

Elemental composition of Arctic soils and aerosols in Ny-Ålesund measured using laser-induced breakdown spectroscopy



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ABSTRACT

Two laser-induced breakdown spectroscopy (LIBS) systems (soil LIBS and aerosol LIBS) were used to determine the elemental composition of soils and ambient aerosols less than 2.5 μm in Ny-Ålesund, Svalbard (the world's most northerly human settlement). For soil LIBS measurements, matrix effects such as moisture content, soil grain size, and surrounding gas on the LIBS response were minimized. When Ar gas was supplied onto the soil sample surfaces, a significant enhancement in LIBS emission lines was observed. Arctic soil samples were collected at 10 locations, and various elements (Al, Ba, C, Ca, Cu, Fe, H, K, Mg, Mn, N, Na, O, Pb, and Si) were detected in soils. The elemental distribution in arctic soils was clearly distinguishable from those in urban and abandoned mining soils in Korea. Moreover, the concentrations of most of anthropogenic metals were fairly low, and localized sources in extremely close proximity affected the elevated level of Cu in the soil samples derived from Ny-Ålesund. The number of elements detected in aerosols (C, Ca, H, K, Mg, Na, and O) was lower than those determined in soils. The elements in aerosols can mainly originate from minerals and sea salts. The elemental distribution in aerosols was also clearly distinguishable from that in soils, suggesting that the resuspension of local soil particles by wind erosion into aerosols was minimal. The daily variation of particle number concentration (RSD = 71%) and the elements in aerosols (RSD = 25%) varied substantially, possibly due to fluctuating air masses and meteorological conditions.

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1. Introduction

The Arctic is extremely sensitive to minute climatic changes and effects of human activity; with its historically pristine conditions, the Arctic is recognized as an important region for predicting global climate changes [1–5]. Studies have demonstrated that arctic environments (air, snow, water, and soil) can be influenced by long-range transported contaminants [6,7]. Heavy metals in multimedia can serve as an indicator of the growing pollution in the Arctic derived from anthropogenic sources. Both local and remote sources can contribute to heavy metals in soils and aerosols. Atmospheric deposition of long-range transported anthropogenic aerosols may play a crucial role in the enrichment of heavy metals in soils in the Arctic [8–10]. In Ny-Ålesund, Svalbard, which is the world's most northerly human settlement, the first coal mining activity began in 1916 and stopped in 1963 [11]. Heavy metals in soils in Ny-Ålesund may still be affected by coal waste materials. Therefore, determining heavy metals in soils and aerosols is essential to understanding anthropogenic pollution in the Arctic.

In general, elements in soils and aerosols are determined by atomic absorption spectroscopy and inductively coupled plasma–optical emission spectroscopy (ICP–OES) or –mass spectrometry [12,13]. However, these techniques are relatively time-consuming, labor-intensive, and



Fig. 1. Map of soil and aerosol sampling sites in Ny-Ålesund.

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Table 1
Description of sampling sites for soils and aerosols.

Sample type	Sampling location in the map	Description
Soil (loamy sand)	A, B	Town in Ny-Ålesund (78.6° N, 11.6° E)
Soil (loamy sand)	C, D, E	Road in Ny-Ålesund (78.6° N, 11.6° E)
Soil (loamy sand)	F, G	Plain in Ny-Ålesund (78.6° N, 11.6° E)
Soil (sand)	H, I	Seashore in Ny-Ålesund (78.6° N, 11.6° E)
Soil (loamy sand)	J	Airport in Ny-Ålesund (78.6° N, 11.6° E)
Soil (loamy sand)	–	Urban (Gwangju) in Korea (35.2° N, 126.8° E)
Soil (sandy loam)	–	Abandoned mining (Hongchun) in Korea (37.7° N, 127.6° E)
Aerosol	K	9 samples (September 14, 2012, to September 22, 2012) at Gruvebadet station in Ny-Ålesund (78.6° N, 11.6° E)

costly [14–16]. During sample preparation and pretreatment processes, the consumption of high-purity solvents is inevitable, leading to the generation of chemical waste and possible sampling artifacts [16–18]. Laser-induced breakdown spectroscopy (LIBS) has been used as a tool

for multielement detection of diverse samples in aerosol, solid, liquid, and gas phases [19–24]. The sample size can be as small as the laser spot size (i.e., laser focal area). LIBS can detect even light elements (e.g., H, He, Li, C, N, and O) [25,26], and it is a relatively simple and cost-effective technique, with little or no sample preparation required [27–30]. Studies have demonstrated that elemental concentrations in soils determined by LIBS were consistent with data from conventional methods [31–33]. However, soils intrinsically consist of nonhomogeneous materials [34,35], and the complex soil matrix tends to hinder the accurate quantification of elemental composition of soils by LIBS [36,37]. Water content, grain size, and cohesion in soils can affect LIBS emission lines [38–40]. Furthermore, the surrounding gas can influence the emission characteristics of LIBS during plasma expansion and cooling processes [41–43].

