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Effect on narcissus plant by exhaust emissions derived from diesel engine

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Abstract Polluted narcissuses by exhaust emissions derived from a diesel engine twice a day were investigated by XRF, SEM-EDX and TEM analyses. Polluted narcissus was characterized by no flower, deformed leave and the change of color from green to yellow and black. S was increased about 6 times. About 33 % of S-coated carbonaceous soots was retained through breath holes by narcissus, causing the normal breath and photosynthesis of narcissus damaged. This could be a major factor of narcissus growing abnormally during a short period (2 months).

Key words : exhaust emissions, diesel engine, narcissus, retention, SEM-EDX, TEM

Introduction

Carbon-, sulfur-, and nitrogen-containing particles account for most of the anthropogenic pollution in the atmosphere (Navakov et al. 1974; Ibusuki 1987; Kasahara et al. 1993; Wang and Sakamoto 1994). A major source of these pollutants is fossil fuel combustion and exhaust emissions derived from vehicle engine, especially from diesel engine (Bulter and Crossley 1981; White et al. 1983; Stober 1986; Sagai et al. 1993; Eiden et al. 1994; Nakajima and Kato 1994). They produce not only the primary particulate carbonaceous emissions (soot) and gaseous hydrocarbon, but also large amounts of SO_2 and NO_2 gases (Tartarelli et al. 1978; Nakajima and Kato 1994). Chemical analyses have revealed that exhaust emissions of diesel engines are mainly composed of elemental carbon (41% on the average), organic material (39% on the average), variable amounts of SO_2 and NO_2, and minor metals (Hildemann et al. 1991; Tazaki et al. 1995). It has been indicated that exhaust emissions derived from diesel engine vehicle is 30-100 times higher than gasoline vehicle (Sagai et al. 1993; Nakajima and Kato 1994). Diesel exhaust particles in the atmosphere on Tokyo take about 30-40% of total dispersive particle matter (Sagai et al. 1993). A large number of studies have revealed the fact that vehicles are the main source of heavy metal and acid gases (SO_2 and NO_2) pollution in ecosystems (Bulter and Crossley 1981; Markert 1993). For example, a close relationship exits between the intensity of vehicle traffic and metal accumulation by plants, and lead levels in the plants growing alongside the highway with a heavy traffic load are three times higher than that in the plants from rural road sides in India (Markert 1993).

However, these studies are almost limited in chemical analyses of bulk plant leave, microanalyses and observations on polluted plants by electron microscopy on the μm and nm levels are rarely reported. Narcissus is one of plants first flower blooming in spring after winter snow melt. It grows actively in spring season and has relatively short period of growth in comparison with other plants such as legumes. It is favorable to observe directly acute pollution from a special exhaust emissions such as diesel engine without other serious impact from atmospheric pollution. Therefore, narcissus is considered as one of good samples in this investigation. We also selected other plants such as legumes as monitor of atmospheric pollution in the plant garden of Faculty of Science, Kanazawa University. Some results will be reported in another paper. In this paper, a

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Table 1. Chemical composition of narcissuses by XRF (wt%)

Element	Normal Narcissus	Polluted Narcissus
Na	0.04	0.12
Mg	0.05	0.20
Al	-	0.10
Si	tr.	0.17
P	0.03	0.08
S	0.06	0.37
Cl	0.30	0.52
K	0.29	0.48
Ca	0.19	1.30
Ti	-	tr.
Mn	-	tr.
Fe	-	0.02
Cu	-	tr.
Zn	tr.	tr.
$C_6H_{10}O_5$	99.05	96.62

case of acute pollution of exhaust emissions from a diesel engine on fresh narcissus during a short period (2 months) was described through XRF, EDX microanalyses and SEM, TEM observations. Major factor causing narcissus leave to grow abnormally was discussed.

