

Regular Article

## $^{210}\text{Pb}$ and Major Ion Concentrations in Aerosols Collected in Qingdao, a Seaside Area of China

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This study aimed at understanding the atmospheric concentrations of  $^{210}\text{Pb}$  and major ions in aerosols in Qingdao, China, including their seasonal variations and relationships with weather data and to identify the sources of atmospheric sulfur as a part of the Japan-China joint project, "Aeolian Dust Experiment on Climate Impact (ADEC)". The sampling period was from beginning of May 2001 to beginning of March 2002; and a high air-volume sampler was used with a polyflon filter. Atmospheric concentrations of  $^{210}\text{Pb}$  ranged from  $0.15 \pm 0.03$  to  $6.63 \pm 0.26$  mBq  $\text{m}^{-3}$  with the mean ( $\pm$  S.D) of  $0.93 \pm 0.21$  mBq  $\text{m}^{-3}$  and they showed a clearly seasonal variation with high values in winter to spring and low values in summer to autumn, the lowest values were observed during the rainiest period. Total suspended particles (TSP) ranged from 27.17 to 289.43  $\mu\text{g m}^{-3}$  with an average of 123.99  $\mu\text{g m}^{-3}$  which exceeded the World Health Organization (WHO) guideline level for maximum annual exposure of 10 and 20  $\mu\text{g m}^{-3}$  for  $\text{PM}_{2.5}$  and  $\text{PM}_{10}$  respectively. The concentrations of  $\text{Cl}^-$ ,  $\text{NO}_3^-$ ,  $\text{SO}_4^{2-}$  and  $\text{NH}_4^+$  were high in winter and low in autumn.  $\text{Mg}^{2+}$  and  $\text{Ca}^{2+}$  concentrations did not show any seasonal variation.  $\text{Ca}^{2+}$  shown a strong correlation with TSP ( $r = 0.81$ ,  $p < 0.01$ ) this revealed that soil particles were mainly the source of TSP. The strong correlation found ( $r = 0.76$ ,  $p < 0.01$ ) between  $\text{SO}_4^{2-}$  and  $^{210}\text{Pb}$  shown that they were originated mostly from anthropogenic activities the same conclusion was deduced based on the  $\delta^{34}\text{S}$  sulfate measurement results.

**Key words:** lead-210, major ion concentrations, total suspended particles, air-volume sampler

### 1. Introduction

The pollution issue is a problem facing the world recently. Air pollution can occur from nature and anthropogenic

and one of the air pollution caused naturally is Asian dust which can transport very far from the mainland of China to Japan. To find out the effect of this natural phenomenon on the quality of human life, especially those affected by this natural phenomenon, in 2000 the Aeolian Dust Experiment on Climate Impact (ADEC) project was formed<sup>1)</sup>. Qingdao city is one of the network site of ADEC project.

Dust is air pollution containing particles of Pb-210

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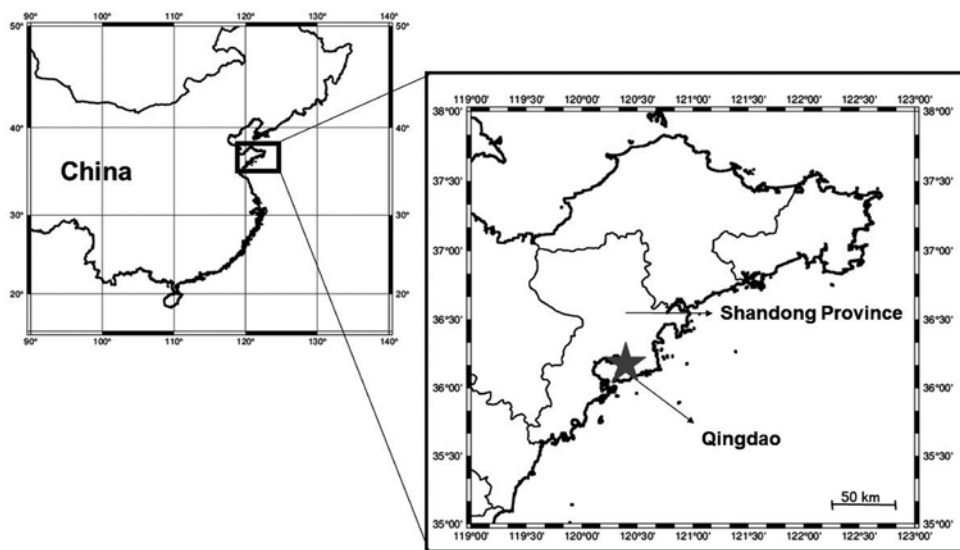


Fig. 1. Location of the study area.