In this study, elements including heavy metals in soils and aerosols in Ny-Ålesund, Svalbard, were determined using two LIBS systems (soil LIBS and aerosol LIBS). First, matrix effects, such as water content and grain size in soils, and surrounding gases (air versus Ar) were examined in soil LIBS measurements. The spatial distribution of elements in soils in Ny-Ålesund was determined to examine the effects of local sources on soils, and this distribution was compared with those in urban and abandoned mining soils sampled in Korea. Additionally, elements in arctic aerosols were determined by aerosol LIBS and compared with those in arctic soils.

2. Materials and method

Soil and aerosol sampling was conducted in Ny-Ålesund, Spitsbergen, Svalbard (78.6 N, 11.6 E). International observation stations and a

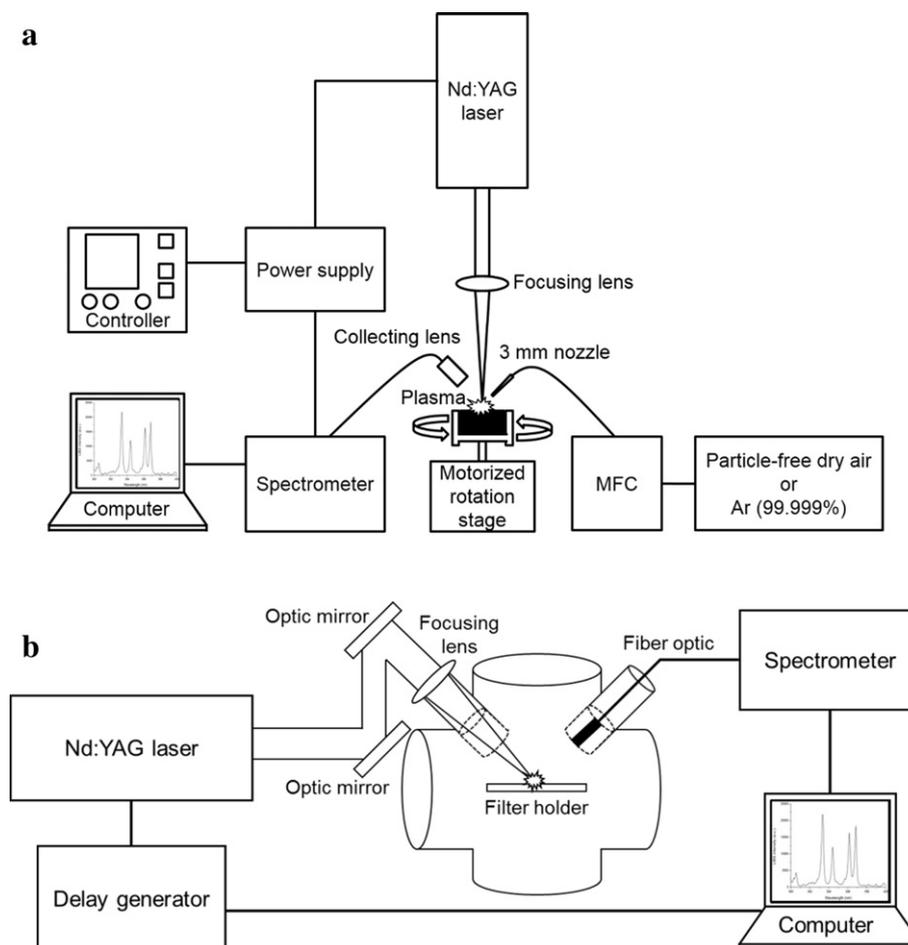


Fig. 2. Schematics of the LIBS systems (soil LIBS and aerosol LIBS) to determine elemental composition of (a) soils and (b) aerosols.

