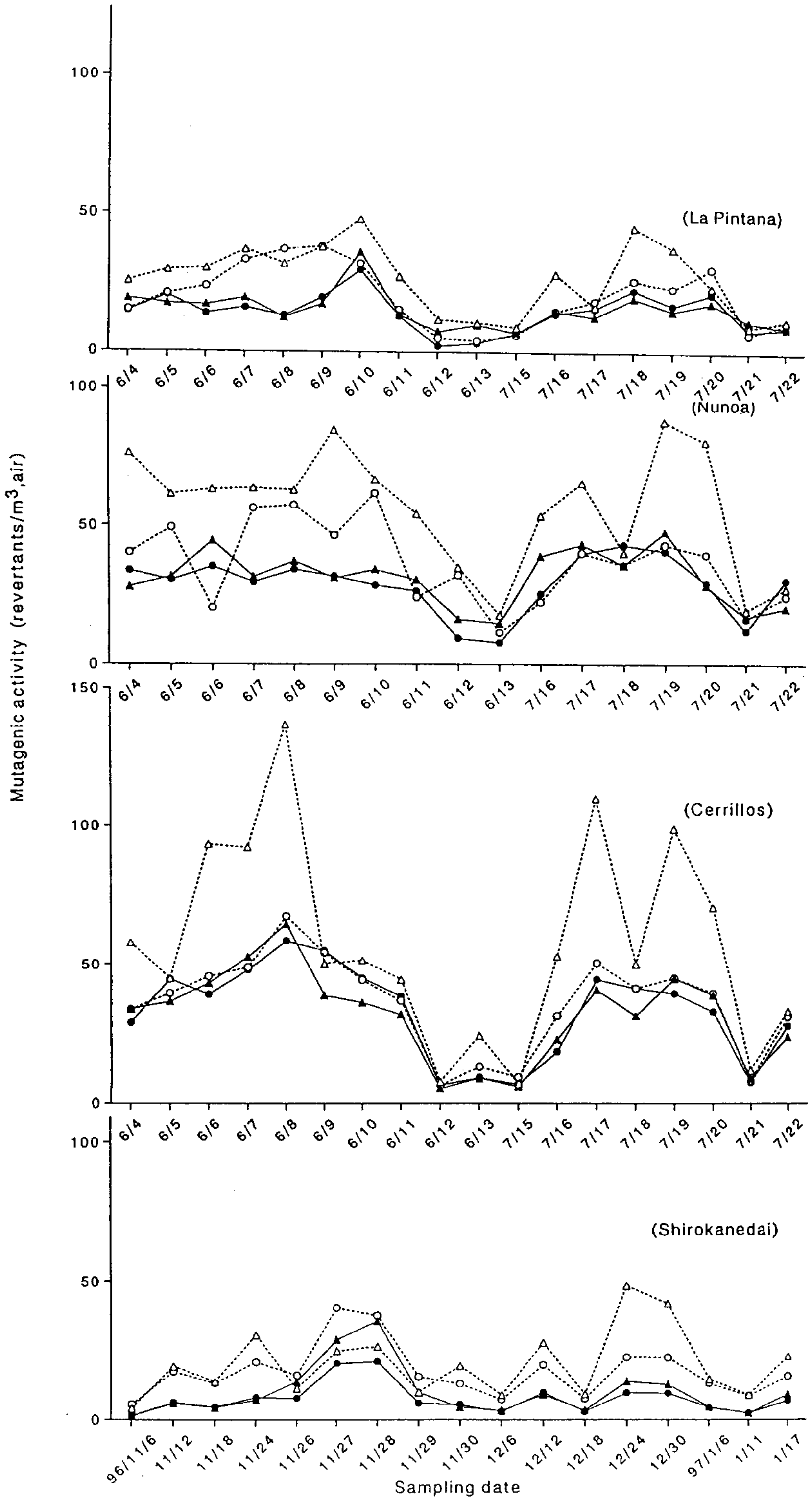

Fig. 3. Daily Variations of Mutagenic Activities in Airborne Particulate Extracts
--△--, TA100–S9. ---○---, TA98–S9. —▲—, TA100+S9. —●— ,TA98+S9.

tricts (Nunoa and Cerrillos) were higher than in a suburban district (La Pintana), but in the Tokyo area, not such a large difference of these concentrations was found in this report between urban districts (Yoyogi and Shirokanedai) and a suburban district (Sagamihara city). The concentrations of four-ring PAHs were higher in the Tokyo area than in Santiago, while the reverse was true for five-or-more-ring