( $^{210}\text{Pb}$ ) which can affect human health. Airborne  $^{210}\text{Pb}$  ( $T_{1/2} = 22.3$  years) is produced from the radioactive decay of  $^{222}\text{Rn}$  in the  $^{238}\text{U}$  series, and it becomes readily attached to suspended particles and precipitation elements<sup>2)</sup>.  $^{210}\text{Pb}$  has been used as a tracer to study atmospheric dynamics in long-range air mass transport, wet or dry deposition rates<sup>3)</sup>, etc. For that purpose, some research studies have looked into the relationships between  $^{210}\text{Pb}$  concentrations in the atmosphere and weather parameters<sup>4,5)</sup>.

In the other hand a rapid economic growth has increased the consumption of fossil energy resources and of industrial raw materials. Despite the fact that some sulfur dioxide ( $\text{SO}_2$ ) and particulate matter occur naturally in the atmosphere in large amounts, contributions from human activities are generally of prime importance in urban areas. In particular, the combustion of fuels for heating and power generation is considered responsible for most of the sulfur dioxide and particulate pollution to which the general population is exposed<sup>6-8)</sup>. The 2005 WHO air quality guidelines offered global guidance on thresholds and limits for key air pollutants that pose health risks, based on expert evaluations of current scientific evidence for particulate matter (PM), ozone ( $\text{O}_3$ ), nitrogen dioxide ( $\text{NO}_2$ ), and sulfur dioxide ( $\text{SO}_2$ )<sup>9)</sup>. Sulfur compounds occurring naturally in the atmosphere come from various sources such as: the  $\text{SO}_4^{2-}$  of sea spray; biogenic sulfur  $\text{H}_2\text{S}$  and dimethyl sulfide (DMS); and volcanic sulfur  $\text{H}_2\text{S}$  and  $\text{SO}_2$ <sup>10)</sup>. The sulfur isotope ratio  $\delta^{34}\text{S}$  has been used as an indicator to determine the sources and behaviors of sulfur compounds in the environment<sup>11)</sup>. Emitted particles in the atmosphere come in many sizes and shapes and chemical components can be directly emitted by sources such as industrial

emissions, fossil fuel combustion, or wildfire combustion, but some are products of chemical reactions in the atmosphere. The main species of interest are  $\text{NO}_3$ ,  $\text{SO}_4^{2-}$ , and  $\text{NH}_4^+$ , due to their effects on environment and human health. Cations, such as  $\text{Mg}^{2+}$  and  $\text{Ca}^{2+}$ , are used as tracers for the determination of the  $\text{SO}_4^{2-}$  concentration in the atmosphere that originates from the sea<sup>12)</sup>.

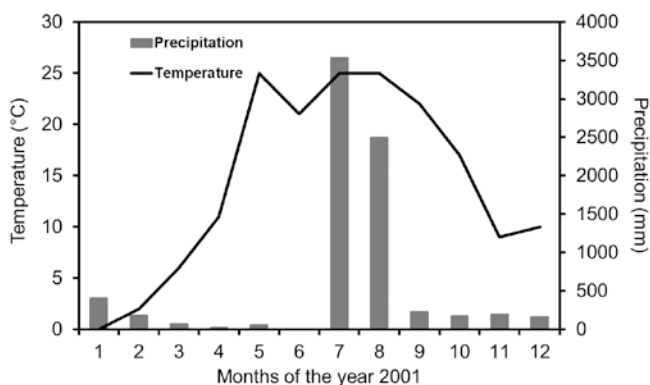
During 2001 to 2002, aerosol samples were collected in Qingdao, China as part of the ADEC project, and total suspended particles (TSP) data were reported<sup>13)</sup>. In this study  $^{210}\text{Pb}$  concentration and major ion concentrations in aerosol samples collected at Qingdao, China are reported with  $\delta^{34}\text{S}$  of sulfate to provide understanding of their seasonal variations, relationships with weather parameters and to identify the sources of atmospheric sulfur.

## 2. Experimental

### 2.1. Study area

Qingdao is a city located in Shandong Province, China, which is a principal administrative division of several counties (Fig. 1). The city (population more than 8,700,000) has a combination of sea coast and mountains and a diverse northern temperate zone climate<sup>14)</sup>. The city of Qingdao has a tropical climate which includes humidity, mild temperatures, and with four clear seasonal changes. During spring, the temperature slowly gets warmer; this usually occurs a month later in the non-coastline areas. During summer, it is muggy and wet while in the autumn it is cool and arid. Winters are usually cold.