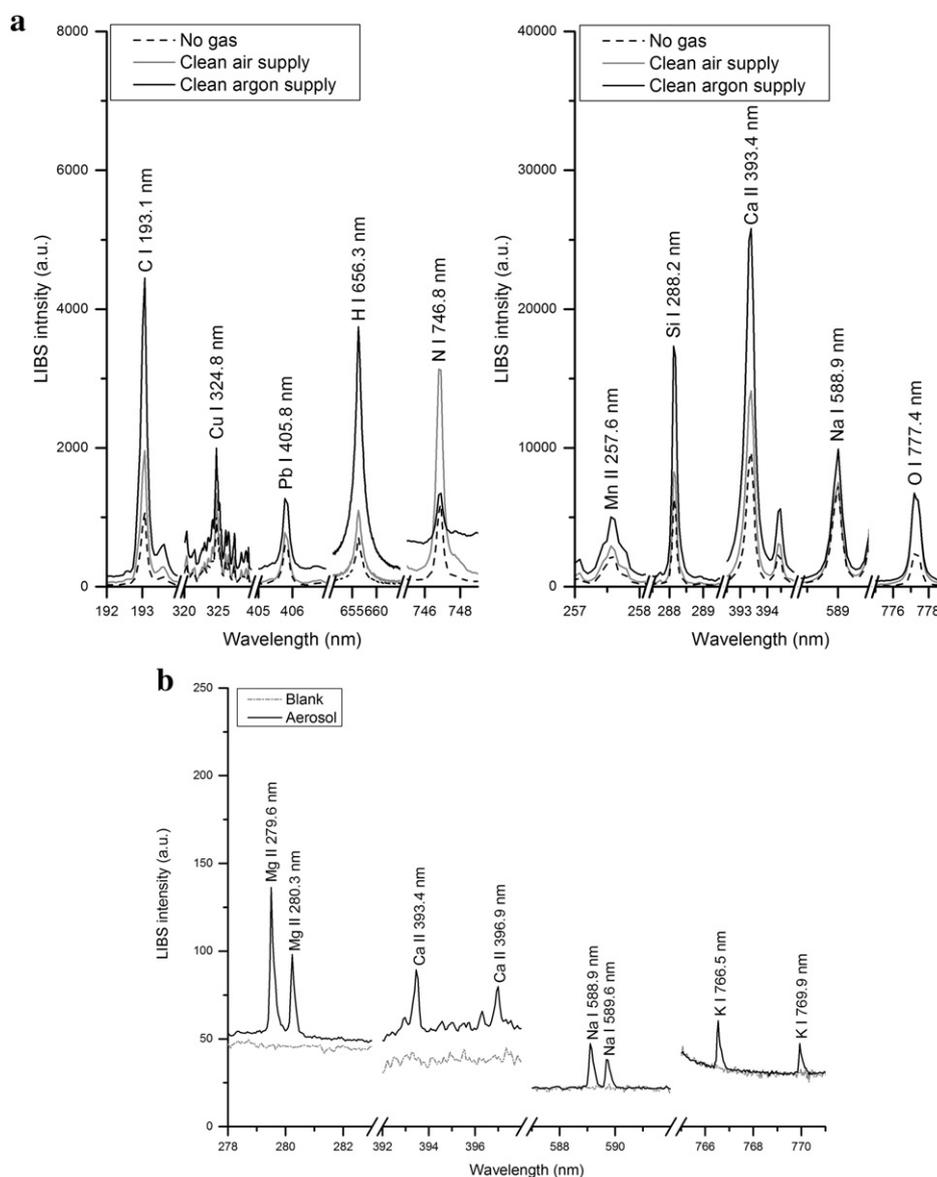


Fig. 3. Examples of LIBS spectra of (a) soil and (b) aerosol samples.

small town are located in Ny-Ålesund, and the area is generally considered representative of remote Arctic environments. Arctic soil samples were collected at 10 different locations (A to J), and ambient aerosol samples were collected at location K in Ny-Ålesund, as illustrated in Fig. 1. Descriptions of sampling sites are provided in Table 1. Location A and B were in town; C, D, and E were near a road from town to the Gruebadet observation station; F and G were near a plain area; H and I were near a coastal area; J was located at the airport. Soil samples within 5 cm of the soil surface were collected. Moreover, soil samples obtained in urban and abandoned mining areas in Korea were analyzed, and are presented in Table 1. Soil types in Ny-Ålesund were found to be loamy sand and sand, as summarized in Table 1.

All soil samples were dried and sieved through a 200-mesh screen (75 μm). They were weighted equally (1 g) and then prepared as pressed pellets, with a load of 5000 kg applied for 1 min. Consequently, each pellet had a diameter of 13 mm and a height of approximately 3.5 mm. Pellet samples were stored at a constant temperature and relative humidity (RH) in a desiccator before being analyzed by LIBS.

For aerosol samples, the ambient aerosols passed through an impactor inlet and a diffusion dryer, and they were then collected on filters (Zefluor™, Pall Corporation, USA) at a constant flow rate of 25 l per minute (lpm) (i.e., particulate matter less than 2.5 μm (PM_{2.5}) were collected on filter).

Aerosol sampling was performed from 12:00 to 20:00 every day during the sampling period from September 14, 2012, to September 22, 2012. The aerosol samples were stored at a constant temperature and RH in a desiccator before being analyzed by LIBS. To determine number concentration of particles in sizes from 10 to 470 nm in real time, a scanning mobility particle sizer (SMPS) (TSI 3034, USA) was used.