Table 2. Mutagenic Activities in Airborne Particulate Extracts

Sampling station	n	Mutagenic activity (rev./m^3)											
		TA100−S9			TA100+S9			TA98−S9			TA98+S9		
		G.m.	Max	Min	G.m.	Max	Min	G.m.	Max	Min	G.m.	Max	Min
La Pintana	18	23.0	48.0	9.2	14.3	35.9	7.1	16.5	38.0	4.2	12.3	29.4	2.2
Nunoa	17	51.4	87.3	18.0	29.8	47.6	15.0	33.4	61.4	11.6	26.3	43.0	7.9
Cerrillos	18	43.8	136.4	7.0	25.5	64.6	5.3	29.9	67.4	6.4	26.6	58.5	6.4
Santiago	53	37.0	136.4	7.0	22.1	64.6	5.3	25.3	67.4	4.2	20.4	58.5	2.2
Shirokanedai	17	16.7	48.2	4.0	6.9	35.6	1.2	15.1	40.4	5.4	6.0	21.0	1.5
Yoyogi	4	34.1	48.7	23.6	39.9	59.6	21.3	41.6	67.4	26.4	21.8	33.2	13.3
Sagamihara	4	19.3	25.8	15.5	23.3	30.1	17.8	29.8	41.3	21.0	13.1	22.9	8.6
Tokyo area	25	19.2	48.7	4.0	11.1	59.6	1.2	19.8	67.4	5.4	8.3	33.2	1.5

G.m.: geometric mean.

Table 3. Multiple Correlation between PM10, Mutagenic Activities and PAH Concentrations in Santiago(Chile) Air

	BghiP	BaP	BkF	BaA	Pyrene	TA98+S9	TA98−S9	TA100+S9	TA100−S9
PM10	0.698	0.747	0.786	0.746	0.703	0.839	0.766	0.815	0.698
TA100−S9	0.742	0.752	0.679	0.751	0.636	0.809	0.829	0.894	
TA100+S9	0.863	0.891	0.855	0.885	0.713	0.919	0.801		
TA98−S9	0.690	0.682	0.752	0.696	0.704	0.831			
TA98+S9	0.823	0.899	0.929	0.882	0.748				
Pyrene	0.731	0.748	0.769	0.763					
BaA	0.932	0.950	0.917						
BkF	0.878	0.956							
BaP	0.941								

PM10: Particles collected by a sampler with a 50% inlet cutoff and an aerodynamic diameter of 10 μm. Significant level of correlation was $p < 0.1\%$. $n = 53$.

Table 4. Multiple Correlation between TSP, Mutagenic Activities and PAH Concentrations in Tokyo Area Air

	BghiP	BaP	BkF	BaA	Pyrene	TA98+S9	TA98−S9	TA100+S9	TA100−S9
TSP	0.777	0.741	0.620	0.752	0.849	0.842	0.809	0.866	0.740
TA100−S9	0.928	0.897	0.894	0.883	0.746	0.712	0.720	0.658	
TA100+S9	0.768	0.797	0.571*	0.765	0.661	0.974	0.961		
TA98−S9	0.812	0.859	0.664	0.812	0.621	0.976			
TA98+S9	0.786	0.821	0.617	0.765	0.618				
Pyrene	0.747	0.727	0.630	0.789					
BaA	0.976	0.981	0.919						
BkF	0.950	0.928							
BaP	0.980								

TSP: Total suspended particulates: total airborne particles obtained using a high volume sampler. Significant level of correlation was $p < 0.1\%$ except for $*p < 1\%$. $n = 25$ except for pyrene ($n = 24$).

PAHs: those were higher in Santiago than in the Tokyo area. This suggested that the major air pollution sources are different in the two locations.

The specific mutagenic activity also differed in Santiago depending on the land area: whether agricultural, commercial and residential, or industrial. The mutagenic activities were similar there under the conditions of TA98–S9 mix and TA98+S9 mix, in contrast to the TA98–S9 mix being higher than TA98+S9 mix in the Tokyo area. Diesel-engine traffic is heavier in Santiago,[13] and as though the dynamics of the diesel-engine exhaust particles are not well known,[14] they do contain nitroarenes which are direct mutagens.[14–16] The mutagenic activities were similar under the tow mixes in Santiago, suggesting that other kinds of sources also play some role in the air pollution.

Santiago is surrounded by mountains, rainfall is a sparse (compared with the Tokyo area), traffic jams due to heavy vehicles are common, and the PAH concentrations are believed to be higher[13] in Santiago. In contrast, the Tokyo area receives much rain and is not surrounded by mountains, so the accumulation of PAH is lower.

Continuous PAH monitoring and measuring of mutagenic activity are necessary preventive measures to control air pollution in the Santiago area.

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