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著者	Tazaki Kazue, Wakimoto Rie, Minami Yukiya, Yamamoto Masayoshi, Miyata Koshirou, Sato Kazuhiro, Saji Ichiro, Chaerun S. Khodijah, Zhou Guoping, Morishita Tomoaki, Asada Ryuji, Segawa Hiromi, Imanishi Hiroki, Kato Rie, Otani Yusuke, Watanabe Tomoko
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TRANSPORT OF CARBON-BEARING DUSTS FROM IRAQ TO JAPAN DURING IRAQ'S WAR

Kazue Tazaki[1], Rie Wakimoto[1], Yukiya Minami[2], Masayoshi Yamamoto[3], Koshirou Miyata[1], Kazuhiro Sato[1], Ichiro Saji[1], S. Khodijah Chaerun[1], Guoping Zhou[1], Tomoaki Morishita[1], Ryuji Asada[1], Hiromi Segawa[1], Hiroki Imanishi[1], Rie Kato[1], Yusuke Otani[1], Tomoko Watanabe[1]

[1] Faculty of Science, Kanazawa University, Kakuma, Kanazawa, Ishikawa, 920-1192 Japan

E-mail: kazuet@kenroku.kanazawa-u.ac.jp

[2] Department of Agricultural Science, Ishikawa Agricultural College, Nonoichi, Ishikawa, 921-8836 Japan

[3] LLRL, K-INET, Kanazawa University, Tatsunokuchi, Ishikawa, 923-1224 Japan

Abstract- Rainwater collected during the period of February to April, 2003, at Kanazawa University, the Japan Sea Coast, was investigated by Ion chromatography for the dissolved ions. The filtered samples were evaluated by various kinds of

micro-techniques. The pH, Eh, electrical conductivity (EC), dissolved oxygen (DO), and depleted U (DU) of the rainwater were also measured. The results showed a rare case with low pH and high EC values of rainwater. The NO_3^-, SO_4^{2-}, and NH_4^+ concentrations of rainwater collected on 26th March 2003, showed quite high values after oil field fires in Iraq on 21st March 2003. The powdery dust and carbon-bearing nm sized particles contained in rainwater had characteristics different from the Asian dust (Kosa).

Since the Iraq plunged into the war on 21st March 2003, nine oil field fires were reported in the Rumaylah oil field near the borderline of Kuwait on 25th March 2003. The first precipitation was caught in Kanazawa on 24th March 2003. The pH value of rainwater indicated a strong acid rain (pH 3.6) with black powdery dusts. The acid rain (pH 3.4 - 4.3; 5-17mm) associated with WNW wind (2.7-4.1 m/s) started to fall from 27th March to 2nd April and continued to the first ten days of April in Kanazawa. The EC of rainwater collected from 24th March to 15th April 2003, showed high concentrations of ions, suggesting high contents of water soluble-carbon particles and soot. In the meantime, it was the highest season of sandstorms at bare dried land in Iraq from the end of March to the beginning of April. The westerly wind blew around 5500m high, and the sandstorm with 2000m wide was transported by strong wind to Zagros 3000m

high mountains and easily joined and rose to westerly wind high by a rising air current. The $^{234}U/^{238}U$ activity (around 0.2) in typical depleted uranium (DU) was quite low compared with that (around 1.0) in natural uranium. The powdery dusts and carbon-bearing particles of rainwater were produced by combustion of oil fields in Iraq and they directly cycled in our planet by westerly wind. The results remind us of the scientific values of short-term atmospheric environment records during the Iraq War. This has consequences for primary production of powdery dusts coming from Iraq to the atmosphere over half the globe away.

Key word index: the Iraq War, oil field, soot, acid rain, westerly wind, transportation, high EC, SO_4^{2-}, NO_3^-, NH_4^+, the Japan Sea Coast.

1. INTRODUCTION

Local atmosphere reflects major or minor influences of world environment, as we remember the Gulf War in 1991. More than 700 oil field fires had produced a tremendous amount of carbon soot from Kuwait to the world. On 20th – 25th February

1991, we caught black snow for a week at Matsue, Shimane, the Japanese Sea Coast (Tazaki et al., 1992). It used to take 8 months to recover the fired environment in Kuwait. Again, it happened before forgetting the Gulf War. Since the Iraq plunged into the war on 21st March 2003, nine oil field fires were reported in the Rumaylah oil field near the borderline of Kuwait on 25th March 2003. Some of the oil fields in Mosul, Kirkuk, and Basrah, continuously caused fires afterwards.

In this paper, we reported a short-range transport of carbon-bearing nm-sized particles in powdery dusts and strong acid precipitation during the Iraq War. The powdery dusts were quite different from chemical composition and size distribution of Asian dust (Kosa) aerosol during long-term variation of atmospheric environment (Zhou et al., 1996; Mori et al., 2002 and 2003).

2. MATERIAL AND METHODS

2.1 Sample collection sites

Rainwater was collected daily from the 10 litter beakers on the tray put on the roof (2 m from green grass ground level) of the hut at Kanazawa University, Kakuma, Kanazawa, Ishikawa Prefecture, located on the Japan Sea Side. The rainwater samples were also collected at Hakui, about 10 km SW from Kanazawa University. The polypropylene cylindrical container, 115 mm in diameter and 2 m in height, was used to collect rainwater for ion chromatography analysis at Hakui. Both sampling sites are about 6-10 km from the Japan Sea. Kanazawa city has a population of approximately 450,000. Compared with most big cities on the Pacific Ocean coast of Japan, Kanazawa city has a few pollution sources.

For comparison, rainwater was also collected in Kawabe, Wakayama Prefecture, located on the Pacific Ocean coast of Japan. Kawabe town is a small country site which has a few pollution sources as well.

2.2 Analysis of rainwater

The beakers on the tray were changed every rain event, and the pH, Eh, Electrical Conductivity (EC), dissolved oxygen (DO), and temperature of rainwater were immediately measured using a Twin Cont pH meter (HORIBA). The depleted Uranium (DU) concentration in the rainwater was measured. The dissolved constituents were quantitatively analyzed by ion chromatography, and were calculated by the weight and the concentration of ions.

2.3 Analysis of filtered matters from the rainwater

The rainwater was filtered with a cellulose acetate membrane filter (0.2 mm pore size) using an aspirator. Solid bulk materials left behind after filtration were analyzed under dry condition for mineral composition, micro morphology, and chemistry. The filtered dry samples was cut from each filter, attached to a glass slide, and measured by X-ray powder diffraction (XRD) using a Rigaku, Rint 1200 system X-ray diffract meter with CuKα radiation. Elemental concentration measurement was conducted using energy dispersive X-ray analyzer (EDX; Philips-EDAX PV9800STD) attached to a JEOL-JSM-5200LV scanning electron microscope (SEM).

Carbon concentration measurement and carbon elementary content map of the filter were conducted using electron probe micro analyzer (EPMA: JEOL JXA 8800R Super Probe) at an accelerating voltage of 15 kV. The bulk carbon spherical soot was observed by a JEOL JEM 2000EX transmission electron microscope (TEM).

The 500 mb and 5520-5700 m meteorological maps of westerly wind, indicating the transport systems of dusts from 24^{th} March to 5^{th} April 2003, in both Iraq and Japan Honshu Islands, were provided by Kanazawa meteorological station in Kanazawa, Ishikawa Prefecture, Japan. The trajectory analysis of westerly wind supported evidence of the collected rainwater samples in Japan, which were transported from Iraq to Japan.

2.4 Analysis of DU in rainwater

The rainfall together with dusts collected at two stations (Kanazawa, Ishikawa Prefecture and Kawabe, Wakayama Prefecture) were combined each other, and each composite sample was evaporated to dryness by heating, with an addition of a known amount of ^{232}U as a yield tracer. The purified U and its α-activities were measured by a surface barrier Si detector (Tennelec TC256 spectrometer coupled with a 1K channel pulse height analyzer, Seiko EG % G Model 7800) for 5-10 days (Yamamoto, 1992).

3. RESULTS AND DISCUSSION

3.1 Characteristics of the rainwater

The period of rainwater collection in Hakui, Kanazawa, Japan, from February to April 2003, is given in Table 1. The quantity of rainwater, its pH, EC, and water temperature (WT) indicated a rare case, showing high EC and low pH values, after the Iraq War started and the oil wells were on fire on 21st March 2003. Moreover, concentration of dissolved ions in the rainwater was quite different from usual values, such as NO_2^-, SO_4^{2-}, and NH_4^+ (Table 2). The total cations and anions were related to the acidity. It was clear that concentrations of NO_2^-, SO_4^{2-}, and NH_4^+ of rainwater collected on 26th

March 2003 were 3-7 times higher than the average before and after Iraq's War (Fig. 1). We collected black rainwater in Kanazawa on 31st March and 1st April 2003 as filtered rainwater at 15:00 and 10:30 on those days, respectively (Fig. 3).

The pH, EC, Eh, and DO of rainwater collected at Kanazawa University during the period of 24th March to 12th April 2003, were measured. The pH of rainwater during this period changed from 3.4 to 6.2 with a characteristic of pH of 7 out of 13 rainfalls being lower than 4. It was noticed that the rainfalls with pH lower than 4 almost occurred during the period of 24th March to 4th April (Table 3).