Fig. 2 displays schematics of the LIBS system for elemental analysis of soil and aerosol samples. For the soil LIBS system, a Q-switched neodymium-doped yttrium aluminum garnet (Nd:YAG) laser (Polaris, New Wave Research Inc., USA) was used as the radiation source. The laser was operated at 90 mJ/pulse, with a pulse width of 4–5 ns at 1064 nm, and the laser repetition rate was set to 1 Hz. A pulsed laser beam was optically focused by a 90 mm focal length plano-convex lens and directed at the sample surfaces so that small amounts of samples could be dissociated and ionized. After laser-induced plasma was generated, atomic and ionic emissions were observed during cooling. The emissions from the laser-induced plasma were collected using a collection lens at a 45° angle, and were then delivered to the spectrometer (Aurora, Applied spectra Inc., USA), measuring emission lines from 190 to 884 nm with a spectral resolution of 0.1 nm and a delay time of 1 μs . Approximately 50 LIBS spectra for each soil sample (50 laser shots) were recorded. During the analysis, a soil pellet placed on the sample holder was automatically rotated to

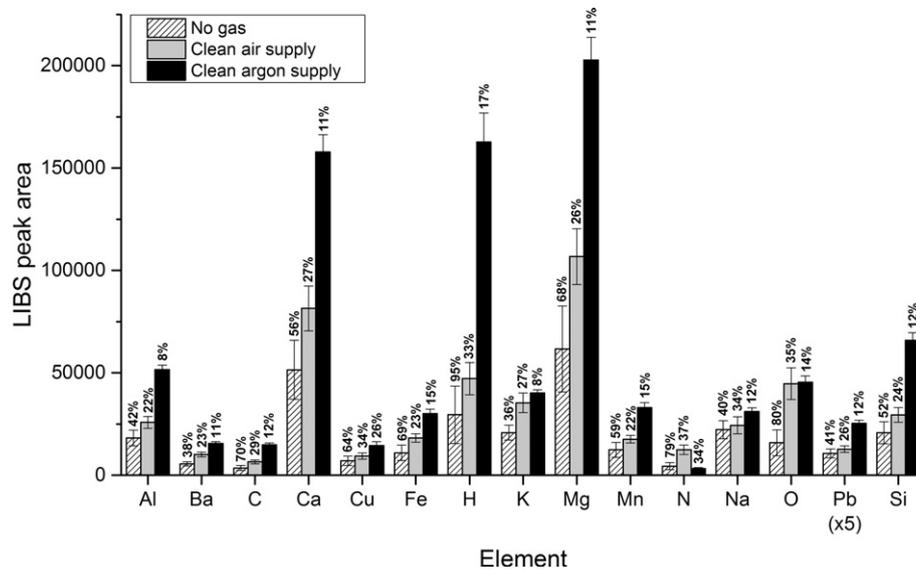


Fig. 4. LIBS emission lines with RSD (%) with different gas supplies (no gas, clean air supply, and clean Ar supply).

expose fresh surface so the crater effect would be negligible [44]. To investigate the effects of surrounding gas on the LIBS emissions, particle-free dry air and Ar (99.999% pure) were supplied into the plasma by using a 3 mm nozzle with a flow rate of 0.5 lpm.

For the aerosol LIBS system [45], a Q-switched Nd:YAG laser (Surelite II-10, Continuum Inc., USA) was used; the laser was operated at 110 mJ/pulse, with a pulse width of 5–7 ns, wavelength of 1064 nm, and repetition rate of 1 Hz. The pulse laser was focused onto the particle samples on the filter by using a plano-convex lens (focal length = 75 mm). A broadband spectrometer (LIBS2000+, Ocean Optics Inc., USA) was used to measure emission lines of 200–980 nm, with a spectral resolution of 0.1 nm. The filter was

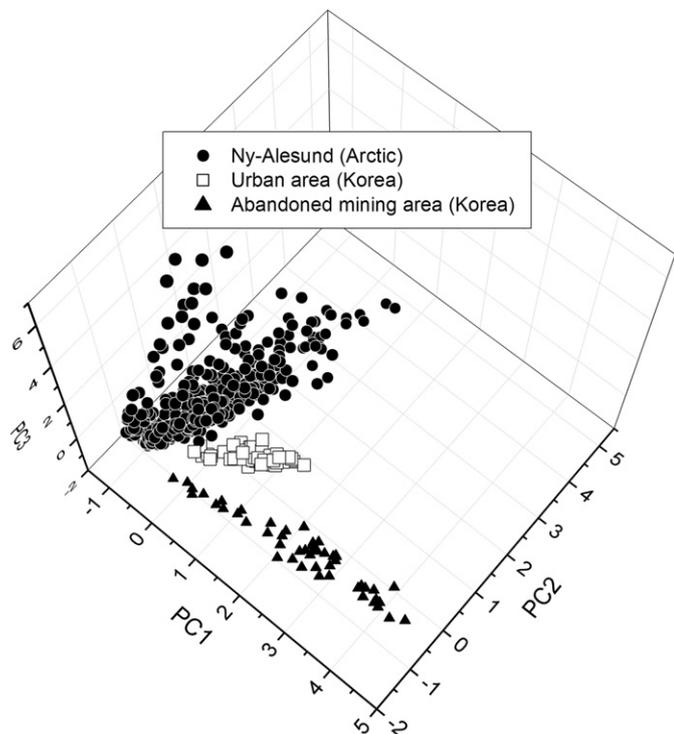


Fig. 5. PCA score plot for soil samples from the Arctic and urban and abandoned mining sites in Korea.

