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Sources Causing Long-Term and Seasonal Changes in Combustion-Derived Particulate Matter in the Urban Air of Sapporo, Japan, from 1990 to 2002

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Abstract: Fifty-one samples were collected seasonally to estimate the amounts of total suspended particulate (TSP) in Sapporo, Japan, from 1990 to 2002. The atmospheric concentration of combustion-derived particulate (P_c) was calculated based on the NP method using 1-nitropyrene and pyrene. The atmospheric TSP and P_c concentration ranges were between 31–121 $\mu\text{g m}^{-3}$ of air (Mean \pm standard deviation (SD) = 58.2 \pm 20.2 $\mu\text{g m}^{-3}$) and 31–121 $\mu\text{g m}^{-3}$ (Mean \pm SD = 8.2 \pm 6.0 $\mu\text{g m}^{-3}$), respectively. First-order linear regression equations suggested that the P_c fraction decreased faster than TSP. The highest and lowest P_c concentrations were observed in winter and summer, respectively, whereas the highest and lowest TSP concentrations were observed in spring and winter, respectively. The largest and smallest P_c /TSP concentration ratios were observed in winter (0.324) and summer (0.075), respectively. The seasonal fractions of high-temperature combustion-derived particulate (P_h) in P_c ranged from 0.56 (winter) to 0.75 (summer), suggesting that the contribution of vehicle emissions to P_c was always larger than those of coal and biomass combustion. The sources of long-term and seasonal change in P_c were elucidated by analyzing organic source markers. Atmospheric concentrations of polycyclic aromatic hydrocarbons (PAHs), nitropolycyclic aromatic hydrocarbons (NPAHs) and hopanes showed long-term and seasonal changes similar to those of P_c , although biomarkers of biomass and coal combustion, such as levoglucosan, mannosan, and galactosan were not as strongly correlated. These results suggest that the change in the P_c concentration was mainly affected by vehicle emissions rather than by coal and biomass combustion or secondary pollutant formation. The decrease in the P_c over the study period was mainly a result of the Japanese particulate matter/NOx regulations on vehicle exhaust.

Keywords: total suspended particulate; combustion-derived particulate matter; NP method; polycyclic aromatic hydrocarbon; nitropolycyclic aromatic hydrocarbon; vehicle; coal/biomass combustion



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1. Introduction

Air pollution kills millions of people every year. Among airborne pollutants, research has focused on particulate matter (PM), in particular the fine particulates (having a diameter $\leq 2.5 \mu\text{m}$; $\text{PM}_{2.5}$), because of its relationship to respiratory and cardiovascular diseases [1]. $\text{PM}_{2.5}$ contains numerous carcinogens and mutagens such as polycyclic aromatic hydrocarbons (PAHs), e.g., benzo[a]pyrene (BaP), and nitropolycyclic aromatic hydrocarbons (NPAHs), e.g., 1-nitropyrene (1-NP) and dinitropyrenes. However, among the 16 priority PAHs determined by the United States Environmental Protection Agency (US EPA), BaP contributes only 11% to the total cancer risk. The other PAHs of the USEPA PAHs and NPAHs, respectively, contribute 72% and 17%. Moreover, 47% of the direct-acting mutagenicity of PM extracts cannot be attributed to eight of the commonly quantified NPAHs, as

the toxic equivalent is only known for a limited number of NPAHs [2,3]. On the other hand, several oxygenated PAHs, such as the hydroxy PAHs, quinoid PAHs, and hydroxy NPAHs, have demonstrated endocrine-disrupting activity, reactive oxygen species overproduction activity, and indirect-acting mutagenicity [4–6]. The biological activities of PAHs with polar functional groups are higher than those of their parent PAHs [7]. These reports indicate that PM contains many unknown hazardous chemical substances.

In addition to the materials emitted from combustion, PM contains substances generated from plants and animals. However, separating PM into combustion and noncombustion-derived fractions is challenging. The classification of PM into combustion and noncombustion-derived fractions and the knowledge of their sources can significantly facilitate the research on unknown toxic chemicals. Currently, for source analysis, several methods are used, such as receptor models, including chemical mass balance (CMB) and positive matrix factor Analysis (PMF), principal component analysis (PCA) method, and diagnostic PAHs ratio method [8–11]. However, to use receptor models and the PCA method, it is impossible to obtain emission information of vehicles and around the sampling site at that time. The diagnostic PAHs ratio method has problems, such as the inability to calculate the source contribution ratio to PAHs; the main source often differs depending on the type of PAH pair used. Moreover, this method cannot be applicable to combustion-derived particulate and NPAHs [12]. Recently, our group developed a method (the NP method) to quantify the combustion-derived fractions (P_c) and noncombustion-derived fractions (P_n) in PM. We further divided P_c into high-temperature combustion-derived particulate (P_h) and low-temperature combustion-derived particulate (P_l). Major sources of P_h and P_l are vehicles and coal and biomass combustion. The main idea for this method is that the formation of NPAHs relative to PAHs will increase relative to combustion temperature, as the formation of nitrogen oxides and the subsequent nitration of PAHs depends on the combustion temperature. The NP method can be used for PM generated at any place and time because it only requires pyrene (Pyr) and 1-nitropyrene (1-NP) measurements [12,13].

Herein, atmospheric samples were collected every season to determine the total suspended particulate (TSP) in Sapporo from 1990 to 2002. During this period, several important countermeasures were enacted to deal with air pollution in Japan, such as restrictions on vehicle emissions of PM and NO_x gases, progress on vehicle engine performance and fuel quality [7] and the ban on spiked tires in snowy regions [14]. In addition, winter heating mostly switched from coal heating to kerosene or electric heating in Sapporo by the beginning of the 1990s. It is important to clarify how these measures have improved urban air pollution in Japan. This study was conducted to elucidate the factors causing long-term and seasonal changes in TSP and P_c . TSP was divided into P_c and P_n , and P_c was further classified into P_h and P_l using the NP method. The study also examined the contributions of vehicles as well as coal and biomass combustion to P_c by analyzing organic source markers.