Weather data provide useful information to understand



**Fig. 2.** Mean monthly averages of temperature and precipitation in Qingdao, China in 2001.

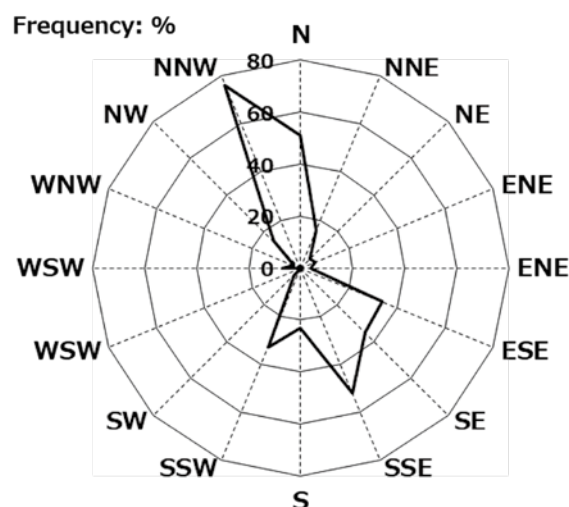
an area's geophysical properties<sup>14</sup>). Figure 2 shows the mean monthly averages of temperature and precipitation in 2001. Temperature varied from 0°C in January to a peak of 25°C during July and August. The most precipitation fell during July and August<sup>15</sup>). In these two summer months, the comparatively large precipitation would cause washout of aerosols from the air.

Figure 3 shows the wind directions in Qingdao during 2001<sup>15</sup>). The wind direction was mainly NNW and SSE. Based on these observations the two usual wind patterns were from the sea to the continent and from the continent to the sea. The wind pattern from the sea occurred at roughly double the frequency of the continental wind pattern.

## 2.2. Sample collection and analyses

The sampling method has been reported in 2018<sup>13</sup>). In brief, aerosol samples were collected using a high-volume air sampler (HV-1000F, Sibata Scientific Co., Ltd., Japan) for 5 days per 1 week during May 2001 to March 2002 at the sampling site on the campus of the Ocean University of China (36°07'N, 120°33'E) in Qingdao City. Aerosol was collected on PF040 polyflon filters (25×20 cm, Advantec Co. Ltd., Japan). The air flow rate was set to 1000 l min<sup>-1</sup>. The filters were dried at 25°C and weighed before sampling. After sampling they were dried again and then weighed. TSP was calculated by dividing the weight difference by the total air flow.

The method for determination of <sup>210</sup>Pb and ion concentrations has been described previously<sup>12</sup>). The filters were cut into 47 mmϕ and were placed into a plastic container (PURATUBO 3-20 type 100 cm<sup>3</sup> U8, Yamayu, Japan). <sup>210</sup>Pb concentration on the filter were measured using an HPGe detector (HP-GE-3018, Canberra, USA) with a multi-channel analyzer for 100,000 s to determine using the full energy peak of 46.5 keV  $\gamma$ -rays. The uncertainty of measurement was determined as less than 6% taking into account of only the counts of background



**Fig. 3.** Wind directions in Qingdao, China in 2001.

and samples.

The concentrations of major ions were determined as follows. The remaining quarter section of filter were cut into fine pieces and put it into a Teflon™ beaker filled with 6 ml of 95% ethanol and 4 ml of distilled water. The water-soluble ionic species were extracted using an ultrasonic treatment for 5 min. After collecting the extract solution into another container, the fine filter pieces were rinsed 3 times with 30 ml distilled water. All rinse solutions were collected and mixed with the extract solution, and the mixed solution was filtered through a 1.2 $\mu$ m membrane filter (RAWP04700: Millipore, Germany). The concentrations of Cl<sup>-</sup>, NO<sub>3</sub><sup>-</sup> and SO<sub>4</sub><sup>2-</sup> were measured by ion chromatography (Compact IC 761; Metrohm, Switzerland). Concentrations of Na<sup>+</sup>, Mg<sup>2+</sup> and Ca<sup>2+</sup> were measured by inductively coupled plasma atomic emission spectroscopy (ICP-AES; SPS7000A; Seiko Instruments Inc., Japan). Concentration of NH<sub>4</sub><sup>+</sup> was measured with a spectrophotometer (Model no. 101: Hitachi, Japan) by indophenol blue absorptiometry.

After chemical analyses, SO<sub>4</sub><sup>2-</sup> was precipitated as BaSO<sub>4</sub> from extracted solution for  $\delta^{34}$ S analysis. For the  $\delta^{34}$ S analysis, the BaSO<sub>4</sub> precipitate was dried and converted to SO<sub>2</sub> through thermal decomposition in vacuum line using a mixture of SiO<sub>2</sub>-V<sub>2</sub>O<sub>5</sub><sup>16, 17</sup>). Subsequently,  $\delta^{34}$ S was measured using a stable isotope ratio mass spectrometer (Optima; Micromass, UK). The Canyon Diablo Troilite (CDT) scale was applied for reporting the  $\delta^{34}$ S value, which is defined as:

$$\delta^{34}\text{S} = \left( \frac{(^{34}\text{S}/^{32}\text{S})_{\text{sample}}}{(^{34}\text{S}/^{32}\text{S})_{\text{std}}} - 1 \right) \times 1000 \quad (1)$$

where  $(^{34}\text{S}/^{32}\text{S})_{\text{sample}}$  and  $(^{34}\text{S}/^{32}\text{S})_{\text{std}}$  denote the  $^{34}\text{S}/^{32}\text{S}$  ratios