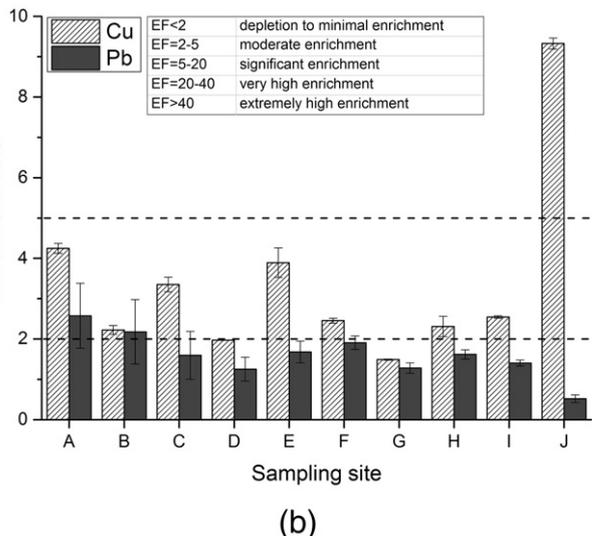
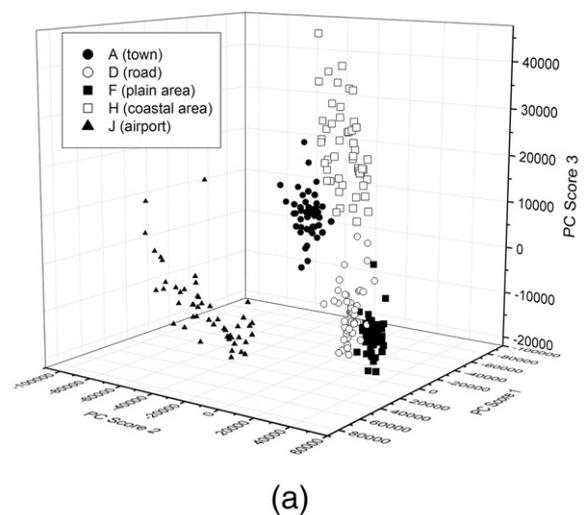


Fig. 6. (a) Scatter plot of three PCs for arctic soils among sites, and (b) comparison of EFs of Cu and Pb for arctic soils among sites [55].

Table 2
Concentrations of elements in soils determined by the ICP–OES.

Soil samples	Concentration determined by the ICP–OES									
	Al (g/kg)	Ba (mg/kg)	Ca (g/kg)	Cu (mg/kg)	Fe (g/kg)	K (g/kg)	Mg (g/kg)	Mn (mg/kg)	Na (mg/kg)	Pb (mg/kg)
A	7.0 ± 0.7	58 ± 5	33 ± 3	73 ± 6	21 ± 2	1.4 ± 0.1	15 ± 2	301 ± 20	427 ± 28	35 ± 8
B	13.3 ± 0.0	97 ± 1	23 ± 0	69 ± 3	39 ± 0	3.4 ± 0.0	14 ± 0	705 ± 3	305 ± 28	57 ± 21
C	11.0 ± 0.7	48 ± 1	35 ± 2	79 ± 1	29 ± 2	1.6 ± 0.1	20 ± 1	351 ± 2	1016 ± 54	30 ± 10
D	10.5 ± 0.1	61 ± 0	12 ± 0	52 ± 0	33 ± 0	1.9 ± 0.0	10 ± 0	472 ± 1	405 ± 51	27 ± 6
E	3.7 ± 0.0	87 ± 0	8 ± 0	74 ± 7	24 ± 0	1.6 ± 0.0	4 ± 0	298 ± 6	457 ± 21	27 ± 4
F	7.2 ± 0.3	48 ± 2	13 ± 1	48 ± 1	24 ± 1	0.9 ± 0.0	8 ± 0	283 ± 10	232 ± 11	31 ± 4
G	10.0 ± 0.1	60 ± 0	14 ± 0	41 ± 0	34 ± 0	1.5 ± 0.0	10 ± 0	579 ± 2	243 ± 10	29 ± 3
H	11.5 ± 0.0	121 ± 0	116 ± 1	45 ± 5	24 ± 0	1.6 ± 0.0	13 ± 0	216 ± 1	2323 ± 23	26 ± 2
I	23.8 ± 0.4	1206 ± 37	79 ± 1	104 ± 2	51 ± 0	2.1 ± 0.0	14 ± 0	482 ± 4	4735 ± 68	48 ± 2
J	11.5 ± 0.1	22 ± 0	5 ± 0	190 ± 1	25 ± 0	0.4 ± 0.0	12 ± 0	240 ± 0	417 ± 10	9 ± 2