2. Materials and Methods

2.1. Sampling

TSP samples were collected in Sapporo (the capital city of Hokkaido, Japan, population = 1,970,000). The average annual, August, and January temperatures were 9.2 °C, 22.3 °C, and −3.2 °C, respectively, and the month with the greatest average snowfall (97 cm) was February [15]. A high-volume air sampler was placed on the roof of the three-story building of the Research Institute of Energy, Environment and Geology, Hokkaido Research Organization, which is located in a residential area approximately 2 km northwest of downtown Sapporo. The 24-h TSP was collected once a week using a quartz fiber filter at an airflow rate of 1.0–1.5 m³ min^{−1} from the spring of 1990 to the autumn of 2002. Filters of 1432 days were obtained during the period. After sampling, filters were stored in a freezer (−20 °C) until analysis. Filters (of 12 to 13 TSP samples) were grouped based on the four seasons of the year, winter (December of the preceding year to February), spring

(March to May), summer (June to August), and autumn (September to November). In total, 51 seasonal TSP samples were obtained over the monitoring period.

2.2. Quantification of Organic Compound Markers

One-eighth of the filters used to collect the TSP samples in each season of the year were cut and placed in a 500-mL glass flask containing dichloromethane (400 mL). The samples were sonicated for 15 min. The extract was filtered twice through three sheets of cellulose fiber filters (Advantec, Tokyo, Japan, No. 5C). The filtrate was evaporated until less than 1 mL remained. Then dichloromethane was added to increase the total volume to 25 mL. An aliquot of the solution was used in the analysis of the chemical compounds described below.

Nine PAHs, fluoranthene (Flu), Pyr, benz[*a*]anthracene, chrysene, benzo[*b*]fluoranthene, benzo[*k*]fluoranthene, BaP, benzo[*ghi*]perylene, and coronene, were quantified according to USEPA methods using a high-performance liquid chromatograph (HPLC) equipped with a fluorescence detector [16]. Deuterated Pyr (Pyr-*d*₁₀) and deuterated BaP (BaP-*d*₁₂) were used as internal standards. A reversed-phase column (Inertsil ODS-P, internal diameter (ID) × length = 4.6 × 250 mm, GL Sciences Inc., Tokyo, Japan) was used as the analytical column. Compounds were separated using a mobile phase gradient of an acetonitrile–water mixture at a flow rate of 1 mL/min. The excitation and emission wavelengths of the fluorescence detector were optimized for each particular PAH.

Four NPAHs, 1-NP, 1,3-, 1,6-, and 1,8-dinitropyrenes, were quantified using an HPLC equipped with a reducer column packed with Pt/Rh-coated particles and a chemiluminescence detector, using 2-fluoro-7-nitrofluorene as an internal standard. Reverse phase columns (Cosmosil 5C18-MS-II, 4.6 (ID) × (250 + 150) mm, Nacalai Tesque, Kyoto, Japan) were used as the analytical columns, and the mobile phase was a mixture of an acetonitrile–imidazole buffer. Further, an acetonitrile solution containing bis(2,4,6-trichlorophenyl)oxalate and hydrogen peroxide was used as the chemiluminescence reagent solution at a flow rate of 1 mL/min [17–19].

17 α (H)21 β (H)-30-norhopane, 17 α (H)21 β (H)hopane, and 17 α (H)-22,29,30-trisnorhopane were quantified using gas chromatography–mass spectrometry (GC–MS, GC: Agilent 7890B, MS: Agilent 5977B, Agilent Technologies Inc., Hachioji-shi, Japan). A DB-5MS capillary column was used as the analytical column (length × ID = 30 m × 0.25 mm, film thickness = 0.25 μ m, Agilent Technologies Inc.). Three sugars, i.e., levoglucosan, mannosan, and galactosan, as well as pinonic acid, were quantified by GC–MS coupled with a solvent extraction–silylation method. The analytical conditions are adopted from previous studies [20–22] with small modifications. Samples used for the analysis of three hopanes were obtained from other TSP samples collected at the same site over the same period.

2.3. Calculation of Source Contributions Using the NP Method

In the NP method, TSP in the urban atmosphere is divided into P_c and P_n . During the combustion process of organic matter, both the formation of nitrogen oxides in the flame gas and the subsequent formation of NPAHs from the parent PAHs are temperature dependent [23,24]. This causes an increase in the NPAH to parent PAH concentration ratios with the increase in the combustion temperature. High combustion temperatures occur in vehicle (diesel and gasoline) engines (2700 °C–3000 °C), which are significantly higher than those used in coal combustion stoves (1100 °C–1200 °C) and wood combustion stoves (500 °C–600 °C) [12]. Depending on these differences, P_c was further divided into P_h and P_l .

When the proportion of P_h in P_c and P_c in P in the atmosphere are x ($0 < x < 1$) and y ($0 < y < 1$), respectively, Equations (1)–(3) can be written as follows:

$$[1\text{-NP}] = [1\text{-NP}_h][P_c]x + [1\text{-NP}_l][P_c](1 - x) \quad (1)$$

$$[\text{Pyr}] = [\text{Pyr}_h][P_c]x + [\text{Pyr}_l][P_c](1 - x) \quad (2)$$

$$y = [P_c]/([P_c] + [P_n]) \tag{3}$$

During the sampling period, petroleum and coal were the largest primary energy sources in Japan [25]. In Sapporo, most petroleum was used in transportation (viz. vehicles), whereas coal was used in power plants, factories, and household heating. We previously obtained the concentrations of 1-NP and Pyr in PM emitted from vehicles and coal boilers/stoves, which were common during the study period [12,13]. As a result, the following equations are available.

$$[1-NP_h]/[Pyr_h] = 0.425 \tag{4}$$

$$[1-NP_l]/[Pyr_l] = 0.0013 \tag{5}$$

Therefore, vehicle emissions and coal combustion were, respectively, regarded as high-temperature and low-temperature combustion sources. x , y and $[P_c]$ can be obtained by Equations (1)–(3) with values from (4) and (5).