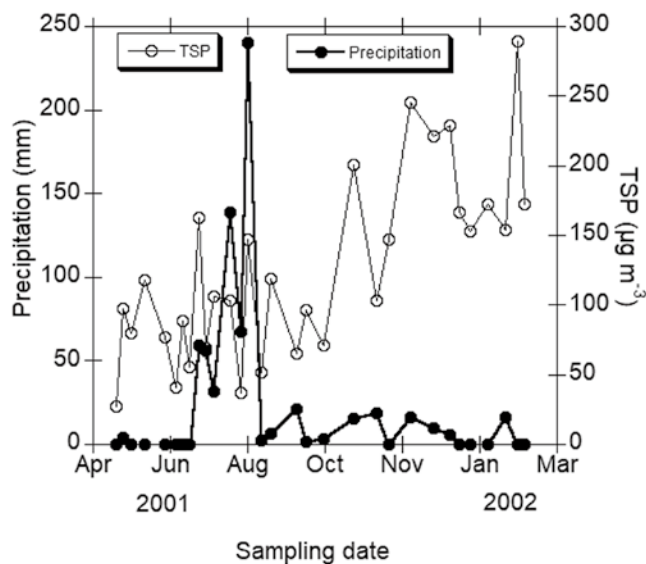


Fig. 4. TSP and precipitation distributions in Qingdao, China.

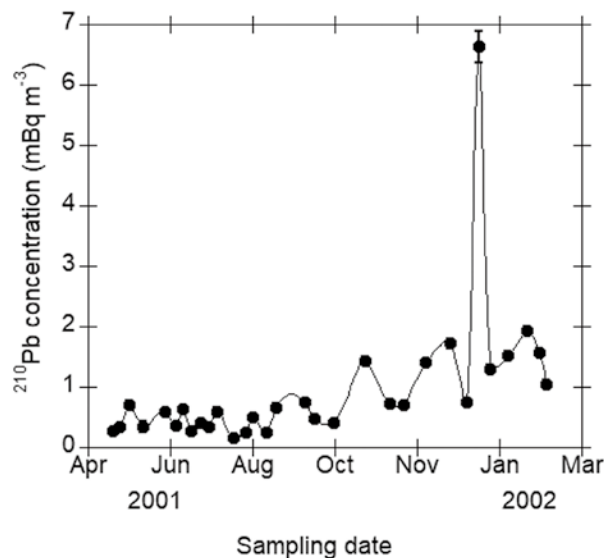


Fig. 5. Temporal variation of  $^{210}\text{Pb}$  atmospheric concentration in Qingdao, China.

of sample and standard, respectively.

### 3. Results and discussion

#### 3.1. Variation of TSP

Figure 4 shows the variation of TSP reported by Kanai *et al.*<sup>13)</sup> combined with the precipitation data reported by the China Meteorological Data Service Center (CMDSC)<sup>15)</sup>. No significant washout phenomenon for TSP was seen during the rainiest period of July to August (Fig. 4). However, the TSP was higher during winter from November 2001 to the beginning of March 2002 with a range from 27.17 to 289.43  $\mu\text{g m}^{-3}$  and an average of 123.99  $\mu\text{g m}^{-3}$ . At this date there is no recent guideline for the exposure to TSP, however  $\text{PM}_{2.5}$  and  $\text{PM}_{10}$  are include in TSP designation. The WHO guideline levels for maximum annual exposure of  $\text{PM}_{2.5}$  and  $\text{PM}_{10}$  are 10 and 20  $\mu\text{g m}^{-3}$  respectively<sup>9)</sup> the present TSP was higher than these guideline levels. Nevertheless it was below of the Chinese national annual TSP average of 291  $\mu\text{g m}^{-3}$  (range from 32 to 741  $\mu\text{g m}^{-3}$ )<sup>18)</sup>. Furthermore, measurements made in Beijing in 2009–2010 showed daily TSP ranged from 75 to 1350  $\mu\text{g m}^{-3}$  with the average of 275.5  $\mu\text{g m}^{-3}$ <sup>19)</sup>. The results in Beijing were generally much higher compared to those of Qingdao and can be explained by the fact of that Beijing is China's second-largest city and high TSP are generally attributed to coal combustion, vehicular traffic and suspended soil dust. Respective concentrations of TSP measured within the current joint project in Japanese regions of Naha, Fukuoka, Nagoya and Tsukuba in 2001 were: 20–90, 20–140, 30–110 and 25–75  $\mu\text{g m}^{-3}$ <sup>20)</sup>. All were slightly lower than the TSP measured in Qingdao. It has been shown throughout the joint

project that atmospheric dust coming to Japan originates from the eastern Asian continent, it can explain the higher TSP measured in Qingdao compared to those measured in Japanese regions<sup>12, 20–22)</sup>.