divided into five areas for laser shots, and five LIBS spectra were obtained for each filter. A background spectrum was obtained for a blank filter without any particle samples. LIBS signals were acquired under room temperature condition without any gas supply.

ICP–OES (Optima 5300 DV, Perkin Elmer, USA) was used to determine the concentrations of Al, Ba, Ca, Cu, Fe, K, Mg, Mn, Na, and Pb in soils. Oven-dried soils were sieved using a 200-mesh screen (75 μm), and a 0.25 g soil sample was then added into the polypropylene tube with 4 mL of aqua regia (HCl with HNO₃ (3:1)). The polypropylene tubes were stored in a heating block at 70 °C for 1 h. After aqua regia digestion, samples were centrifuged for 5 min. Supernatant solutions were diluted and then analyzed by ICP–OES.

Principal component analysis (PCA) was applied for chemometric analysis of samples using LIBS GD&T software (version 1.0, New Folder, USA). A full spectrum, from 190 to 884 nm, was used as the input variable. PCA was used for data reduction by abbreviating complicated spectral data into simplified data (i.e., principal components) with a minimal loss of information.

3. Results and discussion

Examples of LIBS spectra for soils are displayed in Fig. 3a. In soil samples, various elements, namely Al (396.2 nm), Ba (493.4 nm), C (193.1 nm), Ca (393.4 nm), Cu (324.8 nm), Fe (274.7 nm), H (656.3 nm), K (766.5 nm), Mg (279.6 nm), Mn (257.6 nm), N (746.8 nm), Na (588.9 nm), O (777.4 nm), Pb (405.8 nm), and Si (288.2 nm), were detected. Because air breakdown occurs in the LIBS plasma, O and N emission lines are typically observed. To minimize air breakdown and enhance LIBS intensity, Ar was supplied to the sample surface, and the resulting spectra are illustrated in Fig. 3a. With an Ar

supply, the LIBS intensity of N was significantly reduced. Without soil samples, C and H were not observed, suggesting that C and H were derived from organic matter in the soils. For aerosol samples, C (247.9 nm), H (656.3 nm), O (777.4 nm), Mg (279.6 nm), Ca (393.4 nm), Na (588.9 nm), and K (766.5 nm) were detected, suggesting that minerals and sea salts are major constituents of arctic aerosols. Because Zefluor filters used to collect aerosols contain carbonaceous species, carbonaceous aerosols could not be clearly resolved. Fig. 3b displays LIBS spectra for aerosols, including a blank spectrum. The number of elements detected in the aerosol samples was much lower than that in the soil samples; however, all elements in aerosols were also detected in soils.

Moisture content in soils [46], grain size of soils [47], and surrounding gases [41] can affect LIBS emissions (i.e., soil matrix effect). The moisture in soils can absorb part of the incident laser energy, thus reducing the intensity of the LIBS spectra [37,48]. The mass of soils ablated by the laser can vary with soil grain size [37]. To minimize the effects of soil moisture content and grain size on the LIBS performance, soil samples were dried and sieved through a 200-mesh screen (75 μm). Subsequently, soil samples were pressed into pellets to enhance sensitivity and reproducibility [37,38,49,50]. Pelletizing can also produce enhanced physical resistance to mechanical shocks during the laser–sample interaction [38,51]. The effect of gas on the LIBS emission line is illustrated in Fig. 4. When air and Ar were blown onto the sample surface, the LIBS emission lines were significantly enhanced. This might have been because the blowing of gas removed any particles produced during the laser ablation process, causing the prevention of laser or emitted-light decay. Studies have reported that particles produced above the sample surface from successive laser ablation could interact with subsequent laser beams, resulting in a decay in emission intensity [52,53]. Consequently, the laser energy reaching the sample surface decreased, reducing the energy available to ablate the sample. Additionally, a higher enhancement in LIBS emission lines (except N and O emission lines) was found with Ar gas than with air. With Ar, the emission line of N, which is a main constituent of air, was substantially reduced. The expansion of plasma can be suppressed by Ar that has a higher mass density than that of air (1.784 g/l for Ar and 1.292 g/l for air at standard temperature and pressure) [43,53]. Therefore, increases in the temperature, electron density, and lifetime of plasma can be achieved, leading to the enhancement of the LIBS emission. When the relative standard deviation (RSD) values of emission lines were compared, the use of Ar also yielded led to substantially lower RSD than that produced using air. Reproducible results were obtained for all soil samples. Subsequently, the LIBS data with Ar are discussed.