3. Results and Discussion

3.1. Relationship between the TSP and P_c Concentrations

Atmospheric concentrations of TSP and P_c calculated by the NP method were between 31–121 $\mu\text{g m}^{-3}$ and 2–27.2 $\mu\text{g m}^{-3}$, respectively, and the P_c /TSP ratios were 0.043–0.495 from spring 1990 to autumn 2002 (Table 1). Figure 1 shows the seasonal TSP concentrations from spring 1990 to autumn 2002 as well as the annual mean concentrations from 1991 to 2002. Figure 2 shows the P_c concentrations during the same period as the TSP samples. The first-order regression equations of TSP and P_c were $Y = -2.600X + 5248$ ($R^2 = 0.401$) and $Y = -0.673X + 1353$ ($R^2 = 0.921$), respectively. Both had negative slopes, suggesting that TSP and P_c concentrations decreased over the study period. However, P_n did not show a similar tendency to that of P_c . For example, the annual mean concentrations of P_c and P_n were 14.0 and 8.0 $\mu\text{g m}^{-3}$, respectively, in 1991 and 3.8 and 8.3 $\mu\text{g m}^{-3}$, respectively, in 2002. These results indicate that the long-term change in the TSP concentration can be mainly attributed to the change in the P_c concentration.

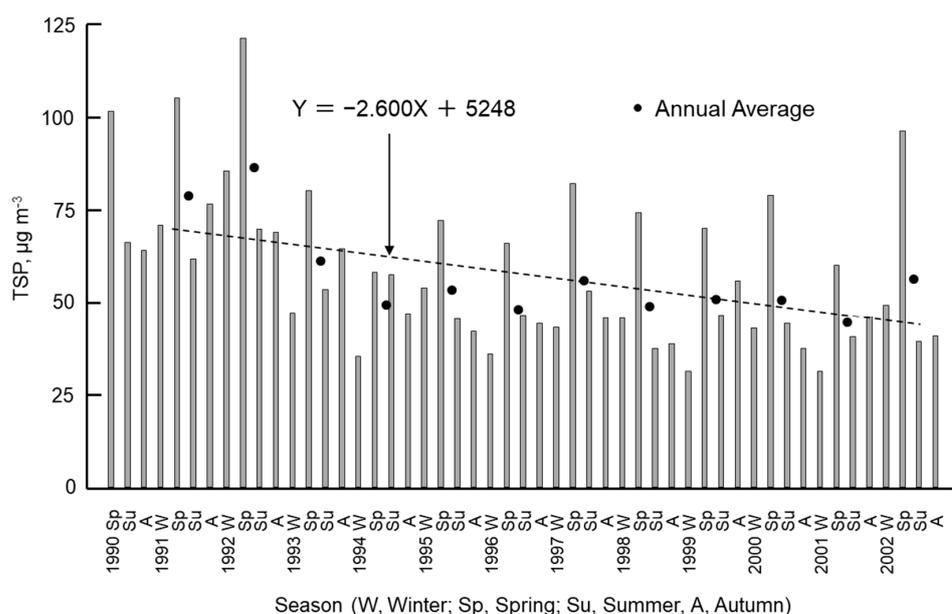


Figure 1. Atmospheric concentration of TSP in Sapporo from 1990 to 2002 by season.

Table 1. Atmospheric concentrations of TSP and P_c in Sapporo (1990–2002).

Year	Season	TSP ($\mu\text{g m}^{-3}$)	P_c ($\mu\text{g m}^{-3}$)	P_c/TSP^a
1990	spring	101.6	5.8	0.057
	summer	66.0	3.6	0.055
	autumn	64.1	6.7	0.104
1991	winter	70.8	26.1	0.369
	spring	105.2	11.2	0.106
	summer	61.8	3.0	0.049
	autumn	76.5	15.6	0.204
1992	winter	85.3	27.7	0.325
	spring	121.3	10.0	0.082
	summer	69.8	4.0	0.058
	autumn	68.8	6.2	0.091
1993	winter	47.0	15.7	0.335
	spring	80.0	8.1	0.101
	summer	53.5	3.4	0.335
	autumn	64.4	10.4	0.161
1994	winter	35.2	17.4	0.495
	spring	58.2	8.8	0.151
	summer	57.5	3.1	0.054
	autumn	46.8	6.6	0.141
1995	winter	53.8	23.5	0.438
	spring	72.2	5.5	0.076
	summer	45.4	4.1	0.091
	autumn	42.1	6.3	0.150
1996	winter	35.8	12.5	0.350
	spring	65.9	13.7	0.208
	summer	46.5	7.7	0.165
	autumn	44.1	5.6	0.127
1997	winter	43.0	16.0	0.371
	spring	81.9	8.0	0.098
	summer	53.1	4.3	0.083
	autumn	45.5	7.0	0.154
1998	winter	45.6	15.5	0.340
	spring	74.3	5.5	0.074
	summer	37.3	7.8	0.208
	autumn	38.6	4.1	0.106
1999	winter	31.2	8.8	0.282
	spring	69.9	7.1	0.102
	summer	46.4	2.0	0.043
	autumn	55.7	5.9	0.106
2000	winter	42.7	8.5	0.200
	spring	78.8	6.1	0.078
	summer	44.0	2.3	0.051
	autumn	37.3	3.3	0.089
2001	winter	31.1	8.1	0.260
	spring	59.9	3.4	0.057
	summer	40.4	2.1	0.053
	autumn	46.0	2.0	0.044
2002	winter	49.3	5.1	0.104
	spring	96.2	5.4	0.057
	summer	39.2	2.0	0.050
	autumn	40.7	2.8	0.069

a: $P_c/\text{TSP} = y$ in Equation (3).