Samples and methods

Samples

Narcissus was collected in the parking lot in March 1995 when the flower actively bloom (Fig. 1A). Polluted narcissuses were located in where they were directly subjected by exhaust emission derived from a diesel engine (Fig. 1B, left and 1 C, left). In the area far from the diesel engine car, normal narcissuses were collected to compare with polluted ones (Fig. 1B, right and 1C, right). The distance between exhaust pipe of the diesel car and narcissus was about 1 m. The temperature near the pipe exit was about 25-30℃ and it decreased gradually with the distance. At the area of 1 m from the pipe, the temperature was almost same as surrounding one. Because the diesel car parked in the same spot everynight, narcissuses were at least subjected by its exhaust pollution twice every 24 hours in morning and night (5 min. in each exhaust emission). Such exhaust pollution gave the growth of narcissus a very serious effect. Most of them have been deformed compared to the nearing normal narcissuses which have not been subjected any exhaust pollution. The most obvious difference is that polluted narcissus displayed an abnormal growth with no flower, changes in color of leave into yellow and in some part black (Fig. 1B, left and 1C, left). The dried narcissus leave twists and turns with black spots (Fig. 1C, left).

SEM-EDX analysis

A leaf with an area (8×8 mm) was cut from upper, middle and lower parts of normal and polluted narcissus samples, respectively, and attached to a carbon tape without any treatment. The leave were point- or area-analyzed in or near breath holes, respectively, by SEM-EDX using a JEOL-JSM-5200LV scanning electron microscope with a Phillips-EDAX PV9800 STD energy dispersive X-ray analyzer at an accelerating voltage 15 kV. A part of polluted narcissus leave was cut with the same area (8×8 mm) and washed using 200 ml distilled water for 2 hours, then suspension was filtered with a membrane filter (0.45 μm of pore diameter) using an aspirator. The variation of S concentration in polluted narcissus before and after washing was investigated by SEM-EDX method. X-ray spectrum was obtained for 200 sec. analytical time. The analysis can only be performed for elements with $Z>11$ and lighter elements such as C, N and O can not be detected. Conversion of intensities into concentrations was accomplished using a standardless ZAF correction program set in computer. The concentrations of elements were normalized as wt% on the dry matter basis.

XRF analysis

Normal and polluted narcissuses were dried at a room temperature without any treatment. The leave were cut from upper, middle and lower parts of both and crushed, respectively. The cru-