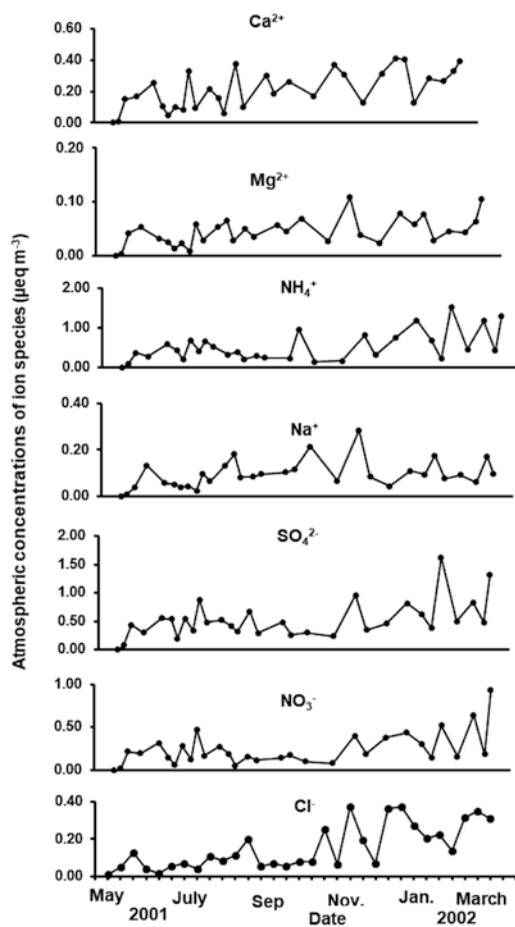
#### 3.2. Temporal variation of $^{210}\text{Pb}$ atmospheric concentration

Figure 5 shows the temporal variation of the atmospheric concentration of  $^{210}\text{Pb}$  in the study area. The  $^{210}\text{Pb}$  concentration ranged from  $0.15 \pm 0.03$  to  $6.63 \pm 0.26$   $\text{mBq m}^{-3}$  with the mean ( $\pm$ S.D.) of  $0.93 \pm 0.21$   $\text{mBq m}^{-3}$ . That was comparable to the concentration measured in the coastal city of Xiamen in the Southeastern of China from 2013 to 2015 which ranged from 0.17 to 3.31  $\text{mBq m}^{-3}$  with the mean of  $1.26 \pm 0.78$   $\text{mBq m}^{-3}$  and Rokkasho, Japan from July 2000 to March 2005 which ranged from 0.18 to 2.17  $\text{mBq m}^{-3}$  with the mean of 1.01  $\text{mBq m}^{-3}$ <sup>23, 24)</sup>. However, the concentration measured from January 2016 to February 2017 in Shanghai, the China's largest city located south of the study area ranged from 0.29 to 6.10  $\text{mBq m}^{-3}$  with the mean of 2.07  $\text{mBq m}^{-3}$  higher than the values of Qingdao<sup>25)</sup>. Furthermore, Table 1 summarizes the  $^{210}\text{Pb}$  concentrations obtained in the present work to reported data from sampling sites around the world, and the mean value in Qingdao was comparable to most of those reported values.

Regarding seasonal variation of  $^{210}\text{Pb}$  in the atmosphere, its concentration in winter was high, with a peak in January 2002, and it was low in summer with the lowest value determined in late July. That distribution pattern suggested the impact of washout phenomenon due to the heavy summer rains (Fig. 3). Based on the present observation, the impact of washout phenomenon on atmospheric  $^{210}\text{Pb}$  concentration was significant. A study

**Table 1.** Summary of  $^{210}\text{Pb}$  activity concentrations in the atmosphere of the present study with reported data from sampling sites around the world

Study area	Sampling period	Activities range (mBq m <sup>-3</sup> )	Mean (mBq m <sup>-3</sup> )
Xiamen, China <sup>24)</sup>	2013–2015	0.17–3.31	1.26 ± 0.78
Michigan, USA <sup>26)</sup>	1999–2001	0.30–4.22	1.16 ± 0.81
El-Minia, Egypt <sup>27)</sup>	Jan.–Dec. 2002	0.17–4.49	1.20 ± 0.15
Kanpur, India <sup>28)</sup>	Jan. 2007–Apr. 2009	0.50–4.80	1.80 ± 1.10
Lodz, Poland <sup>29)</sup>	2008–2009	0.17–1.85	0.56
Islamabad, Pakistan <sup>30)</sup>	2007–2009	0.06–0.76	0.28 ± 0.15
Malaga, Spain <sup>31)</sup>	2009–2011	0.40–0.95	0.55
Mt. Cimone, Italy <sup>32)</sup>	1998–2011	0.05–2.30	0.46
Granada, Spain <sup>33)</sup>	Jan. 2010–Dec. 2014	0.16–1.31	0.62 ± 0.18
Hangzhou, China <sup>34)</sup>	Jan. 2016–Sep. 2017	0.24–27.95	3.39
Changbai, China <sup>35)</sup>	Not given	0.10–1.92	0.81
Shanghai, China <sup>25)</sup>	Jan. 2016–Feb. 2017	0.29–6.10	2.07 ± 1.28
Rokkasho, Japan <sup>23)</sup>	July 2000–Mar. 2005	0.18–2.17	1.01
Kumamoto, Japan <sup>36)</sup>	Dec. 2001–Nov. 2003	0.32–1.30	0.89
Qingdao, China (Present work)	May 2001–Mar. 2002	0.15–6.63	0.93 ± 0.06