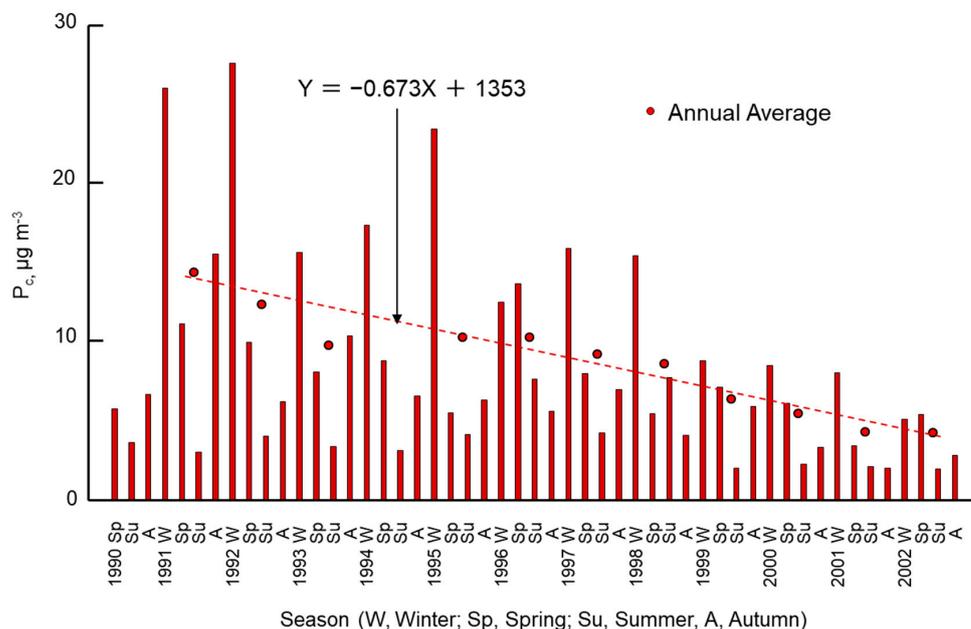


Figure 2. Atmospheric concentration of P_c in Sapporo from 1990 to 2002 by season.

The seasonal changes in the TSP and P_c concentrations differed (Table 2). The highest and lowest TSP concentrations were obtained in spring and winter, respectively, whereas the highest and lowest P_c concentrations were obtained in winter and summer, respectively. However, an almost constant P_n concentration was obtained in all seasons except in winter, where the concentration was 32% lower than the annual concentration. Thus, the largest and smallest fractions of P_c in TSP (P_c/TSP) were obtained in the winter (0.324) and summer (0.075), respectively. The relative standard deviation ($RSD = SD/Mean$) of the annual mean P_c concentration (0.732) was almost two times larger than that of TSP (0.374). These results indicate that the seasonal change in the TSP concentration was also mainly attributed to P_c .

Table 2. Seasonal atmospheric concentrations of TSP, P_c , and P_n concentrations as well as P_c/TSP ratio in Sapporo.

Season	TSP ($\mu\text{g m}^{-3}$) ^a	P_c ($\mu\text{g m}^{-3}$) ^a	P_n ($\mu\text{g m}^{-3}$) ^a	P_c/TSP
Winter	47.6 ± 16.2	15.4 ± 7.4	5.9 ± 3.6	0.324
Spring	82.0 ± 18.9	7.6 ± 2.8	9.4 ± 4.1	0.093
Summer	50.8 ± 10.4	3.8 ± 1.9	9.4 ± 3.1	0.075
Autumn	51.6 ± 12.9	6.4 ± 3.5	10.8 ± 3.0	0.124
Annual	58.2 ± 20.2	8.2 ± 6.0	8.7 ± 4.2	0.141
RSD ^b	0.347	0.732	0.483	

a: Mean ± SD standard deviation (SD), b: Relative SD = (Mean/SD).

3.2. Factors Affecting the P_c Concentration

The factors involved in the long-term and seasonal changes in the P_c concentration were studied. As described in Section 2.3, P_h and P_l , which are emitted from vehicles and coal/biomass combustion, respectively, were calculated using the NP method. Herein, the fractions of P_h in P_c of the 51 TSP samples were calculated based on Pyr and 1-NP concentrations. The largest and smallest seasonal mean fractions of P_h in P_c were obtained in the summer (0.75) and in the winter (0.56), respectively (Figure 3), suggesting that the contribution of vehicles to P_c was always larger than those of coal and biomass combustion in Sapporo. This is despite the increase in heating from coal and firewood combustion in the winter and the increase in post-harvest biomass combustion in the autumn.

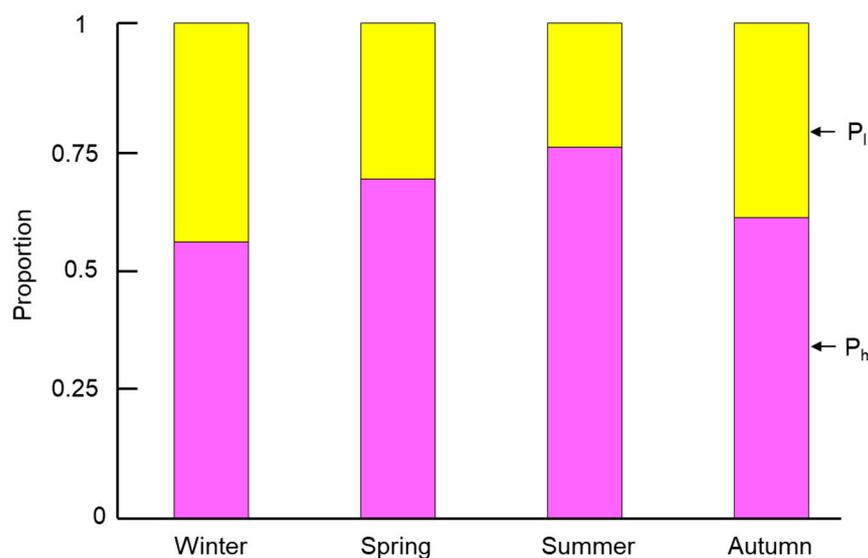


Figure 3. Fractions of P_h and P_l in atmospheric P_c in Sapporo over the four seasons. Symbols: P_h , emitted from the high-temperature combustion source (vehicles); P_l , emitted from low-temperature combustion sources (coal and biomass combustion).

In Japanese cities, the main sources of PAHs and NPAHs are vehicle emissions as well as coal and biomass combustion. Among these primary sources, vehicles emit larger amounts of NPAHs and hopanes [22,26]. Biomass combustion emits several sugars, such as levoglucosan, mannosan, and galactosan, whereas coal combustion emits much smaller amounts. Several organic acids, such as pinonic acid, also form in the atmosphere [27]. Therefore, PAHs, NPAHs, and hopanes are markers of P_h ; levoglucosan, mannosan, galactosan, and PAHs are markers of P_l ; and pinonic acid is a marker of P_n .