The EC of the rainwater changed from 9.2 μS/cm to 360 μS /cm, and a high EC concentration of rainwater particularly occurred during the period of 24th March to 2nd April. The highest EC concentration (360 μS /cm) occurred in the rainfall of 1st April with a pH value of 3.6 (Table 2), indicating that a lot of water soluble materials dissolved in the rainwater. The Fig. 2 showed a relationship between pH and EC of the rainwater during the period of 24th March to 5th April. Rainwater with low pH was generally consistent with high EC concentration, suggesting that water soluble materials which dissolved in the rainwater were responsible for the low pH of the rainwater.

The first precipitation was caught at Kanazawa University on 24th March 2003. The result revealed a strong acid precipitation of the rainwater as indicated by pH of 3.6 with black powdery dusts. The acid rain (pH 3.4 - 4.3; 5-23 mm) associated with WNW wind (16.0 m/s) continued to the first ten days of April at Kanazawa University during the 9 oil field fires in Iraq. The EC of rainwater also showed high concentrations. In the meantime, it was the highest season of sandstorms at bare dried land in Iraq from the end of March to the beginning of April. During the oil well fires, the Eh and DO values were about 300 mV and 11-12 mg/l, respectively, showing relatively higher values than that of normal periods (260 mV and below 10 mg/l).

The wind speed of sandstorm was usually over 7 m/s within a given period of the end of February and July in Iraq. The sandstorm with strong hot westerly wind was the worst period on 25th March 2003. It was reported that the visibility was only 100 m in Persian Gulf, and 2 days later the atmosphere in Iraq got clearer (Chamot, 2003).

During Iraq's war operations at that time, munitions containing depleted uranium (DU) were used by US force at a number of sites in Iraq. To check whether DU, as well as Aeolian dust, were transported from this conflict area to distant Japan or not, we also attempted to analyze uranium by using the above mentioned precipitation samples. The concentrations of ^{238}U in the samples collected at Kanazawa University (total volume: 14.58 L) and Kawabe town, Wakayama Prefecture (5.27 L) were found to be 0.12±0.01 and 0.26±0.02 mBq/L, respectively. The activity ratios of $^{234}U/^{238}U$ and $^{235}U/^{238}U$ were

1.16±0.05 and 0.040±0.006 for the sample in Kawabe town, and 1.25±0.08 and 0.050±0.011 for the sample at Kanazawa University. The contamination of DU from the conflict of Iraq might be, if any, negligibly small on undetectable level.

3.2 Characteristics of filtered materials from the rainwater

(1) Carbon particles

Rainwater collected at Kanazawa University during the period of 24th March to 12th April was filtered with the 0.2 mm membrane filters for the analysis of SEM-EDX, TEM, EPMA, and XRD. The membrane filters showed a very black color with a low pH of the rainwater during the starting days of the rainfalls, for example, the 24th, 27th, 29th, and 31st of March and 1st of April, suggesting that the rainwater or cloud contained a lot of carbon-bearing particles and water soluble materials at the first days of rainfalls (Fig. 3). According to the analysis of the filter for rainwater collected 24th March, 1st April, and 8th April 2003, the black color of the filter resulted from a large quantity of carbon-bearing particles with a nm size which was composed of carbon films of 99 wt% and sulfur species about 1 wt% as shown by the carbon content mapping of EPMA (Fig. 4). The rainwater collected on 1st April 2003 showed low pH values of 3.4-3.6 and high EC concentration of 360 μS /cm, indicating that the water-soluble materials resulted in the acidity of the rainwater. The XRD analysis of the carbon-bearing particles, collected on 24th March, 1st April, and 8th April 2003, indicated mainly amorphous materials without any carbonate minerals (Fig. 5). The EPMA pattern indicated chemical composition of filtered dusts that contained large amounts of C, O, Si, Al, K, and Fe (Fig. 6). The Au peak was due to coating materials. The carbon in the strong acidic rainwater was mostly organic carbon because of no crystalline carbonate minerals in it.

It has been reported that an essential part of the total carbon (TC) consists of compounds soluble in water. The water-soluble carbon compounds appear to accumulate as particles with diameters between 0.18–0.68 μm. However, ultra-fine carbon particles are also substantially composed of water-soluble species. One can speculate that water soluble carbon particles play a role in fog and cloud formation (Temesi et al, 2003; Robert et al., 2002). It has also been revealed that the water-soluble organic compounds in soot samples are produced from oxidation of soot particles at Kanazawa University. The concentration of water-soluble carbon compounds also varies by season with rain in warm season (April–September) having somewhat higher concentrations relative to winter rain events (October–March). Concentrations of water soluble carbon compounds in rainwater are also influenced by storm origin with maritime events having significantly lower levels relative to terrestrially influenced storms (Kim et al., 1999; Kim et al., 2000). In the case of the rainwater during the 24th March to the first ten days of April at Kanazawa University, high concentration of nm-sized carbon-bearing particles and low pH suggested that the sandstorm had a relatively low affection to the components of the rainwater. The high concentration of carbon-bearing particles might be related to the combustion of Iraq oil field and they formed as cloud condensation nuclei and were transported by wind (Novakov and Penner, 1993; Blando and Turpin, 2000). The NO_3^-, SO_4^{2-}, and NH_4^+ concentrations of rainwater collected on 26th March 2003 showed quite high values after oil field fires on 21st March 2003, which supported the events.

(2) Powdery dusts

With respect to the high concentration of carbon-bearing particles, some non-carbon particles with size between 1 and 10 μm were observed (Fig. 7). EPMA and EDX analyses showed that these spherules were mainly composed of Si or Si-Al (Fig. 6, Fig. 7). At the same time, XRD analysis showed an amorphous refraction without quarts, feldspar, and calcite peaks, suggesting that these spherules (glass or mullite), a characteristic of fly ashes, resulted from combustion (Fig. 5). It was noted that Cl and Ca elements in powdery dusts were not detected. These two components were common in the Asian dust (Kosa; yellow sand) particles (Chang et al., 2001; Fang et al., 2001; Seto et al., 2002; Terada et al., 2002; Kim et al., 2002).

Compared with the Asian dust, the powdery dust from the rainwater had a different characteristic, containing no Ca and other soil elements such as Fe and Al (Mori et al., 2002, 2003). The estimated concentration of Al in Kosa source aerosol was 5.3 x 10^3 µg m^{-3} and the aerosol mass concentration was 9.0 x 10^4 µg m-^{3}. The concentrations dropped by one order of magnitude as the dust was transported from the interior of China to Japan. The Al concentration in the size-separated coarse particles was larger than 2.1 µm in aerodynamic diameter. The mass size distribution for the aerosol collected at Yamaguchi during the dust event had two peaks, one at 0.43-0.65 µm and the other at 3.3-4.7 µm. Dust storm particles over China and Japan had different shape and composition. Dust particles over China had irregular shape and mainly contained crustal elements (Zhou et al., 1996).

In this study, SEM and TEM analyses showed that most of the nm-sized powdery dusts had diameters many times smaller than a coarse particle grain, suggesting that they were very readily transported with air currents and long-range transported with the windy clouds. This was also similar to an aerosol that was observed during the previous oil fired dust event in Gulf War in February 1991 (Tazaki et al., 1991).

(3) Sulfur-bearing particles, minerals and aerosol dusts of the Middle East Region

Some sulfur-bearing particles of filtered matters of the rainwater were detected by EDX analysis (Fig. 7 C and D). S-bearing particles showed irregular forms, and contained the main Si, Al components with a small amount of K, Ca, Fe components besides sulfur, suggesting that these S-bearing particles were mainly soil particles with coating of sulfur (Fig. 7D). Transmission electron microscopic analysis revealed that the surface of fly ashes and some spherical particles were mainly covered with the sub-micron sized sulfur matters (Fig. 8). It has been known that emissions from combustion of oil and coal contain a lot of sulfur and carbon soot that are easily absorbed by soil particles during a long-range transportation (Friedlander, 1978; Kleefeld et al., 2002).

Detailed mineralogical investigations of dust fallout deposits collected at eleven locations in Kuwait have been reported by Khalaf et al. (1979, 1985). The dust fallout deposited in Kuwait is quartzitic calcareous sandy silt (dolomite, gypsum) and is mostly derived from the dry Mesopotamian flood plain in the middle and south of Iraq. The occurrence of sand-size particles is attributed to acquirement from local recent surface deposits.

It has been reported that both annual cycle-amplitudes and effects of precipitation amounts are significant for the four ions at almost all sites. The maximum concentrations of nss-SO_4^{2-} and -Ca^{2+} occurred from winter to spring at most sites during the period of Asian dust (Seto et al., 2002). The comparative analyses generally suggest that Asian dust events are prominent sources for major crust components in the fine particle fraction of PM which includes many soil minerals such as quarts, feldspar, calcite, and some iron minerals.

It has been known that mass concentration in Asian dust–storm events was roughly 3–5 times higher than that of the highest concentration measured in non-Asian dust storm seasons. Single particles were generally sharp-edged and irregular in shape and mostly contained crustal elements such as Si, Fe, Ca, and Al (Zhou et al., 1996). During the dust storm in Beijing, aerosol concentrations were one or two orders of magnitude larger than typical one. The enrichment factors of pollution elements during the dust storm were distinctly less than those before and after dust storm. Particles had more than 40% Si content that constituted nearly 50% of the coarse single particles in Asian dust storm events. X-ray spectrometry also showed a pronounced increase in the relative abundance of Al, Fe, Ca, S, and Cl in the Asian dust samples if compared with the non-Asian dust event samples. The high abundance of Cl in the dust samples suggested that the aerosols experienced long-range transport by way of the sea. In this study, these results might reveal that the powdery dusts with carbon-bearing particles and sulfur-bearing particles derived from the Middle and Near East by westerly wind.