**Fig. 6.** Distributions of ion species concentrations in Qingdao, China.

within the present joint project conducted in Okinawa Prefecture in Japan indicated a similar impact on  $^{210}\text{Pb}$  concentration by the washout phenomenon<sup>12)</sup>. It was reported that the  $^{210}\text{Pb}$  concentration ranged from 0.10 to 1.52 mBq m<sup>-3</sup> (mean, 0.64 mBq m<sup>-3</sup>) in Okinawa. That is, the concentration found in Qingdao is slightly higher than that in Okinawa. The lower concentration in Okinawa can be explained by the fact that the Prefecture is an island and there are heavy rainfalls in summer from typhons.

### 3.3. Temporal variation of ion species atmospheric concentrations

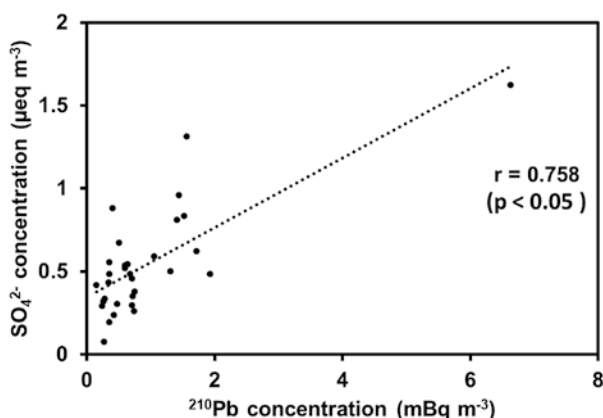
Figure 6 displays the atmospheric concentrations of ion species, the concentrations of Cl<sup>-</sup>, NO<sub>3</sub><sup>-</sup>, SO<sub>4</sub><sup>2-</sup> and NH<sub>4</sub><sup>+</sup> were high in winter and low in autumn. However, Mg<sup>2+</sup> and Ca<sup>2+</sup> concentrations did not show any seasonal variation.

Ion concentrations had the following ranges: for Cl<sup>-</sup> from 0.01 to 6.63 µeq m<sup>-3</sup>; for NO<sub>3</sub><sup>-</sup> from 0.02 to 0.93 µeq m<sup>-3</sup>; for SO<sub>4</sub><sup>2-</sup> from 0.08 to 1.62 µeq m<sup>-3</sup>; for Na<sup>+</sup> from 0.01 to 0.28 µeq m<sup>-3</sup>; for NH<sub>4</sub><sup>+</sup> from 0.09 to 1.53 µeq m<sup>-3</sup>; for Mg<sup>2+</sup> from 0.00 to 0.11 µeq m<sup>-3</sup>; and for Ca<sup>2+</sup> from 0.01 to 0.43 µeq m<sup>-3</sup>. The Table 2 shows correlation coefficients between ion species concentrations TSP and  $^{210}\text{Pb}$ . Ca<sup>2+</sup> shown a strong correlation with TSP ( $r = 0.81$ ,  $p < 0.05$ ) this revealed that aerosols particles in the study area were made out from aeolian dust, it is well known that the source of Ca<sup>2+</sup> is mainly soil particle. SO<sub>4</sub><sup>2-</sup> was strongly correlated with NH<sub>4</sub><sup>+</sup> and NO<sub>3</sub><sup>-</sup> ( $r = 0.83$ ,  $p < 0.05$  and  $r = 0.84$ ,  $p < 0.05$  respectively), NH<sub>4</sub><sup>+</sup> and NO<sub>3</sub><sup>-</sup> were also strongly correlated ( $r = 0.84$ ,  $p < 0.05$ ). These correlations suggested that, those chemical components were present in air in form of (NH<sub>4</sub>)<sub>2</sub>SO<sub>4</sub> and NH<sub>4</sub>NO<sub>3</sub>. Na<sup>+</sup> showed a good correlation with Mg<sup>2+</sup> ( $r = 0.80$ ,  $p < 0.05$ ) which had