Figure 4 shows that the atmospheric concentrations of the total six PAHs (T-PAH), four NPAHs (T-NPAH), and three hopanes (T-Hopane) decreased over the study period, showing the same seasonal change (high in winter and low in summer) as that of P_c in Sapporo. Figure 5 shows that the atmospheric concentrations of levoglucosan, mannosan, and galactosan also decreased in the same period. However, they show different decreasing rates. The relative slope, i.e., the slope of equation/average concentration, of the first-order linear regression equation was calculated for each marker compound. Relative slopes of T-PAH, T-NPAH, and T-Hopane are within a range of $-0.131/\text{year}$ to $-0.099/\text{year}$, which is steeper than that of P_c ($-0.082/\text{year}$). However, the relative slopes of levoglucosan, mannosan, and galactosan are in a range of -0.036 to $-0.040/\text{year}$, which is less steep than that of P_c (Table 3). The pinonic acid concentration, whose relative slope ($0.007/\text{year}$ in Table 3) is close to zero, did not show such a long-term change (Figure 5). Moreover, the correlation coefficients between the T-PAH, T-NPAH, and T-Hopane concentrations and the P_c concentration are in the range of 0.8898–0.9433, which are significantly larger than the other chemicals (Table 4).

The total atmospheric concentrations of T-PAH, T-NPAH, and T-Hopane were significantly lower than that of P_c ($\leq 1\%$ of P_c), and the three sugars and the pinonic acid exhibited low total concentrations similar to that of T-PAH. Despite the very small fractions of these compounds in P_h , their strong correlations with P_c indicate that vehicles were a main contributor to the long-term decrease in the P_c concentration in Sapporo. However, the contribution of coal and biomass combustion to this decrease was not as strong as that of vehicles. Since the 1990s, the Japanese government has started to gradually strengthen the PM/NO_x emission regulations for new vehicles. For PM emissions from heavy-duty diesel vehicles, the regulation value in 1999 was reduced to 36% of the 1994 level. The NO_x regulation value was tightened several times since 1974. It was reduced to 52% in 1989 and 33% in 1999 [28]. This countermeasure decreased the urban atmospheric concentrations of

NPAHs and PAHs by approximately 1/10 over a decade [29]. Thus, the decrease in P_c in Sapporo can be mainly attributed to the PM/NO_x emission regulations for new vehicles, which are reflected in the significant decrease in atmospheric concentrations of T-PAH and T-NPAH (Figure 4). Several decades ago, in the colder regions of Japan, numerous vehicles were equipped with spiked tires in winter and early spring, which significantly increased the PM concentration in the urban atmosphere in spring. The atmospheric TSP concentration was higher than $100 \mu\text{g m}^{-3}$ in Sapporo in the winters from 1990–1992 and decreased quickly to $80 \mu\text{g m}^{-3}$ or less over three years from 1993 to 1996 despite the high P_c concentrations (Figure 1). This can be attributed to the regulation of spiked tires, which was started by the Sapporo city government in 1989 [14]. After the ordinance came into effect, the percentage of vehicles with spiked tires in Sapporo city decreased from 48.6% in 1990 to 2.4% in 1993.

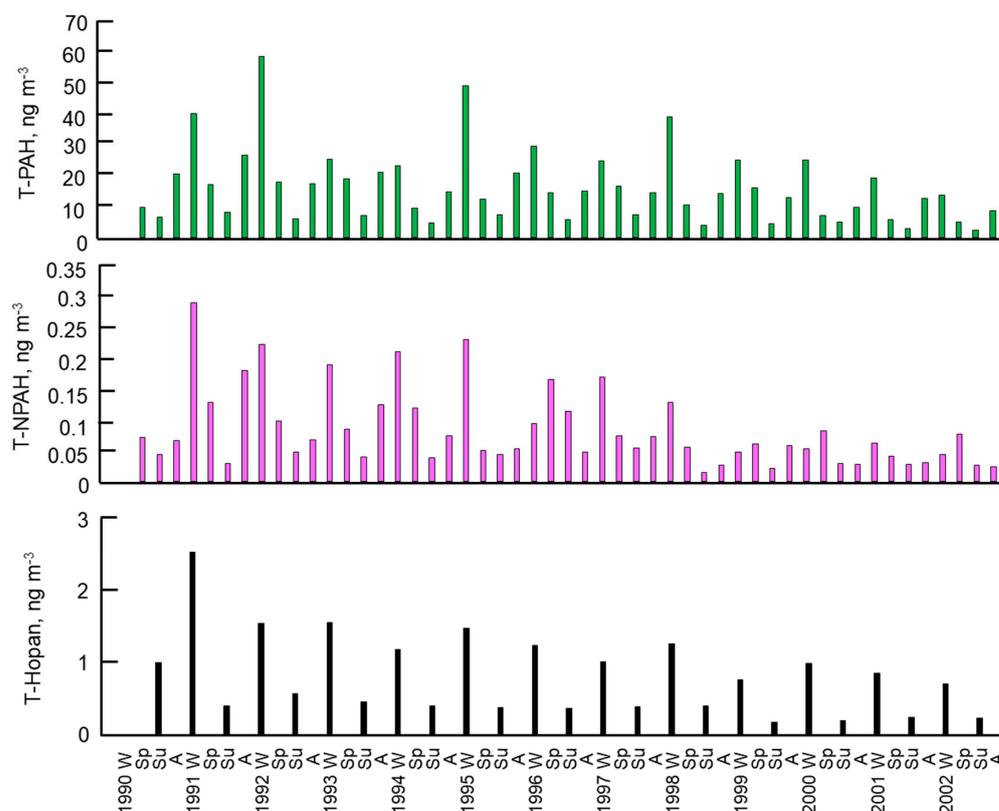


Figure 4. Atmospheric T-PAH, T-NPAH, and T-Hopane concentrations in Sapporo from 1990 to 2002 by season. Abbreviation: T-PAH = fluoranthene + Pyr + benz[*a*]anthracene + chrysene + benzo[*b*]fluoranthene + benzo[*k*]fluoranthene + benzo[*a*]pyrene + benzo[*ghi*]perylene + coronene, T-NPAH = 1-NP + 1,3-dinitropyre + 1,6-dinitropyre + 1,8-dinitropyre, T-hopane = 17 α (H)21 β (H)-30-norhopane + 17 α (H)21 β (H)hopane + 17 α (H)-22,29,30-trisnorhopane.