3.3 Meteorological data during Iraq's War

Since 1984 Department of Environmental Science, Ishikawa Research Laboratory for Public Health and Environment has been observing the acid precipitation for 20 years. The average pH value of each precipitation was constantly 4.5 – 4.6 every year. On rare occasions, the rainwater indicated strong acidic pH of 3.86 (EC 4.3 μS/cm) in January and pH 3.55 (EC 3.7 μS/cm) in July 1996. For 20 years in Kanazawa (the Japan Sea Coast), such a strong acid rain seldom occurred only in winter (November and December) and summer (July and August) (Kitamura, 1989). The common average pH in March 2001 was 4.7 (EC 40 μS/cm), whereas pH 4.4 (EC 40 μS/cm) occurred in Kanazawa in April. The averages of precipitation at Kanazawa University area in 2002 were as follows; precipitation 2,828 mm, pH 4.52, EC 39.0 μS/cm, SO_4^{2-} 27.3 μmol/L, NO_3^- 18.2 μmol/L, and NH_4^+ 20.6 μmol/L.

In this study, it was the first case that low pH values (3.4 – 3.5) and high concentration of EC (360 μS/cm) in the rainwater were detected at Kanazawa

University on 1st April 2003. The strong acidic rain associated with high EC concentration suggested a large quantity of water-soluble materials in it. The SO_4^{2-}, NO_3^-, and NH_4^+ of rainwater collected on 26th March 2003 were 3-5 times higher than the average in 2002. In the meantime, yellow sand did not arrive in Kanazawa from China, based on the weather map and visibility. If yellow sand arrived in Kanazawa, the pH of rainwater increased to 7-8, because calcium contents that derived from desert soils got higher (Terada et al., 2002).

Our AMeDAS (Automated Meteorological Data Acquisition System) weather data in the Kakuma Campus of Kanazawa University associated with the meteorological maps in Kanazawa local weather observatory suggested that the acid rain with carbon-bearing particles might derive from the burning of oil wells in Iraq.

3.4 Sandstorm in Iraq

The storm was captured in a series of images taken by NASA Satellite and predicted by a computer model run by the Air Force. The storm hit its peak, with snow and rain in the north and gale-driven grit blasting along a 300-mile-wide front in southern Iraq on 26th March 2003. Sandstorms periodically attacked to Iraq every week-cycle from SW bare dried land in April. The hot wind (over 7m/s) carried on fine particles (< 0.04 mm in diameter), and blew hard to 1000-2000 m high with clouds of smoke. The sight was enveloped by smoke, and the visibility was sometimes only below 1 m (Revkin, 2003). The highest temperature was 20 ^{o}C in Baghdad and 25 ^{o}C in Kuwait on 29th March under the hot sandstorms (Fig. 9). The rising heat would be the main natural antagonist with daytime temperatures on 27th March throughout the weekend reaching the 90's around Baghdad and topping 100 degrees in the South.

According to the report from Christina Reed (Geotimes May 2003), nine oil well fires burning in Southern Rumaylah blasted flames sometimes 60 m into the air, accompanied by thick black smoke that was caught on satellite images. Smoke plumes from the Greater Burgan oil field south of Kuwait City rose 500 m at their base, high above the workers in the oil field itself. After reaching that height, the plumes created a thick smoke layer, which was capped at 3 km in height by a very strong, and prominent, temperature inversion. The smoke plume was perhaps 50 km in width on any given day, and 2.5 km thick, and looked, from satellite, like a black snake in the desert that blew parallel to the Persian Gulf. Josh Chamot (Geotimes May 2003) also reported that Southwest Iraq was dominated by a dusty desert, as opposed to the coarser and sometimes rocky materials of Saudi Arabia and some of the other regions in the Middle East. The fine sediment is easily caught up by the storm fronts. Transportation of fine-grained particles in suspension frequently occurs during dust storms and usually initiates in Southern Iraq. The particles migrate over Kuwait as thick dust clouds and finally settle in the Northern part of Arabian Gulf (Khalof and Al-Ajimi, 1993).

The most dramatic are the sandstorms, walls of dust and debris moving across the desert and through cities. Every three to five days, a frontal system breaks away from the Mediterranean air mass and travels east. The storms bring rain to the mountains of Turkey and Iran, while the lower elevations of Jordan, Iraq, and northern Saudi Arabia are hit with a dry wind dominated by the Saharan air. Winds are especially severe in March and April as the ground warms, creating more convection and instability, and producing thunderstorms with extremely strong winds. After the systems reach the Persian Gulf, the dust can drop out and the air may pick up moisture, producing thundershowers that often have much lightning, but little rain. In studies of the transport of sandstorms with wind current, geographical features can also be important, with potentially global effects (Khalaf and Al-Ajmi, 1993).

3.5 Westerly wind transportation system

The hot wind blow up to 2000 m high by an up current of air, and joined the westerly wind to transport powdery dusts. The 500 mb and 5520-5700 m meteorological maps of westerly wind indicated the transport systems of dusts from 24^{th} March to 5^{th} April 2003 (Fig. 9). The upper current of air map confirmed that the 5520-5700 m lines crossed over and spread on both Iraq and Japan Honshu Island. The lines on 28^{th} March moved up to the North, whereas the lines on 30^{th} March and 1^{st} April spread over Kanazawa. On the other hand, the line on 3^{rd} April did not cross over on Iraq anymore, suggesting that the powdery dusts were influenced by an air current within 4 days.

The westerly wind transportation system from Iraq to Japan was as follows;

Middle latitude westerly wind; 500mb at height of 5000m; Temperature of Jet current, –20 - -30 ^{o} C.

Kanazawa University (36^{o}40’ North latitude); Temp. 6.1-12.0 ^{o}C, wind direction E – S, Wind Velocity 16.0 m/s on 27^{th} –31^{st} March (Table 3). Air condition at 500 mb and wind speed about 100 m/s.

It takes 1-4 days for the dust to come by air from Iraq to Japan. The black rain that came down in Kanazawa with WNW wind on 24-26^{th} March 2003 was a quite possible (Table 3, Fig. 10).

3.6 Influence of Asian dust (yellow sand) from China

A continuous automatic measurement of meteorological elements has been started at

Kakuma Campus of Kanazawa University since 2nd July 1998. From then on, we have obtained the following data every 10 minutes: wind direction, wind speed, temperature, relative-humidity, depth of snow cover, sunshine direction, amount of precipitation and station pressure. On the Japan Sea side, acid precipitation with pH ranging between 4-5 prevails in winter and it has been revealed that acid precipitation is mainly caused by a high concentration of $SO_4{}^{2-}$ in atmosphere in the Japan Sea Coast. However, during spring, yellow sand particles are frequently transported from the Asian desert areas to the Islands of Japan (Zhou and Tazaki, 1996a). Results from X-ray spectrometry showed a pronounced increase in the relative abundance of Al, Fe, Ca, S, and Cl in the dust samples compared to the non-Asian dust samples (Chang et al., 2001). The high abundance of Cl in the dust samples suggested that the aerosols experienced long-range transport by way of the sea (Fang et al., 2001). For the sample with high yellow sand flux, a high pH correlated to a low EC, suggesting that ion balance was apparently in the side of cations, and the sample also showed relatively large neutralization ability. This might be related to the content of calcite and gypsum contained in the sample (Zhou and Tazaki, 1996b). Solutions of the aerosols that immersed in distilled water gave an average pH of 6.8 for winter samples, 7.2 for spring samples, 6.7 for summer samples, and 6.9 for autumn samples. This suggested that aerosols in spring contained more alkaline materials or carbonate minerals than those in other seasons (Zhou and Tazaki, 1996 a).

It was clear that the low pH of rainwater and high concentration of carbon-bearing particles collected in Kanazawa during the period of 24^{th} March to the first ten days of April had different characteristics from that of Asian dust. On the other hand, the sandstorm occurred within Iraq War at the end of March to the beginning of April in Iraq. Westerly wind carries on powdery dusts with strong acid rain from Iraq to the Japan Sea Coast. Generally, in March and April, the Japan Sea Coast area has a high yellow sand flux from China, so that pH of precipitation should be high. However, at the end of March and the beginning of April 2003, we had a strong acid rain in Kanazawa, Japan. The Kanazawa local weather observatory stated that the sandstorm did not yet occur at Chinese deserts (Taklimakan and Gobi) on 28^{th} March 2003, suggesting that the powdery dusts absolutely came from the sandstorm in Iraq of the Middle East, based on the weather map of upper air current in association with the visibility. However, rough calculations suggested that westerly wind blew about 8000 km/day between 7900 km in distance of Iraq and Japan, and it should transport within 1-4 days. We could catch powdery dusts with carbon soot and nm sized Si-Al spherules with high SO_4^{2-}, NO_3^-, and NH_4^+ in strong acid rain in Kanazawa, Japan, at the end of

March to the beginning of April 2003.