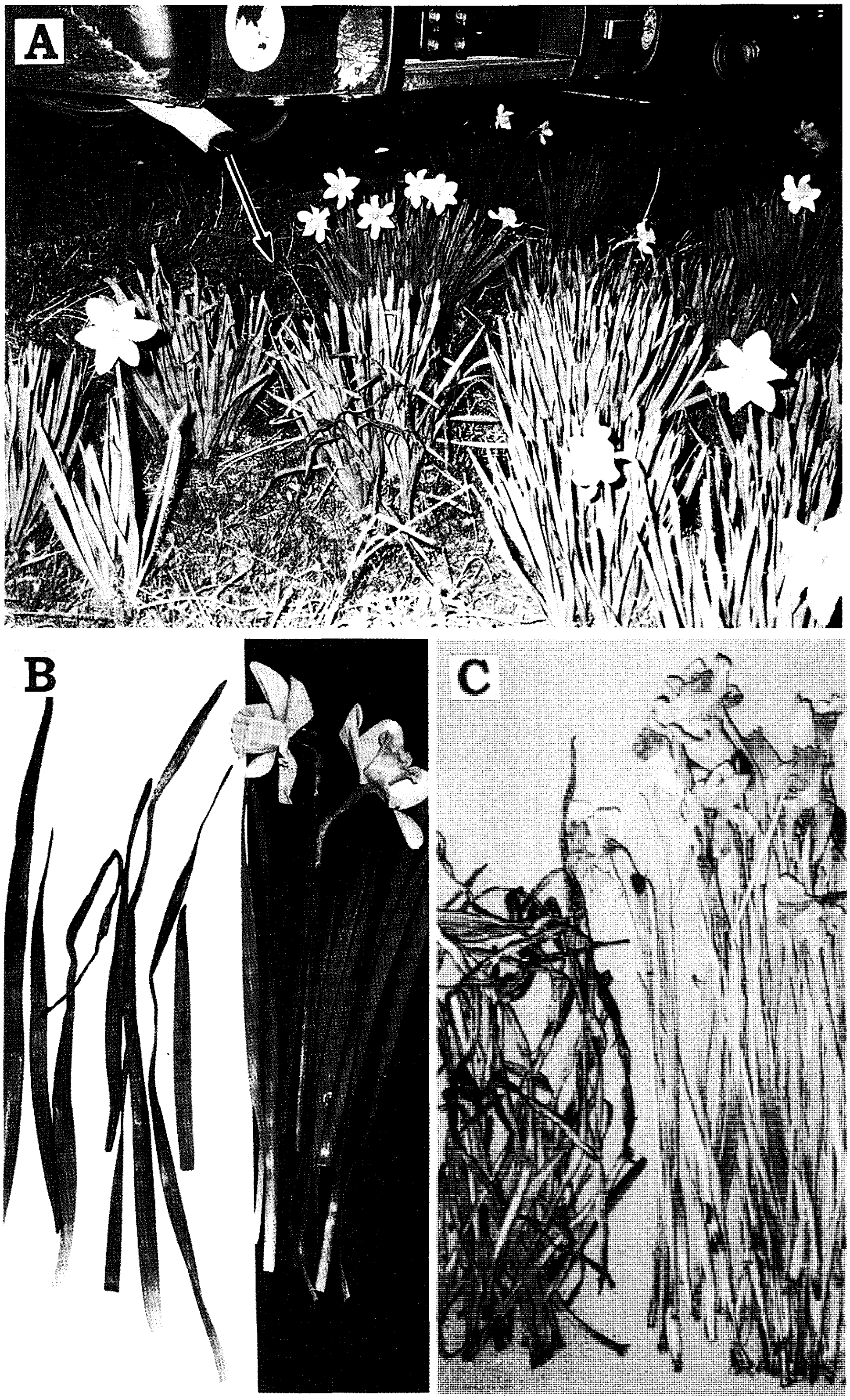

Fig. 1. Parking lot where a diesel engine vehicle parks everyday and narcissuses are subjected by its exhaust emissions twice every 24 hours with 5 min. in each exhaust emission (A). Right side in B and C are normal narcissus before and after drying. Polluted narcissus by the exhaust emissions before and after drying (B and C, left), noticing their shapes with no flowers and changed color.

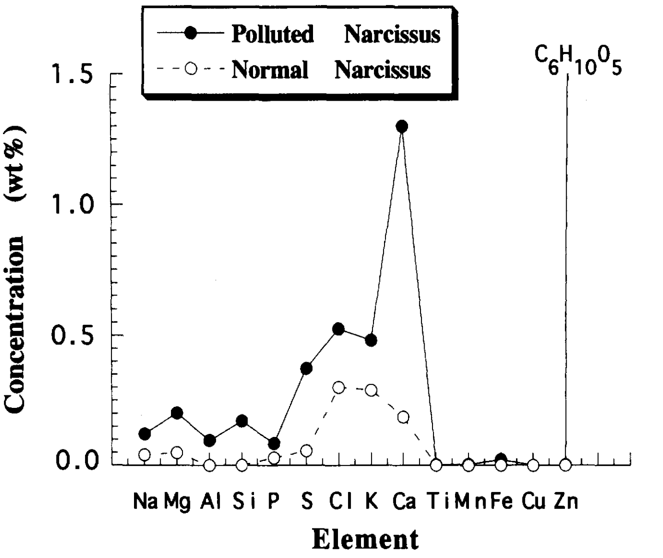

Fig. 2. Variation of chemical compositions between normal and polluted narcissuses, showing an apparent increase of S and Ca in polluted narcissus.

shed sample was pressed to a sample container (32 mm of diameter) and analyzed by XRF, using a JEOL-JSX-3200 Element Analyzer. The analytical condition is as follows: accelerating voltage 30 kV, electron current 1.20-2.76 mA, analytical time 300 sec.