All the combustion source markers exhibited the same seasonal changes as that of P_c , i.e., the highest and lowest concentrations are observed in winter and summer, respectively (Figures 4 and 5). There are several factors for this. First, the largest and smallest fractions of P_1 in P_c were observed in the winter (44%) and the summer (25%), respectively (Figure 3). Moreover, the highest P_c concentration is observed in the winter (Table 2). These results indicate an increase in the P_1 emitted from fuel combustion for winter heating. The combustion temperatures of firewood and kerosene used as fuels for heating are equal to or lower than that of coal heating ($1100 \text{ }^\circ\text{C}$ – $1200 \text{ }^\circ\text{C}$). This suggests that firewood and kerosene combustion for heating emits P_1 that contains significantly smaller (NPAH)/(PAH) ratios than those from coal combustion for heating [12]. Second, the fuel consumption in vehicles worsens in winter. This increases the P_h emissions. Furthermore, PM tends to stay on the

ground surface in the winter due to the formation of an atmospheric inversion layer [26]. These anthropogenic and meteorological factors caused long-term and seasonal changes in P_h and P_l , which might be then reflected in P_c .

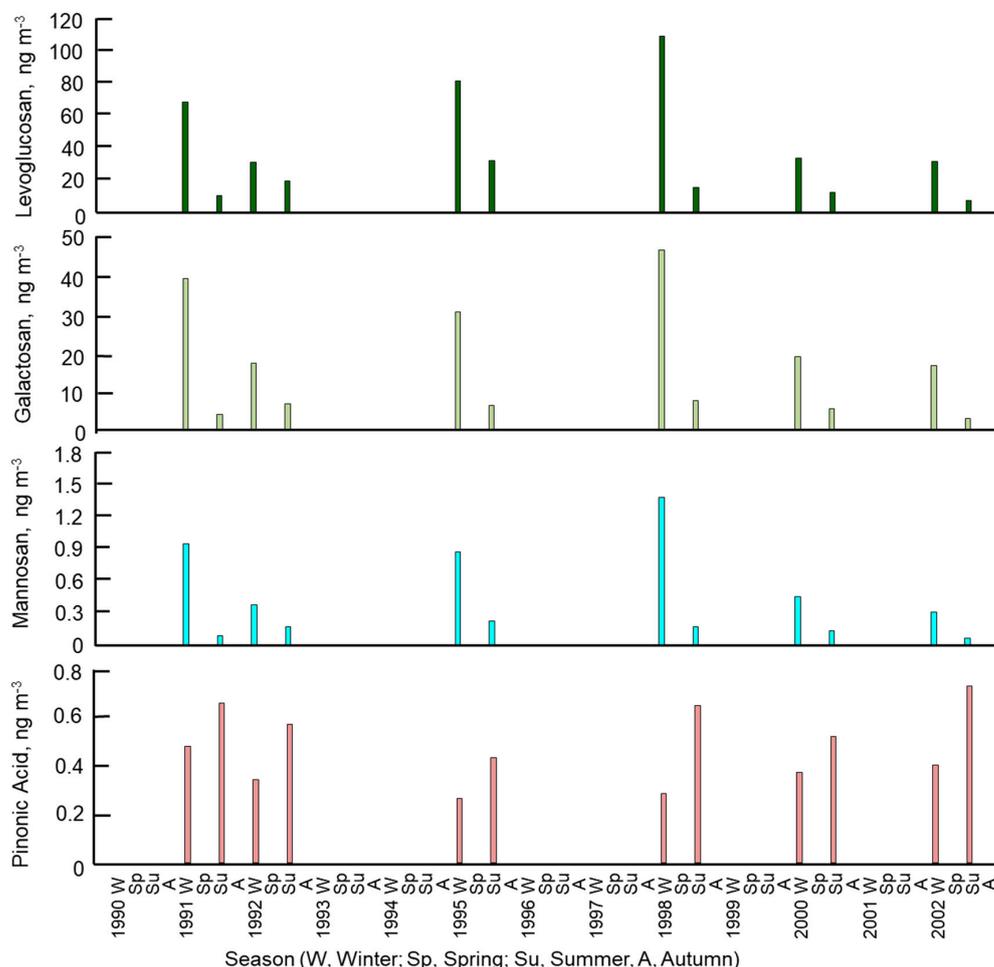


Figure 5. Atmospheric levoglucosan, galactosan, mannosan, and pinonic acid concentrations in Sapporo from 1990 to 2002 by season.

Table 3. Parameters of the first-order linear regression equation for the source markers.

Organic Chemical	Major Source	Equation (Unit of X)	Relative Slope ^a
TSP		$Y = -2.600X + 5248$ ($\mu\text{g m}^{-3}$)	-0.045/year
P_c		$Y = -0.673X + 1353$ ($\mu\text{g m}^{-3}$)	-0.082/year
T-PAH	Vehicle/Coal combustion	$Y = -2.17X + 2194$ (ng m^{-3})	-0.131/year
T-NPAH	Vehicle	$Y = -8.52X + 16545$ (pg m^{-3})	-0.099/year
T-Hopane	Vehicle	$Y = -0.0889X + 178.3$ (ng m^{-3})	-0.123/year
Levoglucosan	Biomass combustion	$Y = -1.33X + 2713$ (ng m^{-3})	-0.036/year
Galactosan	Biomass combustion	$Y = -0.0650X + 131.5$ (ng m^{-3})	-0.039/year
Mannosan	Biomass combustion	$Y = -0.191X + 358.8$ (ng m^{-3})	-0.040/year
Pinonic acid	Secondary formation	$Y = 0.0032X - 5.961$ (ng m^{-3})	0.007/year

^a, Relative slope = slope of the equation/average concentration.

Table 4. Correlation coefficients (R) of the organic chemicals with P_c.