5. CONCLUSION

The conclusions obtained from the study of the pH, EC, and dissolved ions of the rainwater collected during the period of 24th March to the first ten days of April 2003 in Kanazawa, Ishikawa Prefecture were as follows:

(1) A low pH value and high EC concentration of the rainwater, and dissolved ions in the rainwater in Kanazawa during the spring showed a rare case, suggesting no evidence for the local or the Asian dust affection.

(2) High concentration of nm sized carbon-bearing particles and powdery dusts only with Si and Si-Al components showed the characteristics different from that of Asian dust.

(3) Based on the weather map, rough calculations suggested that westerly wind blew about 8000 km/day between 7900 km in distance of Iraq and Japan, and it should transport within 1-4 days. We could catch powdery dusts with carbon soot and Si-Al spherules in strong acid rain in Kanazawa, Japan.

(4) The contamination of depleted Uranium (DU) from the Iraq's War might be, if any,

negligibly small on undetectable level.

The results remind us of the scientific values of short-term atmospheric environment records during Iraq's War. This has consequences for primary production of powdery dusts coming from Iraq to the atmosphere over half the globe away.

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Captions

Fig. 1. Concentration of dissolved ions in rainwater vs. quantity of precipitation collected from Hakui, Ishikawa Prefecture, showing high SO_4^{2-}, NO_3^-, and NH_4^+ on 26th March 2003, just after the start of Iraq's War.

Fig. 2. The pH and EC changes in acid rain with pHs of 3.4 - 4.4, since the Iraq War started on 21st March 2003, the Japan Sea Coast had the first rain on 24th March (pH 3.6), and a continuous acid rainfall for a week (pH 3.4 - 4.4) with carbon soot and melted Si-Al spherules glass, associated with a high electrical conductivity (360 µS/cm). The pH and EC of rainwater collected in Kanazawa are contrary interrelated, indicating a large amount of ions present in the acid rain.

Fig. 3. The precipitation materials of filtered acid rainwater collected in Kanazawa since Iraq' War started on 21st March 2003, showed grayish blown and black in color, suggesting the existence of a large amount of soot and minerals.

Fig. 4. EPMA micro morphology (A and B) and carbon content maps (A' and B') of

filtered acid rainfall (pH 3.4) indicated a high concentration carbon with nm order fine powdery dusts (white portion) in Kanazawa on the Japan Sea Coast on 1^{st} April 2003. The chemistry of the sphere indicated by an arrow in B was composed of Si-Al without carbon (black portion), suggesting the melted secondary products by fire shells in Iraq War.

Fig. 5. X-ray powder diffraction patterns of filtered acid rainwater samples collected in Kanazawa on 24^{th} – April 8^{th} March 2003. The samples are no treatments at all, showing mainly amorphous materials without any carbonate minerals or carbon minerals.

Fig. 6. EPMA analytical patterns of the powdery dusts (in Fig. 3) in Kanazawa on 1^{st} April 2003, showing high contents of Carbon (700cps) and Oxygen (12000cps) in the soot, whereas high concentration of Si (12000cps) and Al (11000cps) at the spherule (an arrow in Fig. 3B). The peak of Au is due to coating material. The Carbon peak indicated mainly amorphous organic carbon according to XRD results.

Fig. 7. Scanning electron microscopy equipped with energy dispersive analysis of the powdery dusts in Kanazawa on 1^{st} April 2003, showing few µm sized spherules. A and

B; Low magnification of general views, showing abundant spherules. C~F; Closed up micrographs of powdery dusts. The EDX data of the spherules indicate Si or Si-Al chemical compositions. Some spherules contain high S (D) and high P, S, and K (C). Traces of Ti and Fe are connected to oil soot.

Fig. 8. Transmission electron micrograph of the S-bearing aggregates of sub-micron particles coated on the surface of fly ashes (A, B, and C) and the carbon spherules (D).

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Fig. 10. Maps showing the 500 mb atmospheric pressure at 5520-5700 m high indicated the stream of West wind from 24th March (21:00) to 5th April (21:00) 2003, showing the currents cross over on both Iraq and Japan under sandstorm conditions in Iraq's War. Distance between Iraq and Japan is 7900 km, and West wind speed is about 100 m/sec. (8000 km/day), therefore the dust should transport within 1-4 days after Iraq's War started and oil field fired.

Table 1. Period of rain collection, quantity of rain water, its pH, EC and WT in Nonoichi, Ishikawa Prefecture, from Feb. to April in 2003.

Start		Finished		Period of rain collection				Quantity of rain water	Rain water		
Date	Time	Date	Time						pH	EC	WT
2003		2003		d	h	m	min	(g)		(μS/cm)	(℃)
Feb. 25	10:30	March 2	17:20	5	6	50	7610	569.4	4.7	26.4	10.6
March 2	17:20	18	16:20	15	23	0	22980	447.7	4.3	64.6	13.1
18	16:20	26	10:05	7	17	45	11145	51.0	3.9	−	−
26	10:05	29	10:15	3	0	10	4330	114.7	4.1	70.0	13.7
29	10:15	April 3	9:50	4	23	35	7175	64.2	−	−	−
April 3	9:50	6	15:55	3	6	5	4685	333.5	4.3	33.5	12.6
6	15:55	10	9:50	3	17	55	5395	183.8	4.5	44.5	16.2
10	9:50	13	10:10	3	0	20	4340	350.8	5.3	6.6	14.6
13	10:10	19	7:25	5	21	15	8475	40.1	−	−	−
19	7:25	22	8:40	3	1	15	4395	691.3	4.7	14.8	16.8
22	8:40	25	13:20	3	4	40	4600	583.8	4.5	22.8	16.7
25	13:20	29	6:25	3	17	5	5345	272.5	6.5	23.6	17.6
29	6:25	30	17:40	1	11	15	2115	284.7	5.8	18.9	18.2
30	17:40	May 6	16:40	5	23	0	8580	198.9	6.8	44.7	19.0

WT ; Water temperature

Table 2. Concentration of dissolved ions in rain water and quantity of precipitation collected from Nonoichi, Ishikawa Prefecture, from Feb. to April in 2003.

Date	Concentration of dissolved ion in rain water											
	H^+	Na^+	K^+	Ca^{2+}	Mg^{2+}	NH_4^+	Cl^-	NO_2^-	NO_3^-	SO_4^{2-}	Cation	Anion
2003	(μeq/l)										(μeq/l)	
Feb. 25	21.4	65.0	2.7	15.0	16.6	23.6	73.8	0.5	19.5	48.5	144.4	142.3
March 2	53.7	236.5	6.4	27.2	56.8	26.1	257.7	0.0	24.5	79.3	406.7	361.5
18	131.8	–	–		–	–	–	–	–	–	131.8	–
26	72.4	92.2	7.2	40.7	28.1	94.1	110.1	0.0	52.3	149.0	334.7	311.4
29	–	–	–	–	–	–	–	–	–	–	–	–
April 3	45.7	17.9	1.6	8.2	6.1	27.5	81.7	0.4	36.5	38.9	107.0	157.4
6	29.5	164.3	5.1	19.6	39.5	19.1	183.1	0.2	14.8	52.9	277.1	251.0
10	4.6	4.1	0.9	26.4	4.9	0.5	5.6	0.5	6.8	9.7	41.4	22.6
13	–	–	–	–	–	–	–	–	–	–	–	–
19	18.6	12.7	1.6	5.3	4.8	7.4	15.9	0.0	11.7	19.2	50.5	46.8
22	33.9	4.7	1.6	5.7	3.6	12.9	6.7	0.0	17.1	28.9	62.3	52.7
25	0.3	–	–	–	–	–	27.1	0.8	19.4	35.0	0.3	82.4
29	1.6	46.3	17.5	26.2	20.9	–	16.9	0.7	11.6	33.0	245.9	62.2
30	0.2	–	–	–	–	–	–	–	–	–	0.2	–

Date	Quantity of precipitation									
	Na^+	K^+	Ca^{2+}	Mg^{2+}	NH_4^+	Cl^-	NO_2^-	NO_3^-	ΣPO_4^{3-}	SO_4^{2-}
2003	(mg/m^2)									
Feb. 25	82.0	5.8	16.5	11.1	23.3	143.7	1.3	66.2	0.0	127.8
March 2	234.6	10.7	23.5	29.8	20.3	394.6	0.0	65.4	0.0	164.3
18	–	–	–	–	–	–	–	–	–	–
26	23.4	3.1	9.0	3.8	18.7	43.2	0.0	35.8	0.0	79.1
29	–	–	–	–	–	–	–	–	–	–
April 3	13.2	2.0	5.3	2.4	15.9	93.2	0.6	72.6	0.0	60.0
6	66.9	3.5	7.0	8.5	6.1	115.1	0.1	16.3	0.0	45.0
10	3.2	1.3	17.9	2.0	0.3	6.7	0.8	14.2	0.9	15.7
13	–	–	–	–	–	–	–	–	–	–
19	19.5	4.2	7.1	3.9	8.9	37.6	0.0	48.3	0.0	61.5
22	6.0	3.4	6.4	2.5	13.1	13.4	0.0	59.7	0.0	78.1
25	–	–	–			25.2	1.0	31.6	28.1	44.2
29	29.2	18.7	14.4	7.0	65.8	16.5	0.9	19.8	24.1	43.5
30	–	–	–	–	–	–	–	–	–	–