Result

Comparative variation between normal and polluted narcissuses

Chemical compositions of normal and polluted narcissuses measured by XRF are listed in Table 1. Original composition of normal narcissus is almost composed of organic substance ($C_6H_{10}O_5$) (99.05% on the dry matter basis) with minor Na, Mg, P, S, Cl, K and Ca, whereas polluted one contains higher amounts of elements other than organic carbon. Figure 2 shows the variation of chemical compositions except organic carbon between normal and polluted narcissuses. It is apparent that these compositions such as S, Cl, K and Ca increase largely in polluted narcissus in comparison with normal one. Particularly, S and Ca compositions are most evident. S concentration is about 6 times higher in polluted narcissus than in normal one. On the other hand, some compositions such as Na, Mg, Si, Al, Mn and Fe also increase in different levels.

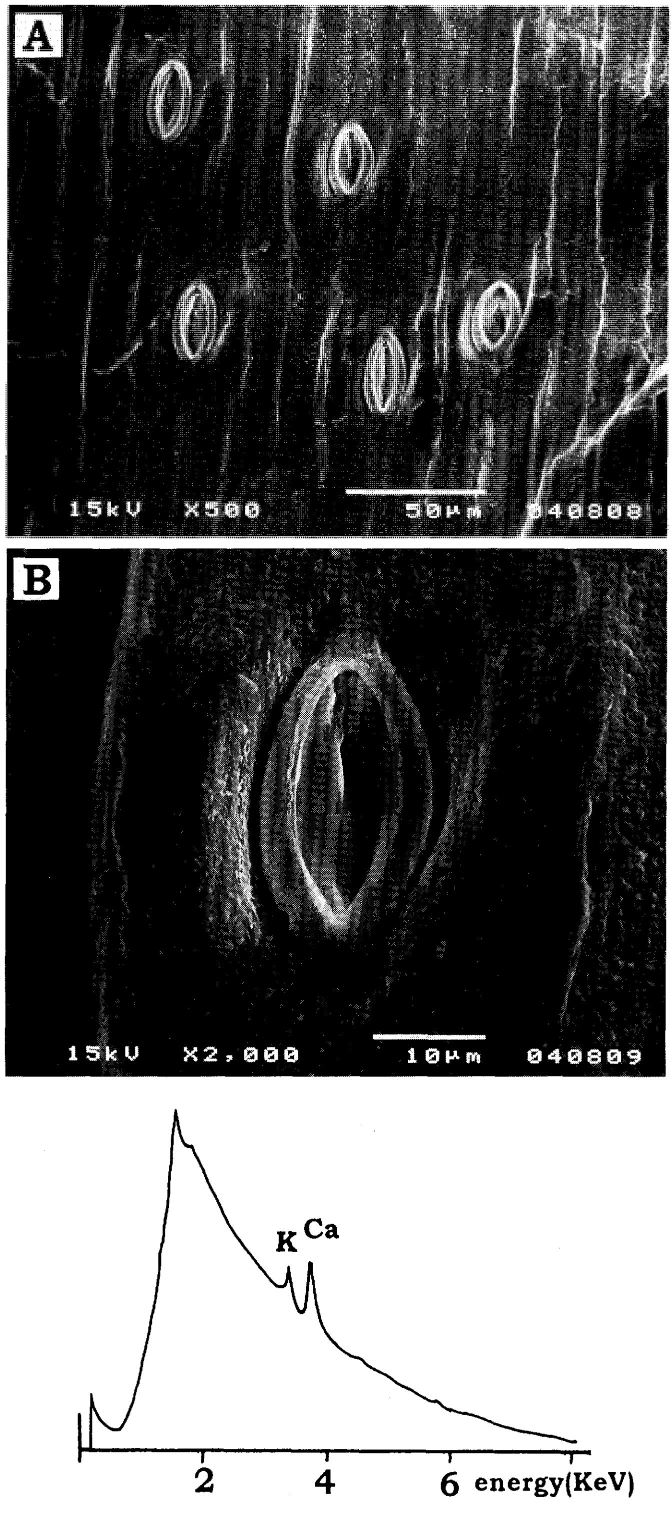

Fig. 3. Scanning electron micrographs and the energy dispersive X-ray analysis of normal narcissus, showing smooth and clear leave (A) and opened non-filled breath holes (B). A high background suggests an original organic composition of narcissus.

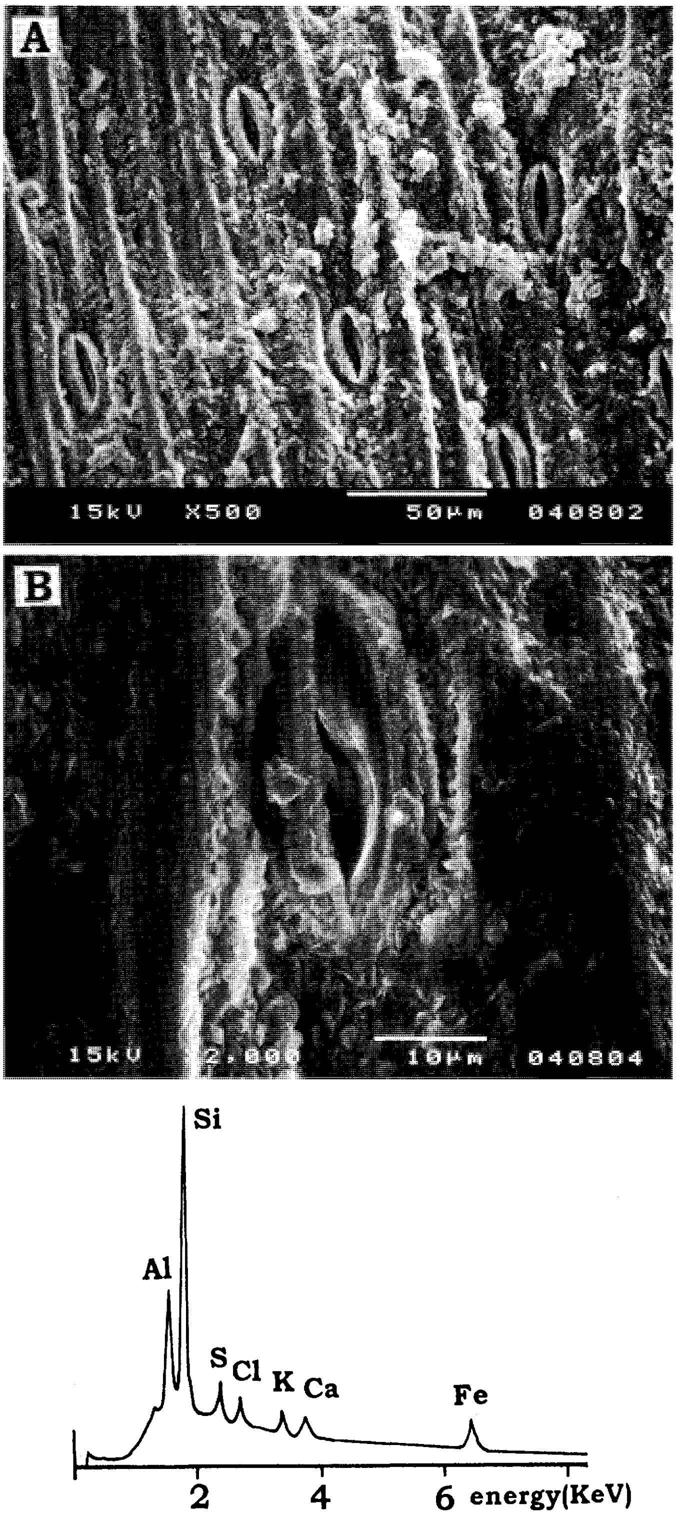

Fig. 4. Scanning electron micrographs and the energy dispersive X-ray analysis of polluted narcissus, showing the increase of Si, Al, S, Cl, K, Ca and Fe compositions. The leave are absorbed by particles (A) and most breath holes are filled by particles (B).