Organic Chemical	R with P _c
T-PAH	0.8937
T-NPAH	0.9433
T-Hopane	0.8898
Levoglucozan	0.6477
Galactosan	0.7271
Mannosan	0.2667
Pinonic acid	−0.7648

This study has clarified that the suppression of PM and NO_x emissions from vehicles drastically reduced the atmospheric concentrations of Pyr, 1-NP, and hopanes emitted from vehicles in Sapporo in the 1990s. However, the emissions from sources with low combustion temperatures have not decreased as quickly. In the future, technological development will be essential for them [30].

4. Conclusions

Atmospheric TSP samples were collected in Sapporo, Japan, every season from 1990 to 2002. P_c in TSP and P_h in P_c was determined by the NP method, and the sources of long-term and seasonal changes in P_h and P_c were elucidated by analyzing organic source markers.

1. The atmospheric TSP and P_c concentrations ranged from 31 to 121 µg m^{−3} (Mean ± SD = 58.2 ± 20.2 µg m^{−3}) and from 31 to 121 µg m^{−3} (Mean ± SD = 8.2 ± 6.0 µg m^{−3}), respectively. The rate of decrease for the latter was steeper than that of the former.
2. The P_c concentration exhibited a seasonal change (highest in the winter and lowest in the summer) and was different from that of TSP (highest in spring and lowest in winter). The largest and smallest P_c/TSP concentration ratios were observed in winter (0.324) and summer (0.075), respectively.
3. The seasonal fraction of P_h in P_c was in a range between 0.56 (winter)–0.75 (summer), suggesting that the contribution of vehicles to P_c was always larger than that of coal and biomass combustion.
4. The atmospheric concentrations of PAHs, NPAHs, and hopanes, which are markers of vehicle emissions, exhibited long-term and seasonal changes similar to P_c with large correlation coefficients (0.9433–0.8898). However, the atmospheric concentrations of levoglucozan, mannosan, and galactosan, which are markers of emissions from coal and biomass combustion, exhibited weaker correlation coefficients with P_c (0.7271–0.2667). Further, the atmospheric concentrations of pinonic acid, which is a marker of the secondary pollutant formation, did not show a similar change to P_c. These results suggest that the change in the P_c concentration was mainly caused by vehicles rather than by coal and biomass combustion and secondary pollutant formation.
5. The significant decrease in the P_c concentration over the study period is mainly attributed to the Japanese PM/NO_x regulations against vehicle exhaust gases.

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References

1. Hayakawa, K.; Nakamura, A.; Terai, N.; Kizu, R.; Ando, K. Nitroarene concentrations and direct-acting mutagenicities in diesel exhaust particulates fractionated by silica gel column chromatography. *Chem. Pharm. Bull.* **1997**, *45*, 18201–18822. [[CrossRef](#)]
2. Kelly, J.; Ivatt, P.; Evans, M.; Kroll, J.; Hrdina, A.; Kohale, I.; White, F.; Engelward, B.; Selin, N. Global cancer risk from unregulated polycyclic aromatic hydrocarbons. *GeoHealth* **2021**, *5*, e2021GH000401. [[CrossRef](#)] [[PubMed](#)]
3. Hayakawa, K.; Onoda, Y.; Tachikawa, C.; Hosoi, S.; Yoshita, M.; Chung, S.W.; Kizu, R.; Toriba, A.; Kameda, T.; Tang, N. Estrogenic/antiestrogenic activities of polycyclic aromatic hydrocarbons and their monohydroxylated derivatives by yeast two-hybrid assay. *J. Health Sci.* **2007**, *53*, 562–570. [[CrossRef](#)]
4. Motoyama, Y.; Bekki, K.; Chung, S.-W.; Tang, N.; Kameda, T.; Toriba, A.; Taguchi, K.; Hayakawa, K. Oxidative stress more strongly induced by ortho- than para-quinoid polycyclic aromatic hydrocarbons in A549 cells. *J. Health Sci.* **2009**, *55*, 845–850. [[CrossRef](#)]
5. Kameda, T.; Akiyama, A.; Yoshita, M.; Tachikawa, C.; Toriba, A.; Tang, H.; Hayakawa, K. Mutagenicities and endocrine-disrupting activities of 1-hydroxy-2-nitropyrene and 1-hydroxy-5-nitropyrene. *J. Health Sci.* **2011**, *57*, 372–377. [[CrossRef](#)]
6. Idowu, O.; Semple, K.; Ramadass, K.; O'Connor, W.; Hansbro, P.; Thavamani, P. Beyond the obvious: Environmental health implications of polar polycyclic aromatic hydrocarbons. *Environ. Int.* **2019**, *123*, 543–557. [[CrossRef](#)] [[PubMed](#)]
7. Hayakawa, K. Review: Environmental behaviors and toxicities of polycyclic aromatic hydrocarbons and nitropolycyclic aromatic hydrocarbons. *Chem. Pharm. Bull.* **2016**, *64*, 83–94. [[CrossRef](#)]
8. Watson, J.G. Chemical Element Balance Receptor Model Methodology for Assessing the Sources of Fine and Total Suspended Particulate Matter in Portland, Oregon. Ph.D. Dissertation, Oregon Graduate Center, Beaverton, OR, USA, 1979.
9. Paatero, P.; Tapper, U. Positive matrix factorization: A non-negative factor model with optimal utilization of error estimates of data values. *Environmetrics* **1994**, *5*, 111–126. [[CrossRef](#)]
10. U.S. Environmental Protection Agency. Positive Matrix Factorization Model for Environmental Data Analyses. Available online: <https://www.epa.gov/air-research/positive-matrix-factorization-model-environmental-data-analyses> (accessed on 2 February 2023).
11. Tobiszewski, M.; Namiesnik, J. Review: PAH diagnostic ratios for the identification of pollution emission sources. *Environ. Pollut.* **2012**, *162*, 110–119. [[CrossRef](#)] [[PubMed](#)]
12. Hayakawa, K.; Tang, N.; Toriba, A.; Nagato, E.G. Calculating sources of combustion-derived particulates using 1-nitropyrene and pyrene as markers. *Environ. Pollut.* **2020**, *265*, 114730. [[CrossRef](#)]
13. Hayakawa, K.; Tang, N.; Matsuki, A.; Inomata, Y.; Toriba, A.; Nagato, E.G. Calculating source contributions to urban atmospheric polycyclic aromatic hydrocarbons and nitropolycyclic aromatic hydrocarbons using 1-nitropyrene and pyrene: An application to an Asian dust event. *Chemosphere* **2021**, *220*, 130662. [[CrossRef](#)] [[PubMed](#)]
14. Sapporo Regional Headquarters, Japan Meteorological Agency, Home Page. 2022. Available online: <https://www.data.jma.go.jp/sapporo> (accessed on 3 February 2023).
15. Hokkaido, Ban of Spike Tires. Available online: <https://www.pref.hokkaido.lg.jp/ks/jss/khz/contents/taiki/jyourei.html> (accessed on 2 February 2023).
16. Wise, S.; Sander, L.; Schantz, M. Analytical methods for determination of polycyclic aromatic hydrocarbons (PAHs)—A historical perspective on the 16 U.S. EPA priority pollutant PAHs. *Polycycl. Aromat. Compd.* **2015**, *35*, 187–247. [[CrossRef](#)]
17. Hayakawa, K.; Kitamura, R.; Butoh, M.; Imaizumi, N.; Miyazaki, M. Determination of diamino- and aminopyrenes by high-performance liquid chromatography with chemiluminescence detection. *Anal. Sci.* **1991**, *7*, 573–577. [[CrossRef](#)]
18. Hayakawa, K.; Murahashi, T.; Butoh, M.; Miyazaki, M. Determination of 1,3-, 1,6-, and 1,8-dinitropyrenes and 1-nitropyrene in urban air by high-performance liquid chromatography using chemiluminescence detection. *Environ. Sci. Technol.* **1995**, *29*, 928–932. [[CrossRef](#)] [[PubMed](#)]
19. Tang, N.; Taga, R.; Hattori, T.; Toriba, A.; Kizu, R.; Hayakawa, K. Simultaneous determination of twenty-one mutagenic nitropolycyclic aromatic hydrocarbons by high-performance liquid chromatography with chemiluminescence detection. In *Bioluminescence and Chemiluminescence, Progress and Perspectives, Proceedings of the 13th International Symposium, Yokohama, Japan, 2–6 August 2004*; Tsuji, A., Maeda, M., Matsumoto, M., Kricka, L.J., Stanley, P.E., Eds.; World Science: London, UK, 2005; pp. 441–444.
20. Kumagai, K.; Tago, H.; Saitoh, Y.; Kudo, S.; Iijima, A. Multicomponent analysis for organic markers in PM_{2.5} by silylated GC/MS method. *J. Environ. Lab. Assoc. (Zenkoku-Kankyouden-Kaishi)* **2017**, *42*, 53–58. (In Japanese)