Fig. 5 displays a PCA score plot used to compare arctic soil samples with soil samples obtained from Korea. The soil samples from Korea were obtained from urban (uncontaminated) and abandoned mining (contaminated with heavy metals) sites. Although they all had similar elements, the data points in the PCA score plot suggest that samples from the Arctic and Korea were clearly distinguishable. Urban soil

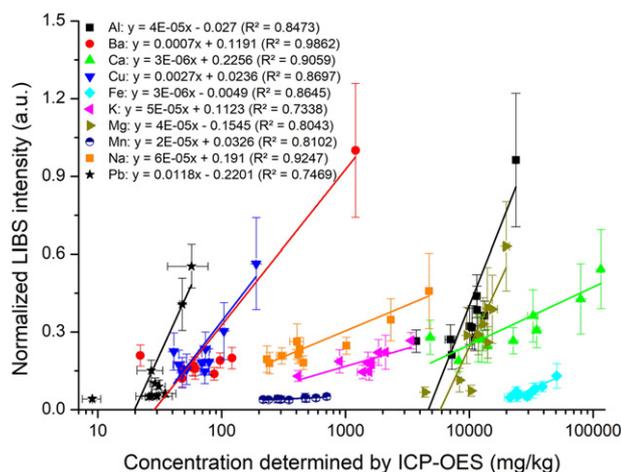


Fig. 7. Comparison of LIBS and ICP–OES data for arctic soils.

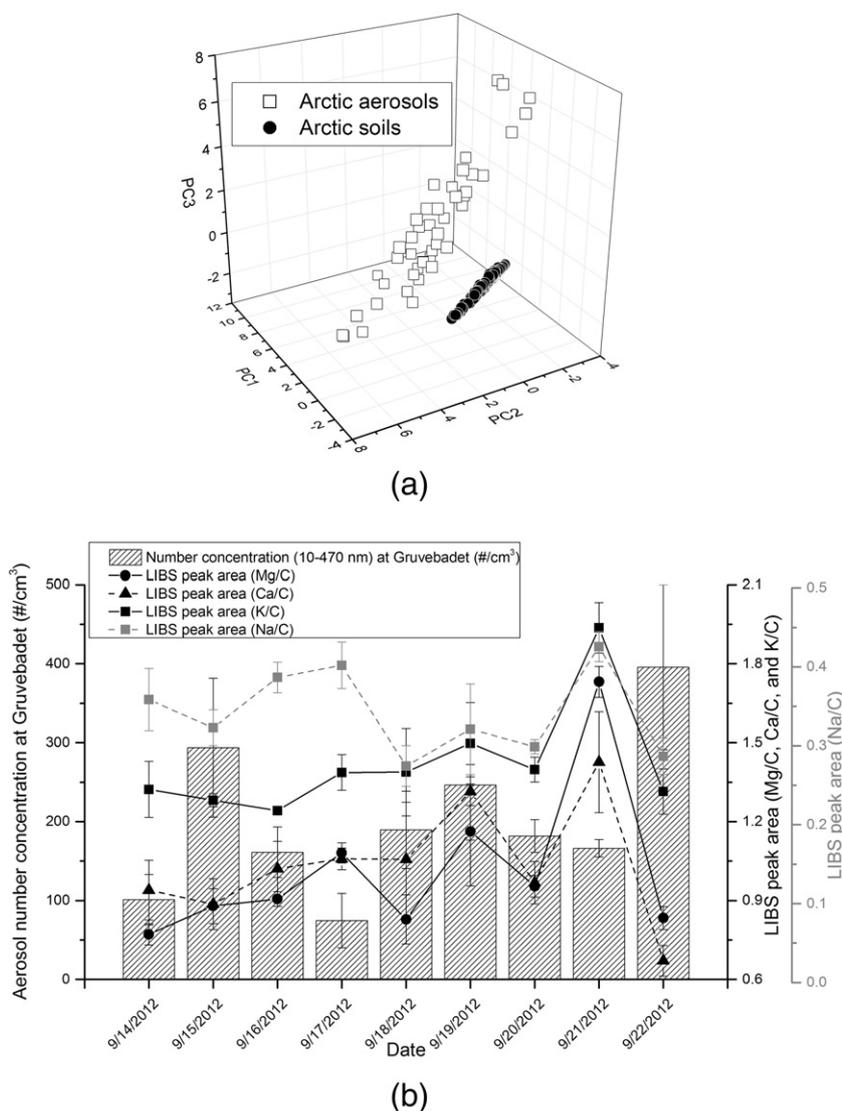


Fig. 8. (a) Scatter plot of three PCs for arctic soils and aerosols, and (b) daily variation of elements normalized by C in aerosols and particle number concentration (10–470 nm).

samples differed from arctic soil samples due to natural differences in geological environments and anthropogenic effects. The soil sample from the abandoned mining site has the largest difference from the arctic soil samples. This occurred because concentrations of heavy metals (Cu = 319 mg/kg and Pb = 1593 mg/kg) are extremely high in the abandoned mining soils and because there are different geological soil properties between the two locations.