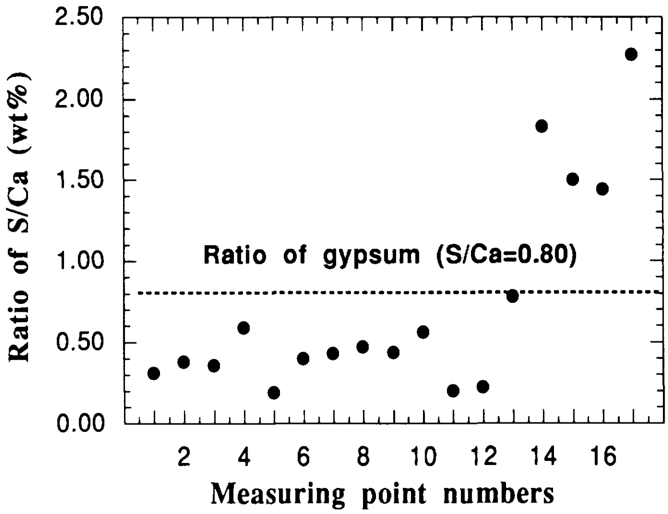

Fig. 5. Ratio of S/Ca in Ca-bearing particles. About 70% of particles have the ratios between 0.20-0.70, showing a serious pollution of S-thin film on the surface by the exhaust emissions of diesel engine.

Microanalyses of normal and polluted narcissuses by SEM-EDX

XRF analysis revealed an apparent increase of out source composition, such as S and Ca, in polluted narcissus. Especially over amounts of S composition could be related to exhaust emission. Therefore, it is necessary to investigate the micro-distribution of S composition in polluted narcissus to understand the factor of its abnormal growth.

1. Normal narcissus

Normal narcissus leave show smooth surface with open pits (breath holes) (Fig. 3A). Breath holes were found not to be filled by particles both internal and external structures (Fig. 3B). The EDX analysis showed a high background with weak K and Ca peaks, suggesting an original composition of narcissus which agreed with XRF results.

2. Polluted narcissus

Polluted narcissus leave show rough surface with numerous granules (Fig. 4A). It is typically characterized by the filling of S pollutants or S-, Al-, Si-containing particles in the breath holes (Fig. 4B). These particles were more commonly observed in the breath holes than other areas of narcissus. EDX analyses showed that they were mainly composed of Mg, Al, Si, Ca and Fe, but were all detected to contain S. Most of road dusts do not contain originally significant S and

Table 2. Chemical composition of exhaust emissions derived from diesel engine vehicles (% of mass)*

Al	Si	P	K	Ca	Ti	V	Cr	Mn	Fe
0.052	0.59	0.028	0.056	0.16	0.030	0.007	0.018	0.009	0.13
Ni	**As**	**Br**	**Ba**	**Pb**	**EC[a]**	**OC[a]**	**Na^{+}****	**Cl^{-}****	**NO_3^{-}****
0.027	0.015	0.001	0.00	0.000	40.5	32.6	0.17	0.28	0.33
SO_4^{2-}**	**NH_4^{+}****	**fine mass emission rate**							
0.22	0.08	408+68 (mg/km driven)							

* after Hildemann et al., 1991; ** measured by IC and others were measured by XRF;
a EC, elemental caobon; OC, organic carbon.

it may resulted from the exhaust emissions according to the chemical compositions of exhaust emissions from diesel engines and road dust (Hildemann et al. 1991; Wang and Sakamoto 1994). Therefore, a ratio of S to one of other elements characterized by road dust composition could imply a level of narcissus pollution subjected by exhaust emissions. Figure 5 shows ratios of S/Ca in Ca-bearing particles. The ratios change ranging from 0.20 to 2.27. About 70% of the particles have the ratios lower than 0.80 of the S/Ca ratio of gypsum (most are between 0.20-0.70). This indicated that these particles were coated at different level by sulfur films implying that narcissus were polluted seriously by exhaust emissions.