– ; not analyzed

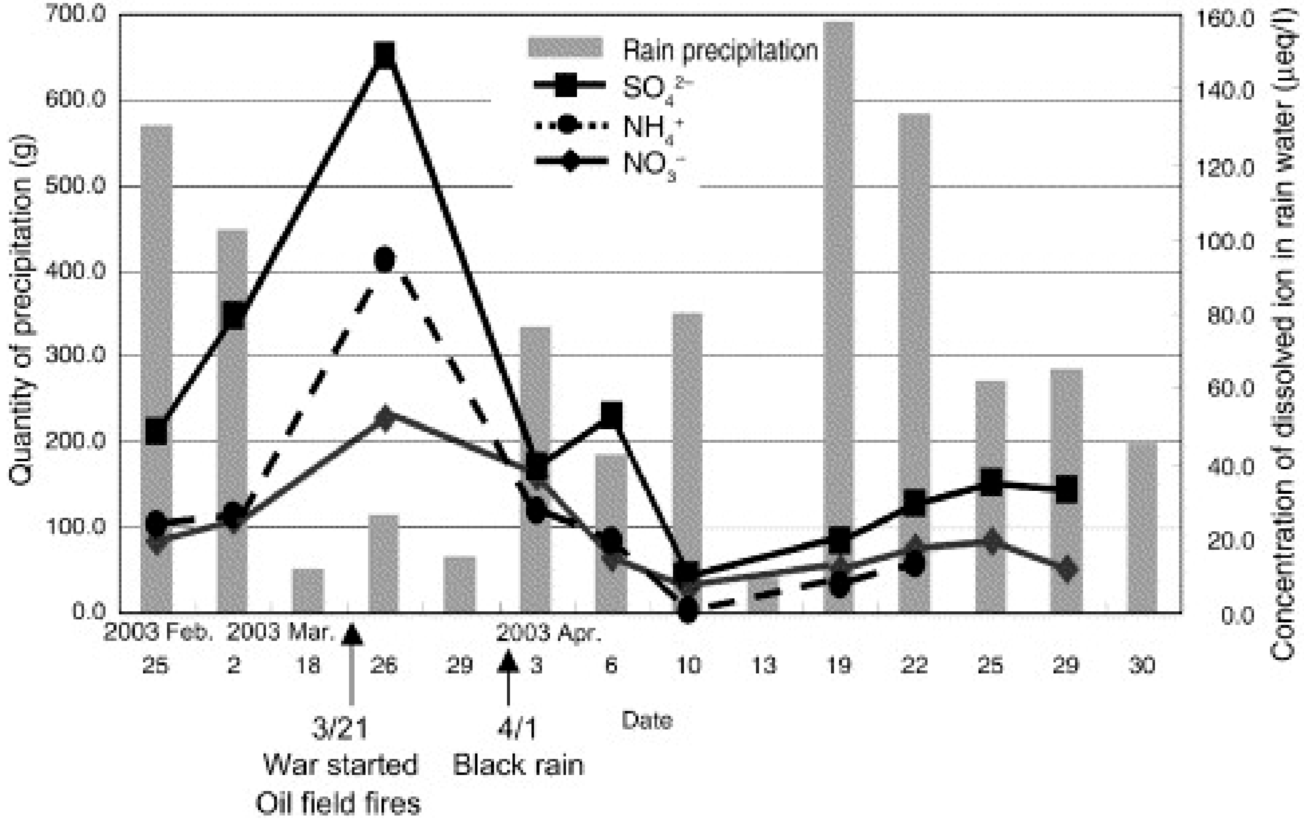

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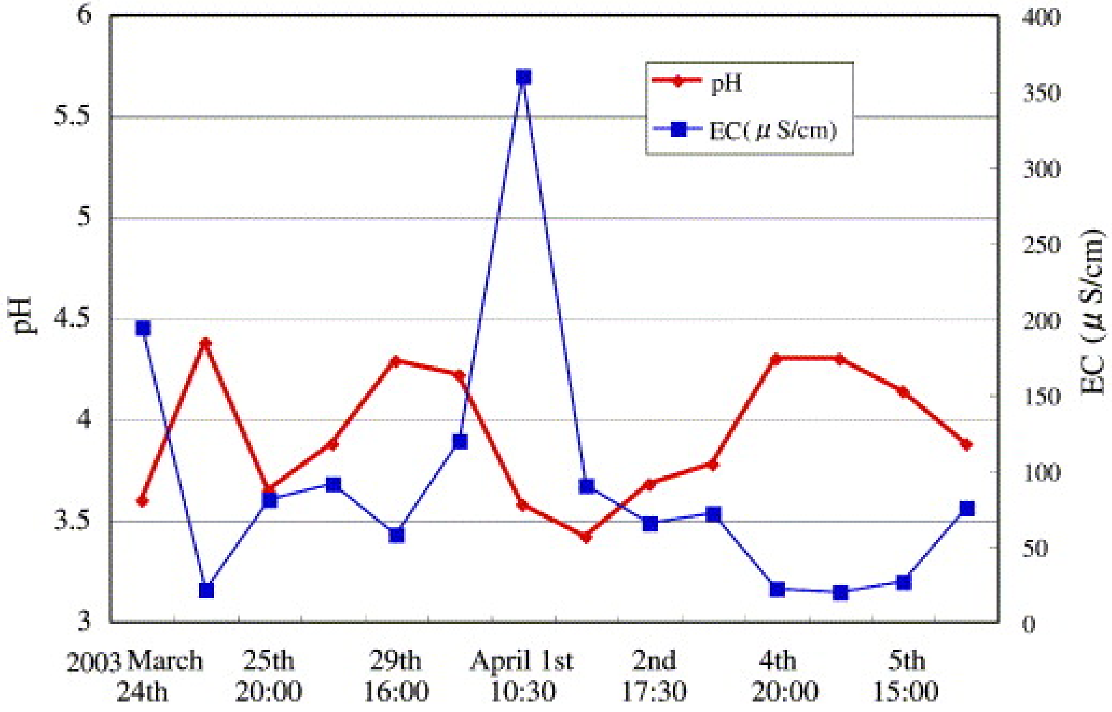
Table 3. The pH, EC, Eh, and DO changes in rain water collected in Kanazawa University, Kakuma, Ishikawa Prefecture, since Iraq War started on March 21st 2003.

Date 2003	Average Temp. ℃	Highest Temp. ℃	Lowest Temp. ℃	Wind direction	Wind velocity (m/s)	Total Precipitation (mm)	Rainwater pH	Rainwater EC (μS/cm)	Rainwater Eh (mV)	Rainwater DO (mg/l)
March 12	1.6	4.6	−0.4	NE	15.9	0.0				
13	2.6	6.8	−0.9	WNW	7.7	0.0				
14	3.3	8.6	−1.6	ESE	15.9	0.0				
15	4.8	11.5	−0.2	NE	15.9	9.0				
17	5.6	9.5	2.9	ENE	15.9	0.5				
18	4.2	8.5	0.1	NNE	16.0	0.5				
19	3.3	7.9	0.5	SSW	15.9	3.0	(3.9)	−	−	−
20	2.9	8.4	−1.5	NW	15.9	0.0				
21	3.6	9.5	−2.8	W	14.7	0.0				
22	3.8	7.4	−0.4	SE	15.9	0.0				
23	4.8	11.1	−1.0	SSW	16.0	0.0				
24	10.1	18.0	2.8	NE	16.0	5.0	3.6	194.5	331	−
25	9.6	14.0	5.2	SSE	16.0	15.0	4.4 , 3.7	21.5 , 80.9	340, 347	9.0 , 8.6
26	8.7	14.4	4.4	WNW	16.0	0.0	−	−	−	−
27	11.3	19.4	5.3	ESE	16.0	17.0	3.9	91.3	390	8.6
28	7.3	11.6	4.4	E	16.0	0.5	4.3	57.9	374	9.7
29	6.1	11.1	0.9	S	16.0	0.0	−	−	−	−
30	8.4	16.1	0.0	ENE	16.0	0.0	−	−	−	−
31	12.0	18.8	6.0	SSE	16.0	1.0	4.2	119.8	270	8.6
April 1	9.2	13.4	6.6	NE	11.5	0.5	3.6	360.0	298	9.9
2	7.5	9.1	6.6	NNE	10.3	5.0	3.4 , 3.7	90.4 , 65.5	289 , 313	11.1 , 9.3
3	9.3	13.7	6.7	NE	11.2	0.0	−	−	−	−
4	8.9	14.1	4.9	ENE	16.0	16.5	3.8 , 4.3	72.1 , 22.3	295 , 296	11.8 , 11.9
5	6.9	7.8	4.7	WNW	16.0	23.5	4.3 , 4.1 , 3.9	20.1 , 27.0 , 75.5	298 , 314 , 296	11.5 , 10.8 , 11.7
6	7.4	11.8	2.9	SE	16.0	0.0	−	−	−	−
7	12.0	19.4	4.1	NE	16.0	0.0	−	−	−	−
8	12.4	19.1	9.0	WNW	20.7	8.5	6.2	64.2	245	10.2
9	6.1	9.0	2.6	ESE	16.0	7.0	4.5 , 3.6	67.7 , 139.2	266 , 277	12.5 , 12.3
10	5.8	10.9	0.9	ENE	13.2	0.0	−	−	−	−
11	10.0	19.1	1.5	ESE	16.0	2.0	4.9	37.3	262	9.9
12	14.1	18.3	11.3	SE	16.0	23.5	6.2	9.2	266	9.3
13	12.4	16.8	6.0	SE	12.7	0.0	−	−	−	−
14	9.8	13.9	4.9	ESE	16.0	0.0	−	−	−	−