21. Ministry of the Environment (Japan). Manual for Measurement of Atmospheric Fine Particulate Matter (PM_{2.5}) Components Technical Committee on Particulate. Available online: <https://www.env.go.jp/air/osen/pm/ca/manual.html> (accessed on 30 November 2022). (In Japanese)
22. Ikemori, F.; Uranishi, K.; Sato, T.; Fujihara, M.; Hasegawa, H.; Sugata, S. Time-resolved characterization of organic compounds in PM_{2.5} collected at Oki Island, Japan affected by transboundary pollution of biomass and non-biomass burning from Northeast China. *Sci. Total Environ.* **2021**, *750*, 142183. [[CrossRef](#)] [[PubMed](#)]
23. Westbald, C.; Levendis, Y.A.; Richer, H.; Howard, J.B.; Carlson, J. A study on toxic organic emission from batch combustion of styrene. *Chemosphere* **2002**, *49*, 395–412. [[CrossRef](#)] [[PubMed](#)]
24. Zajemska, M.; Poskart, A.; Musial, D. The kinetics of nitrogen oxides formation in the flame gas. *Econ. Environ. Stud.* **2015**, *15*, 445–460.
25. BP. Statistical Review of World Energy 2019, 68th Edition. 2020. Available online: <https://www.bp.com/en/global/corporate/energy-economics/statistical-review-of-world-energy> (accessed on 30 November 2022).
26. Hayakawa, K.; Tang, N.; Nagato, E.G.; Toriba, A.; Sakai, S.; Kano, F.; Goto, S.; Endo, O.; Arashidani, K.; Kakimoto, H. Long Term Trends in Atmospheric Concentrations of Polycyclic Aromatic Hydrocarbons and Nitropolycyclic Aromatic Hydrocarbons: A Study of Japanese Cities from 1997 to 2014. *Environ. Pollut.* **2018**, *233*, 474–482. [[CrossRef](#)]
27. Yan, C.; Zheng, M.; Sullivan, A.P.; Shen, G.; Chen, Y.; Wang, S.; Zhao, B.; Cai, S.; Desyaterik, Y.; Li, X.; et al. Residential coal combustion as a source of levoglucosan in China. *Environ. Sci. Technol.* **2018**, *52*, 1665–1674. [[CrossRef](#)]
28. Ministry of Land, Infrastructure, Transport and Tourism, Japan. New Long-Term Regulation Against Vehicles. Available online: https://www.mlit.go.jp/kisha/kisha08/09/090325_.html (accessed on 22 February 2023).
29. Hama, H.; Tokuda, T.; Izaki, A.; Ohno, T.; Watanabe, Y.; Kanda, T.; Tang, N.; Kameda, T.; Toriba, A.; Hayakawa, K. Variation in polycyclic aromatic hydrocarbons and nitropolycyclic aromatic hydrocarbons in airborne particulates collected in urban Kanazawa, Japan, in last 12 years. *J. Jpn. Soc. Atmos. Environ.* **2012**, *47*, 1–8. [[CrossRef](#)]
30. Jia, L.; Cheng, P.; Yu, Y.; Chen, S.; Wang, C.; He, L.; Nie, H.; Wang, J.; Zhang, J.; Fan, B.; et al. Regeneration mechanisms of a novel high-performance biochar mercury adsorbent directionally modified by multimetal multilayer loading. *J. Environ. Manag.* **2023**, *326*, 116790. [[CrossRef](#)] [[PubMed](#)]

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