Figure 6 shows some typical cases of breath holes being filled by S-containing particles. Figure 6A shows that submicrometer particles almostly covered on a breath hole. EDX point analysis revealed a high S concentration with a high background. These S-rich particles are very similar to the exhaust carbonaceous soots of diesel engine (see below). Fig. 6B shows a spherical organic matter with high S concentration and background filled in the breath hole of narcissus. Fig. 6C shows a Fe- and S-containing particle filling in the breath hole.

Retention of narcissus leave for S pollutants

SEM-EDX analyses of polluted narcissus leave before and after distilled water washing showed that a part of S constituents was water soluble and/or was weakly adsorbed on the narcissus leave. Fig. 7 shows changes in S concentration before and after distilled water washing by EDX area analyses in the area of 400×300 μm. After the washing S concentration decreased apparently. But a part of S constituents were not so easily removed by the washing. According to the Fig. 7, about 33% of S constituents were resided after the washing. Table 3 shows compositional characteristics of different areas in narcissus leave after the washing by EDX analyses. EDX spectra from narcissus leave have high backgrounds with higher concentrations of P, S, Cl, K and Ca, whereas the spectra from road dust mostly have low backgrounds, with little P being detected. Only a part of particles contains high S composition. These composition characteristics indicate that S constituents on the road dust are easily removed by water washing, whereas those on narcissus leave or around breath holes are not so easily removed by water washing.

Chemical characteristics of exhaust emissions derived from diesel engine

The analyses by SEM-EDX have shown S constituents present as coatings with a size of submicrometer on narcissus leave and road dust particles. To investigate clearly the origin of these S constituents, exhaust particles from the diesel engine were also collected and investigated by