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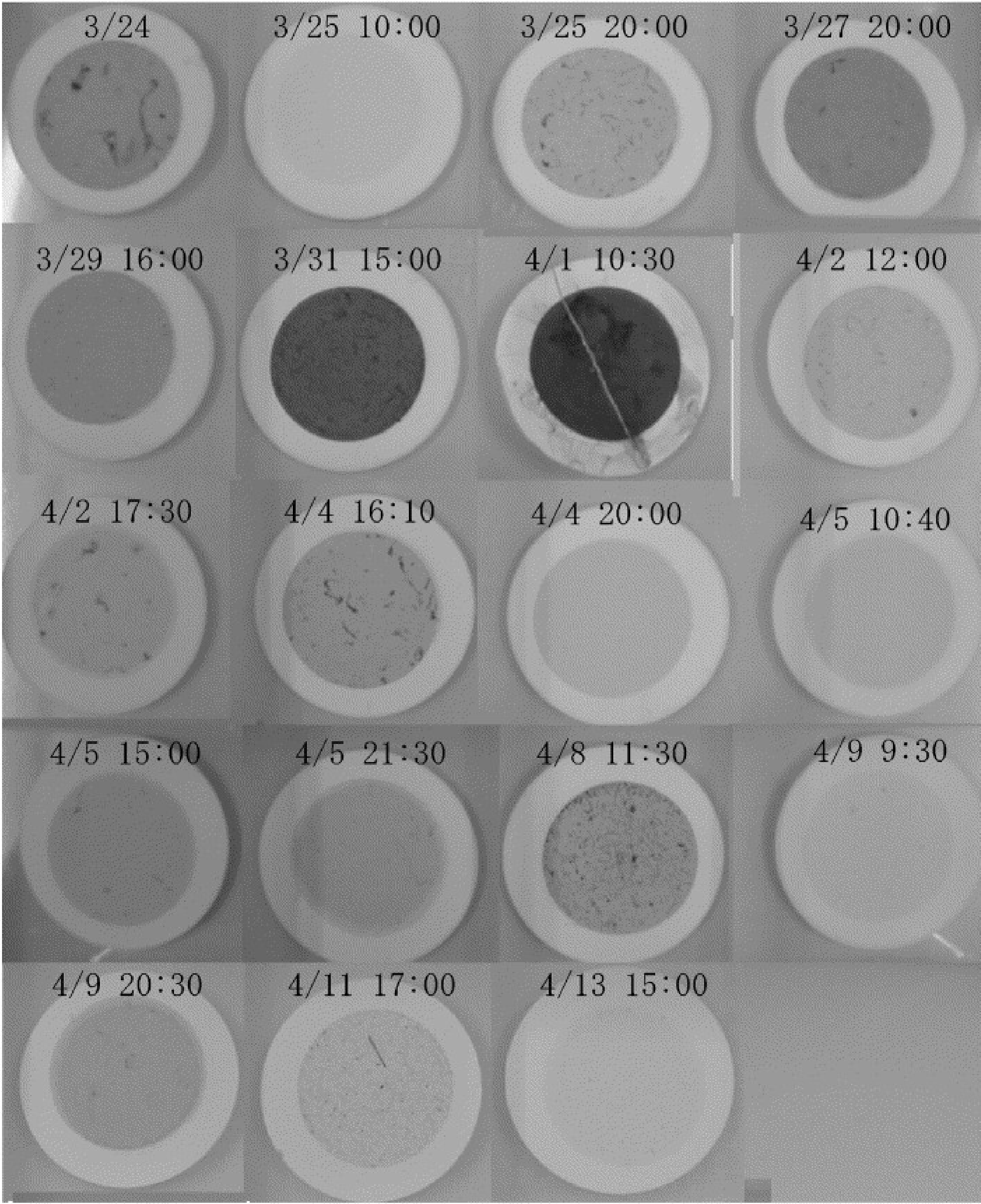
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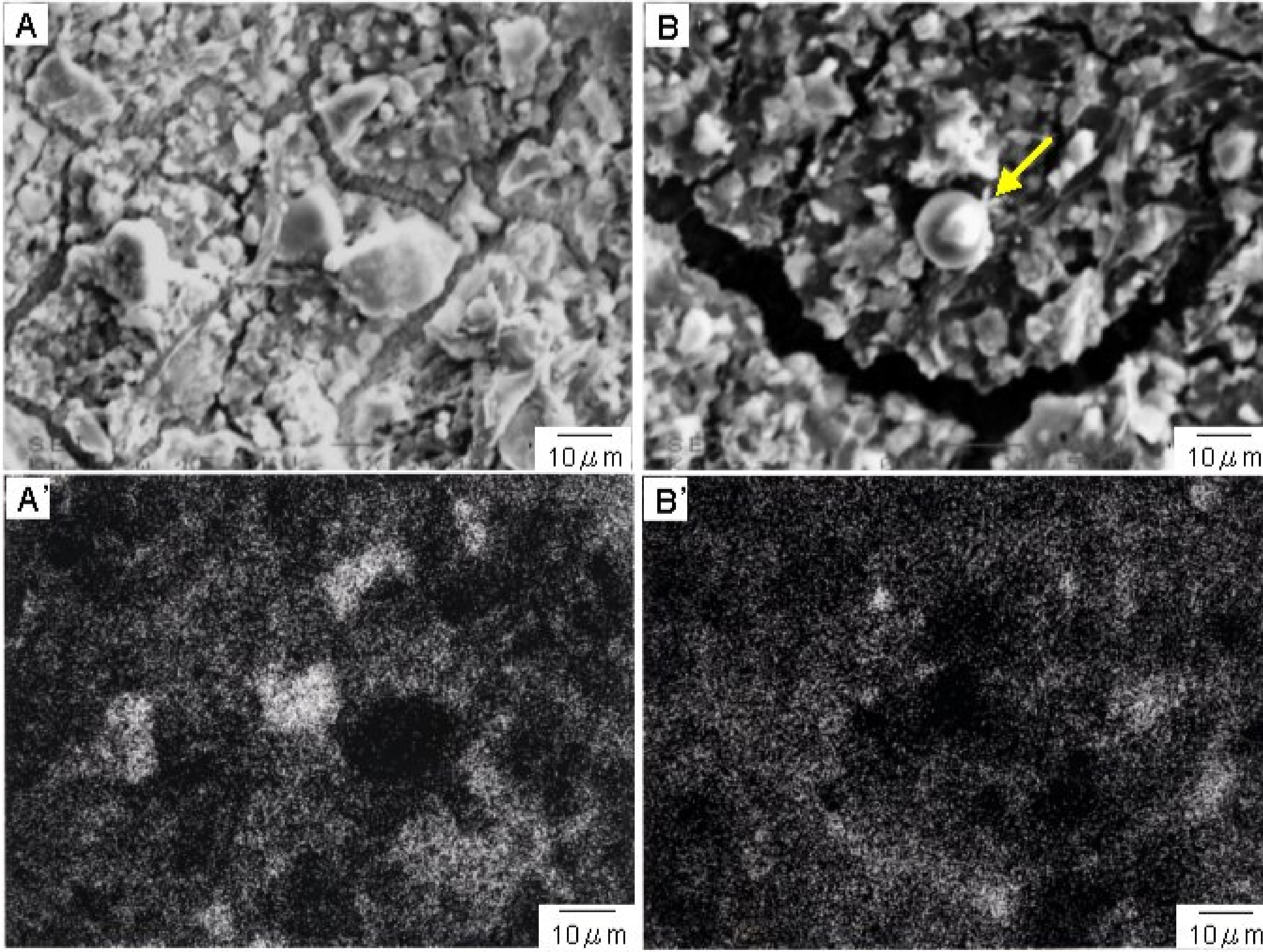
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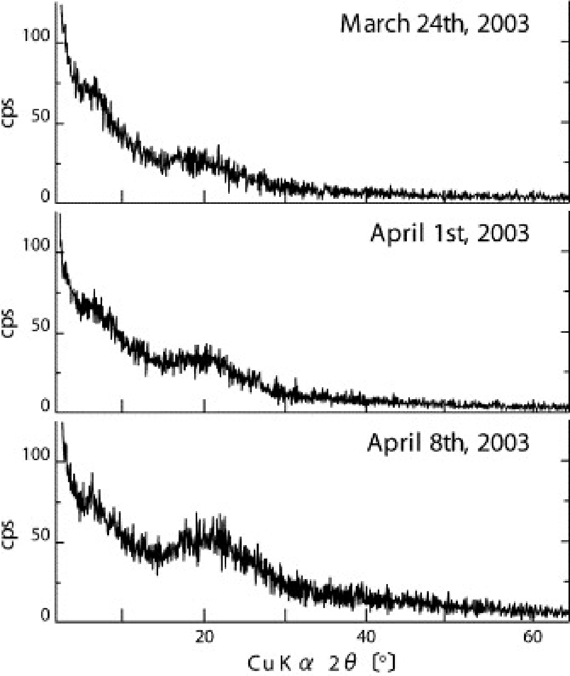