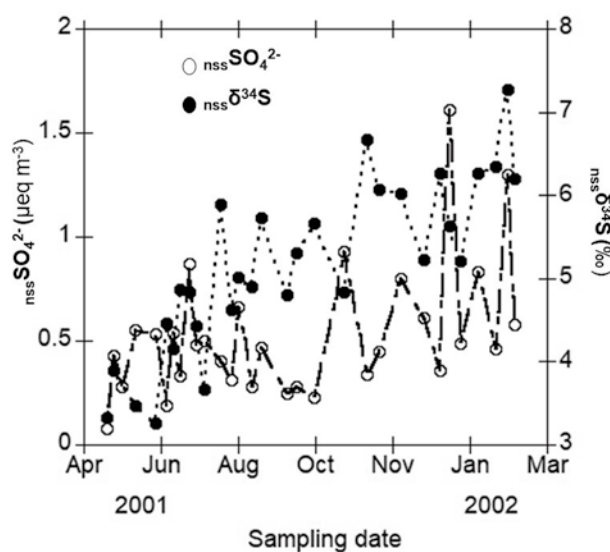


**Table 2.** Correlation coefficients of ion species concentrations  $\delta^{34}\text{S}$  and  ${}_{\text{nss}}\delta^{34}\text{S}$  in aerosol samples collected in Qingdao, China

	Cl <sup>-</sup>	NO <sub>3</sub> <sup>-</sup>	SO <sub>4</sub> <sup>2-</sup>	${}_{\text{nss}}\text{SO}_4^{2-}$	Na <sup>+</sup>	NH <sub>4</sub> <sup>+</sup>	Mg <sup>2+</sup>	Ca <sup>2+</sup>	$\delta^{34}\text{S}$	${}_{\text{nss}}\delta^{34}\text{S}$
TSP	0.80	0.74	0.70	0.69	0.37	0.61	0.76	0.81	0.64	0.61
Cl <sup>-</sup>		0.44	0.46	0.45	0.66	0.40	0.81	0.74	0.64	0.61
NO <sub>3</sub> <sup>-</sup>			0.84	0.84	0.06	0.85	0.76	0.41	0.30	0.43
SO <sub>4</sub> <sup>2-</sup>				1.00	0.14	0.83	0.44	0.39	0.20	0.33
${}_{\text{nss}}\text{SO}_4^{2-}$					0.12	0.83	0.43	0.38	0.19	0.32
Na <sup>+</sup>						0.00	0.80	0.54	0.48	0.32
NH <sub>4</sub> <sup>+</sup>							0.30	0.23	0.22	0.34
Mg <sup>2+</sup>								0.79	0.56	0.51
Ca <sup>2+</sup>									0.55	0.56
$\delta^{34}\text{S}$										0.97



**Fig. 7.** Relationship between  $\text{SO}_4^{2-}$  concentration and  ${}^{210}\text{Pb}$  concentration in Qingdao, China.



**Fig. 8.** Distributions of  ${}_{\text{nss}}\text{SO}_4^{2-}$  concentration and  ${}_{\text{nss}}\delta^{34}\text{S}$  in Qingdao, China.

the same source (sea spray), since one of the two wind patterns (Fig. 3) comes from the sea this result is not surprising. However, a correlation coefficient between  $\text{Na}^+$  and  $\text{Cl}^-$  ( $r = 0.66, p < 0.05$ ) shown that  $\text{Cl}^-$  source was not only from sea-salt but also from anthropogenic activities.

The ion species  $\text{SO}_4^{2-}$  enters the atmosphere from various sources, and may be natural or anthropogenic. Sulfur concentration in aerosols collected for ten years from 1993 to 2003 in Tsuruoka, Japan ranged from 7.6 to 354.4  $\text{neq m}^{-3}$  (16), and this was lower than the concentration in Qingdao. This difference can be explained by abundant anthropogenic emissions from industries and vehicular traffic in Qingdao which is an important economic hub unlike the less industrialized and less populated Tsuruoka. Sulfur in the atmosphere from non-sea salt sulfate ( ${}_{\text{nss}}\text{SO}_4^{2-}$ ), non-sea calcium ( ${}_{\text{nss}}\text{Ca}^{2+}$ ) and  ${}_{\text{nss}}\delta^{34}\text{S}$  were calculated from the conservative assumption that  $\text{Na}^+$  is a sea-salt tracer (see equations (2) and (3)) (12, 16). In Qingdao,  ${}_{\text{nss}}\text{SO}_4^{2-}$  ranged from 0.08 to 1.61  $\mu\text{eq m}^{-3}$ , while in Tsuruoka,  ${}_{\text{nss}}\text{SO}_4^{2-}$  ranged from 3.7 to 335.6  $\text{neq m}^{-3}$ . That followed the same trend as for the total  $\text{SO}_4^{2-}$ ; the sulfur concentration in aerosols collected in Tsuruoka were