LIBS spectral data for arctic soils were further analyzed by chemometrics to classify the samples. The reduction of class information (number of sampling locations) was necessary for further chemometric analysis. Soil samples from the town (A), road (D), plain area (F), seashore (H), and airport (J) locations (5 each) were selected for chemometric analyses. Fig. 6a illustrates the scatter plots for the three major principal components (PCs) (PC1, PC2, and PC3) of the soil samples. As illustrated in Fig. 6, the soil sample from the airport (J) had the most distinct elemental distribution. When the ratios of heavy metals to the reference element (Fe) [54] were compared, the ratio of Cu to Fe was determined to be the highest at the airport site.

Concentrations of elements in soils measured with ICP–OES are presented in Table 2. ICP–OES results indicate that the Cu concentration at the airport site (J) was much higher than those at the other sites, which is consistent with the LIBS results. To estimate the anthropogenic effects on elements in soils, enrichment factors (EFs) for Cu and Pb were calculated using the ICP–OES data. Fe was used as a reference element [54].

Five categories, suggested by Sutherland [55], can be determined based on the EF values, as presented in Fig. 6b. The EF of Cu at the airport site (J) was the highest (9). The EF of Pb for all sites was less than 3. With the exception of the airport samples, the concentration of Cu in most soil samples was substantially lower than regulatory standards (Cu: 270 mg/kg and Pb: 200 mg/kg in USA [56]; Cu: 150 mg/kg and Pb: 200 mg/kg in Korea [37]). Coal mining activity that occurred in this region (1916–1963) had little effect on the present level of surface soil environments at sampling locations. Notably, soil samples from the abandoned mining site in Korea had a Cu concentration of 319 mg/kg and a Pb concentration of 1593 mg/kg. Our data suggest that only anthropogenic sources in extremely close proximity affect the elemental composition of arctic soils. Concentrations of elements measured with the ICP–OES are also compared with the LIBS response for arctic soils as shown in Fig. 7. A linear relationship was found for each element with varying correlation coefficients (0.85–0.99). However, each element had a different slope, suggesting that elements should have their own calibration curves for quantitative analysis by the LIBS.

As discussed previously, fewer elements were found in arctic aerosols than in soils; moreover, minerals and sea salts can be major constituents of aerosols. A comparison of elemental distributions in arctic soils and aerosols in a PCA score plot is displayed in Fig. 8a. The elemental distributions were clearly distinguishable, suggesting that the effect of local soils on the elemental distribution in aerosols (i.e., resuspension

of soil dust) is small. The daily variation of elements (Mg, Ca, Na, and K) in aerosols, normalized by C, is illustrated in Fig. 8b. Note that C is the dominant element in the filter, and was selected as an internal standard element whose concentration should remain to be constant [45,57]. In addition, daily average number concentration of particles with sizes from 10 to 470 nm is included. The particle number concentration (RSD = 71%) and elemental composition in aerosols (RSD = 25%) were highly variable, possibly because of the variation of air masses and meteorological conditions. The daily variation of the mineral components Mg and Ca was higher than that of Na.

4. Conclusion

Elemental composition of arctic soils and aerosols in Ny-Ålesund, Svalbard was determined by two types of LIBS systems. In soil LIBS system, drying and pelletizing of soils, and Ar gas supply were conducted for minimization of matrix effects (moisture content, soil grain size, and surrounding gas). With Ar gas supply, a significant enhancement in LIBS emission lines was observed. Elements of Al, Ba, C, Ca, Cu, Fe, H, K, Mg, Mn, N, Na, O, Pb, and Si were detected in soils sampled at 10 locations at the arctic site. The amounts of most of anthropogenic metals were low, and the elevated level of Cu was found at airport site in Ny-Ålesund, which is consistent with ICP-OES results. Distribution of elements in arctic soils was clearly different from urban and abandoned mining soils. Fewer elements (C, Ca, H, K, Mg, Na, and O) were found in arctic aerosols than in soils. Minerals and sea salts were thought to be major constituents of aerosols. Difference in elemental distribution in aerosols from that in soils suggests that the resuspension of local soil particles by wind erosion into aerosols should be minimal. Daily number concentrations of aerosols and their elements varied substantially which could be affected by varying air masses and meteorological conditions.

Acknowledgments

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