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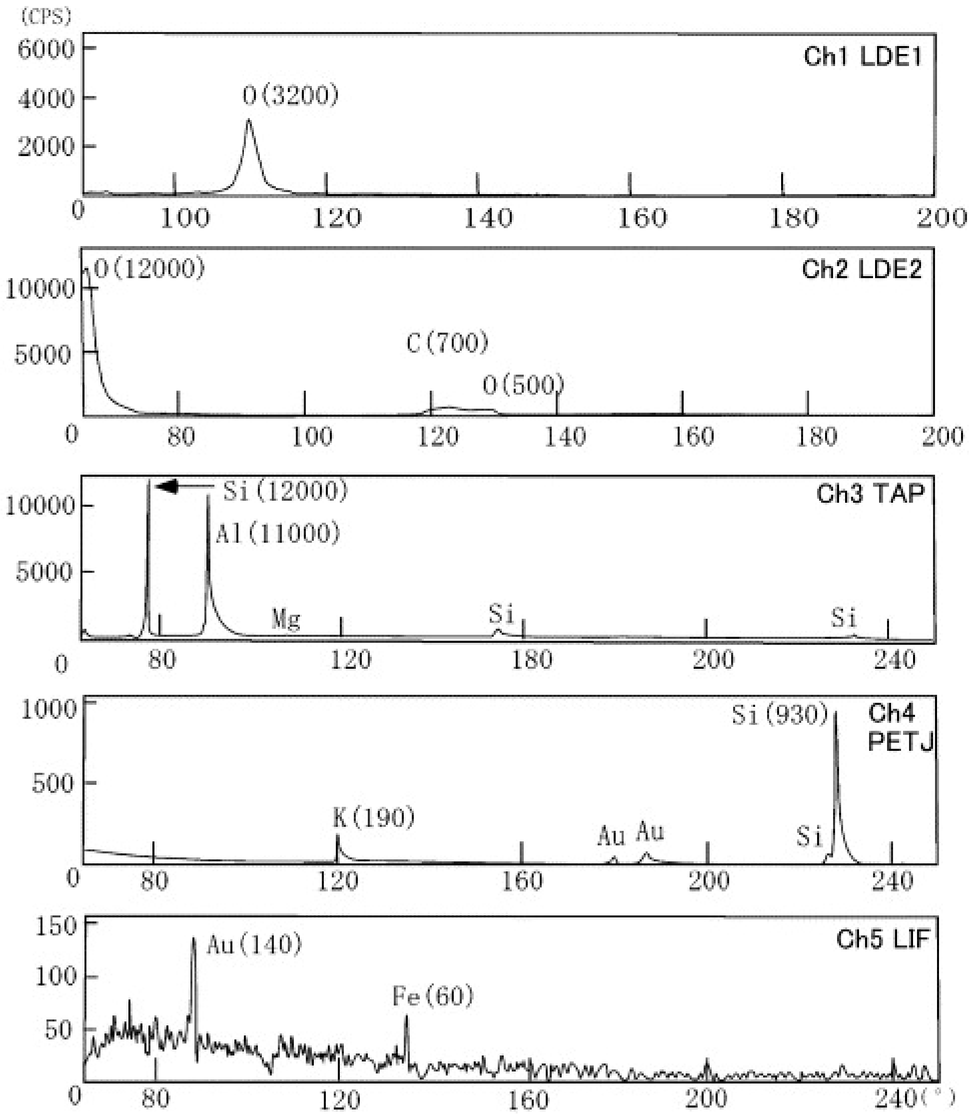
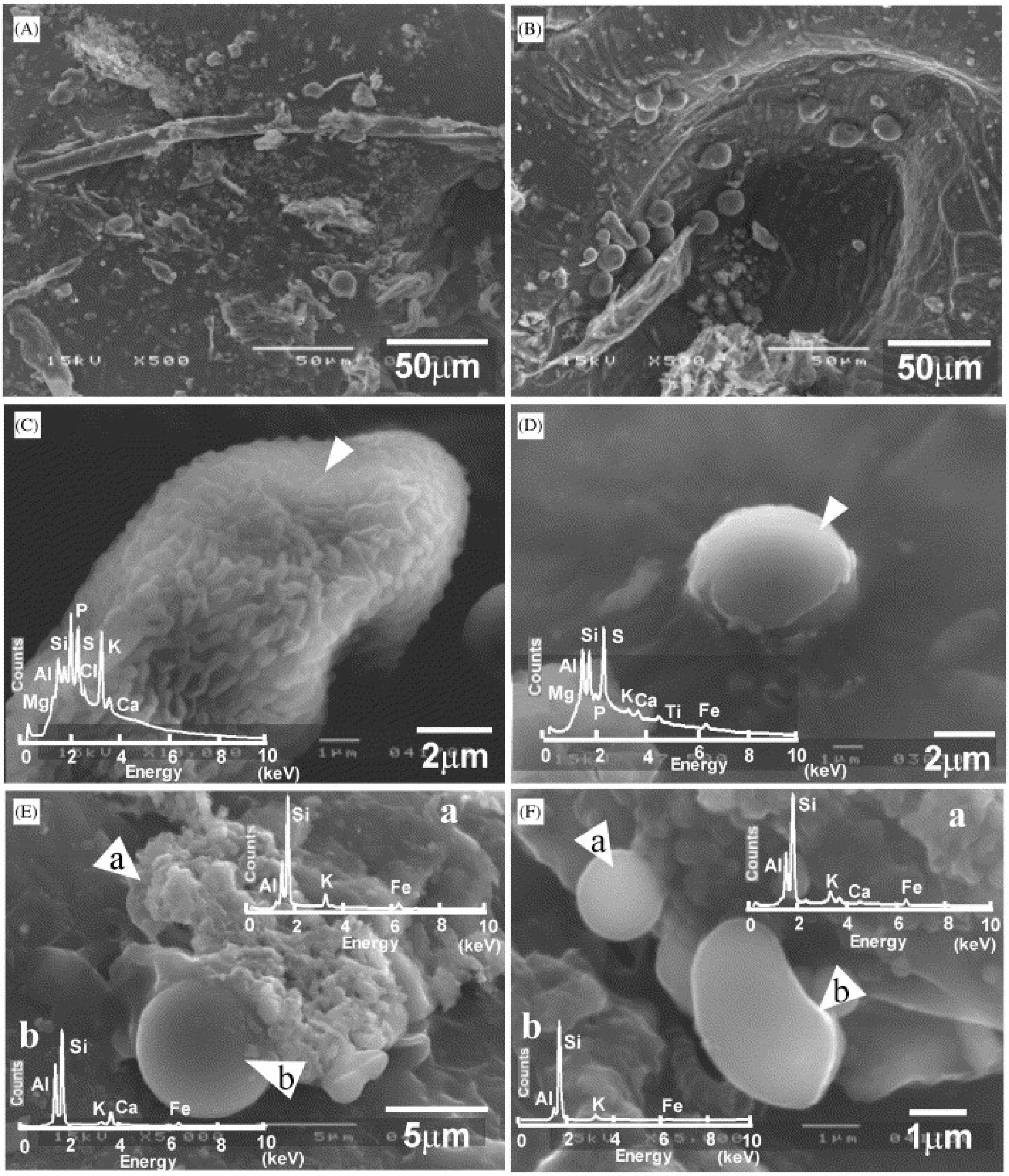


Fig. 6. EPMA analytical patterns of the powdery dusts (in Fig. 3) on 1 April, 2003 in Kanazawa, showing high contents of carbon (700cps) and oxygen (12000cps) in the soot whereas high concentration of Si (12 000cps) and Al (11 000cps) at the spherule (an arrow in Fig. 3B). The peak of Au is due to coating material. The carbon peak indicated mainly amorphous organic carbon because of XRD results. EPMA analysis was carried out on 5 channels from Ch 1 to Ch 5, using different crystalline, such as LDE 1, LDE 2, TAP, PETJ, and LIF, respectively.