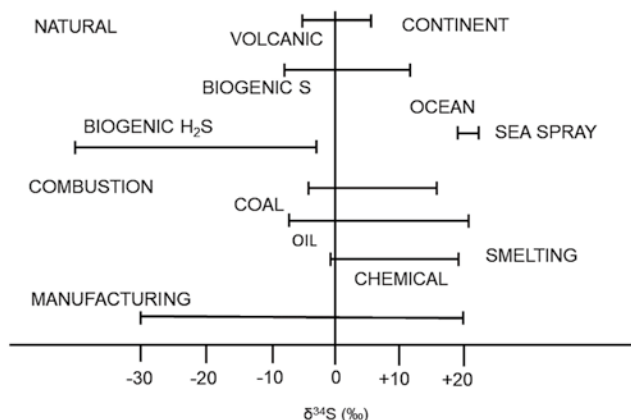
lower than in Qingdao.  $\text{SO}_4^{2-}$  shown a strong correlation with  ${}^{210}\text{Pb}$  ( $r = 0.76, p < 0.05$  see Fig. 7). This strong correlation can be explained by a similar origin from fossil fuel combustion as shown in the study conducted in several Chinese urban sites, coal combustion considerably contributed to atmospheric lead (37).

$${}_{\text{nss}}\text{SO}_4^{2-} = \text{SO}_4^{2-} - (\text{SO}_4^{2-}/\text{Na}^+)_{\text{sea}} \times \text{Na}^+ \quad (2)$$

$${}_{\text{nss}}\delta^{34}\text{S} = \left( \frac{\text{sam}\delta^{34}\text{S} \times \text{sam}\text{SO}_4^{2-} - \text{sea}\delta^{34}\text{S}}{\text{sam}\text{SO}_4^{2-} - \text{nss}\text{SO}_4^{2-}} \right) / {}_{\text{nss}}\text{SO}_4^{2-} \quad (3)$$

where  $(\text{SO}_4^{2-}/\text{Na}^+)_{\text{sea}}$  is the concentration ratio in sea water, and  $\text{sam}\delta^{34}\text{S}$  and  $\text{sea}\delta^{34}\text{S}$  are  $\delta^{34}\text{S}$  values of sample and sea water, respectively.

The  $\delta^{34}\text{S}$  found in Qingdao ranged from 3.46 to 7.36 ‰ and  ${}_{\text{nss}}\delta^{34}\text{S}$  ranged from 3.26 to 7.27 ‰.  $\delta^{34}\text{S}$  and  ${}_{\text{nss}}\delta^{34}\text{S}$  had a strong correlation ( $r = 0.97, p < 0.05$ ); it is suggested that most of the atmospheric sulfur in Qingdao came from



**Fig. 9.** Synopsis of  $\delta^{34}\text{S}$  distributions in major source materials of atmospheric sulfur<sup>38)</sup>.

continental sources rather than from the sea salt. The  $\text{SO}_4^{2-}$  and  $\delta^{34}\text{S}$  variations are shown in Figure 8, and they had similar patterns. Nielsen *et al.*<sup>38)</sup> reported the isotopic composition of the major contributors to atmospheric sulfur, and stated that modern sea water sulfate had a  $\delta^{34}\text{S}$  around 20 ‰. The present study results agreed well with this. Figure 9 presents a synopsis of  $\delta^{34}\text{S}$  distributions in the major source materials of atmospheric sulfur based on Nielsen's work. According to the range of  $\delta^{34}\text{S}$  found in this work ( $3.46 \leq \delta^{34}\text{S} \leq 7.36$  ‰) it can be said that sulfur in the atmosphere of Qingdao probably originates from sources like coal and petroleum combustion, chemical industries, smelting, biogenic activities, and volcanic activity.

#### 4. Conclusion

Aerosol sampling was done in Qingdao, China and the concentrations of atmospheric  $^{210}\text{Pb}$  and ion species were determined with the aim of understanding the local atmospheric environment. The variations of TSP, atmospheric  $^{210}\text{Pb}$  concentration and major ions were observed for the period from May 2001 to March 2002. TSP was found to be lower than the Chinese annual average but higher than those measured in some Japanese region within the current project. The concentrations of  $\text{Cl}$ ,  $\text{NO}_3$ ,  $\text{SO}_4^{2-}$  and  $\text{NH}_4^+$  were high in winter and low in autumn. However,  $\text{Mg}^{2+}$  and  $\text{Ca}^{2+}$  concentrations did not show any seasonal variation. The sulfur content probably originates from sources like coal and petroleum combustion, chemical industries, smelting, biogenic activities, and volcanic activity according to the range of  $\delta^{34}\text{S}$  found in this work. The results suggested that, Qingdao faced to the air pollution phenomenon from fossil fuel combustion and the release of particulate matter in the atmosphere from aeolian dust.

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#### Conflict of Interest

The authors declare no conflicts of interest.

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