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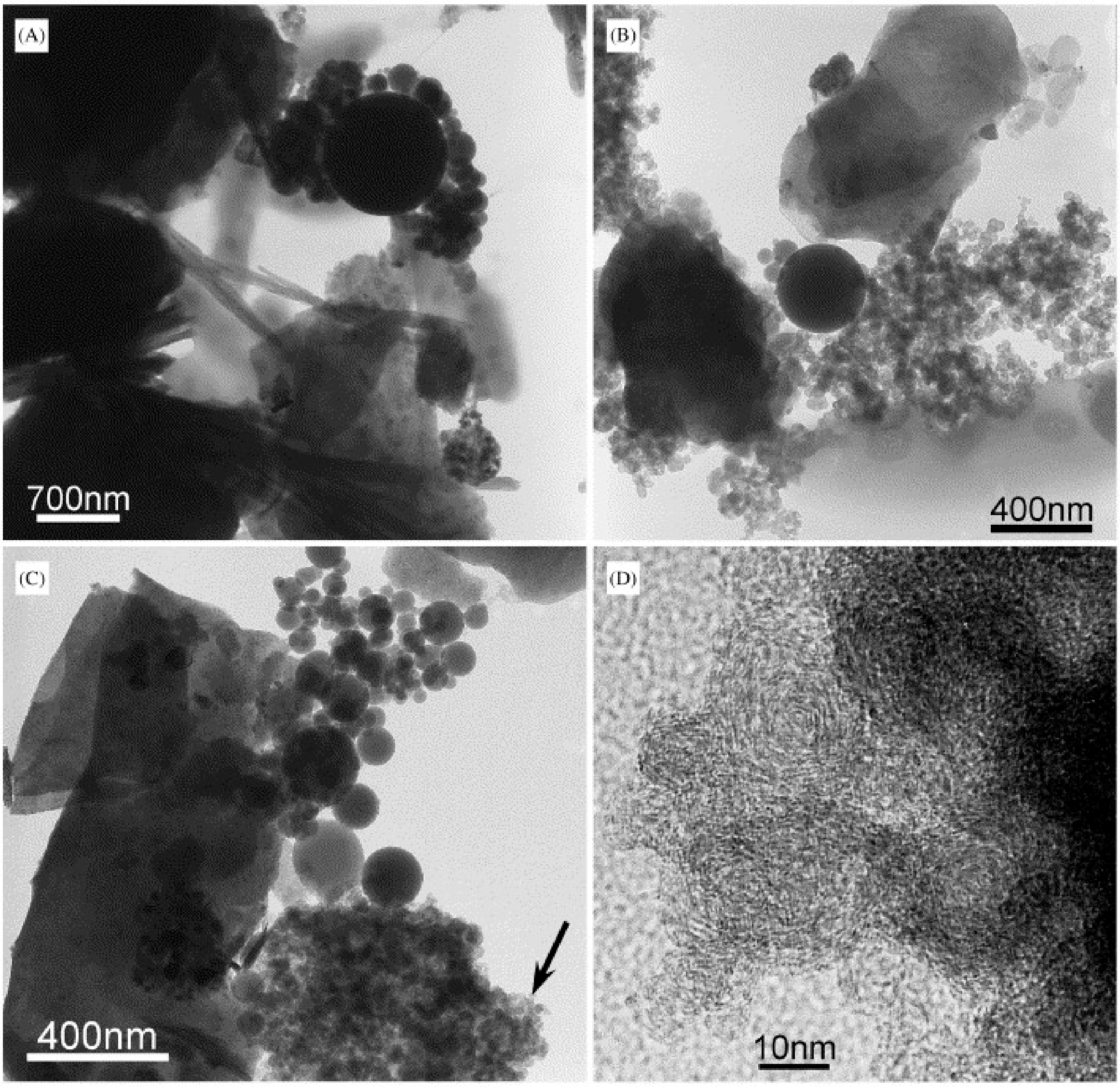

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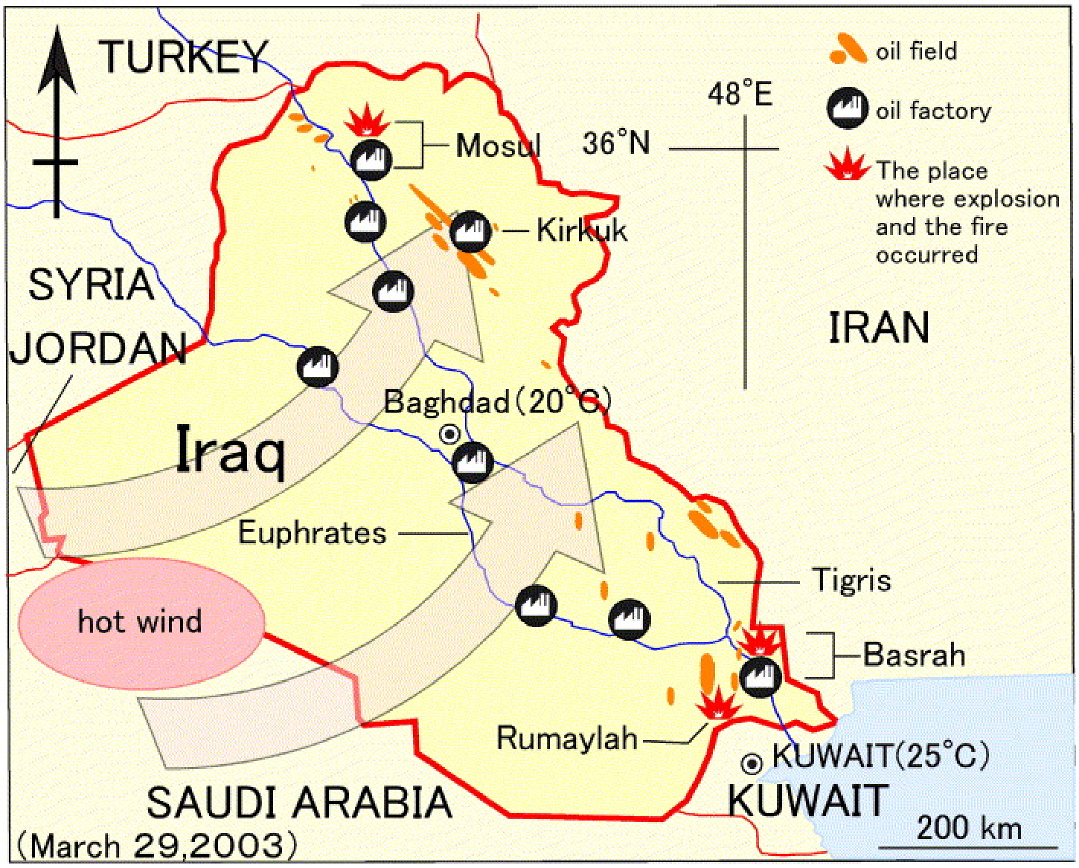

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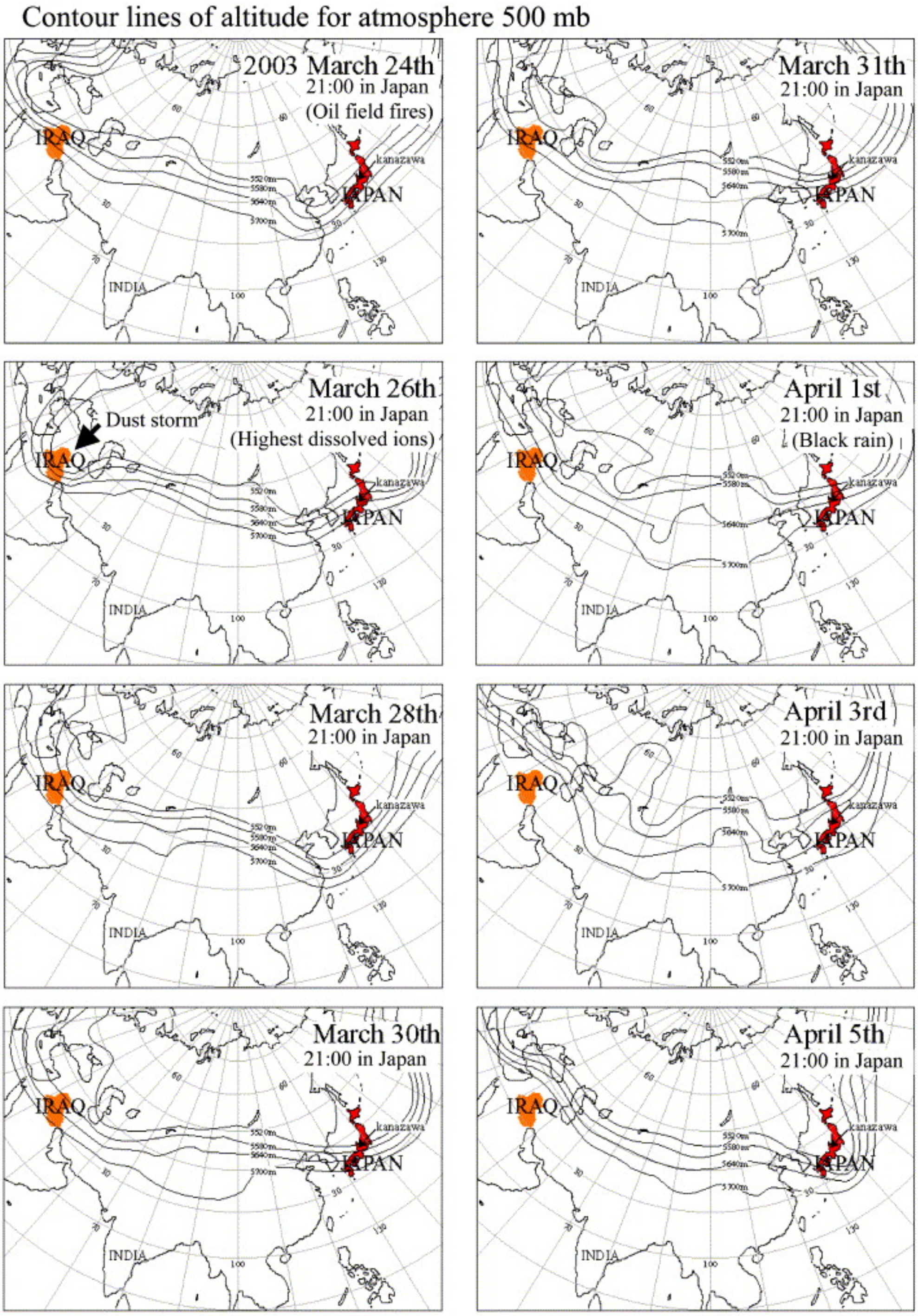

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