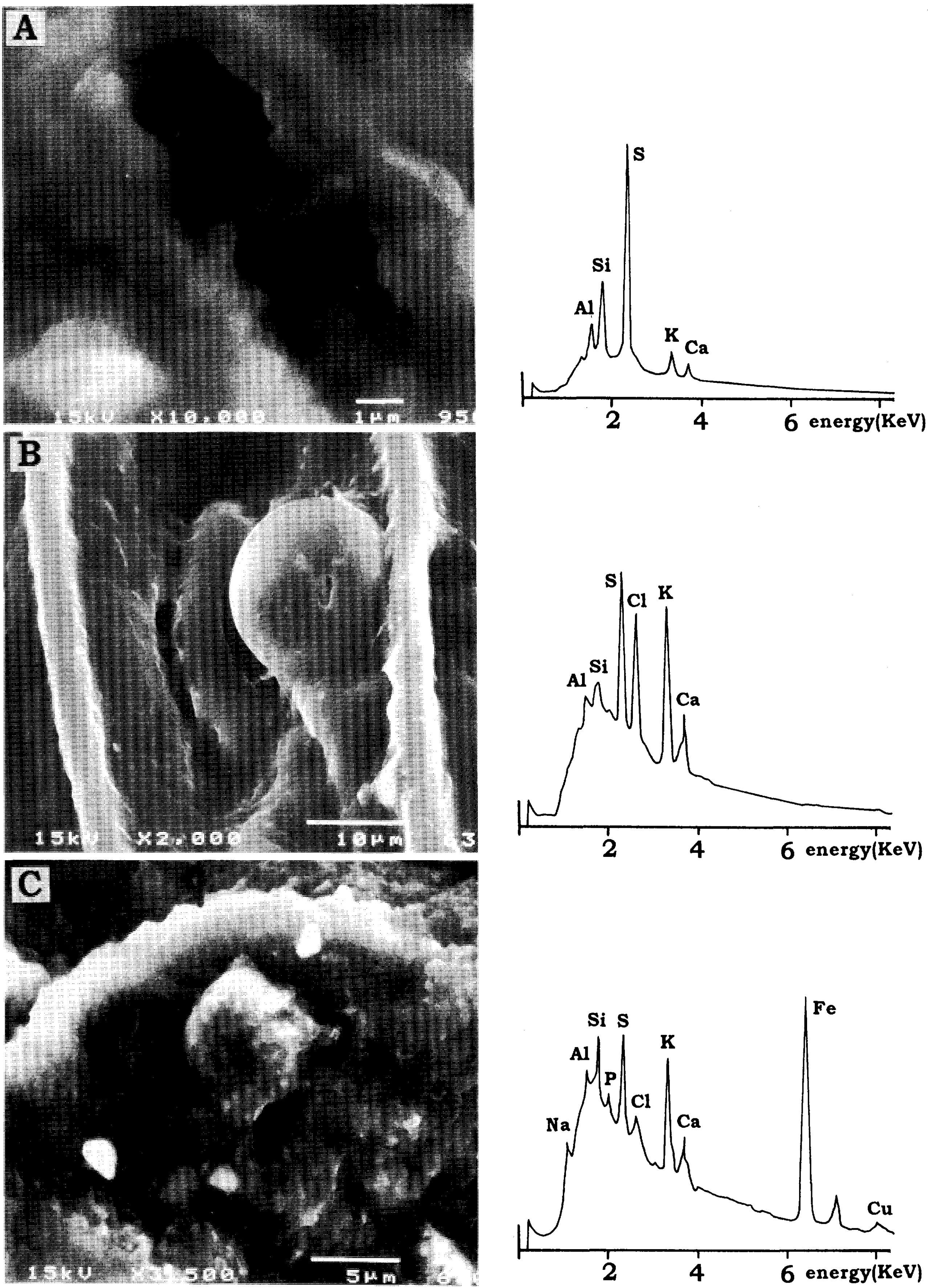

Fig. 6. S-containing particles filled in the breath holes of narcissus, showing submicrometer S-rich carbonaceous soots(A), S-containing organic matter (B) and Fe- and S-containing particles (C).

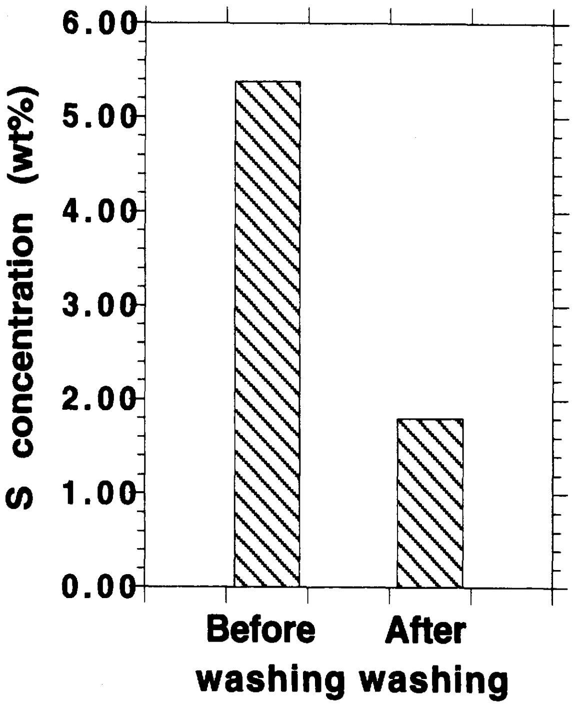

Fig. 7. The change of S concentration before and after distilled water washing by EDX area analysis in the area of 400×300 μm, showing a decreasing of S concentration in the narcissus after the washing. About 33% of S consituents were still resided after the washing.

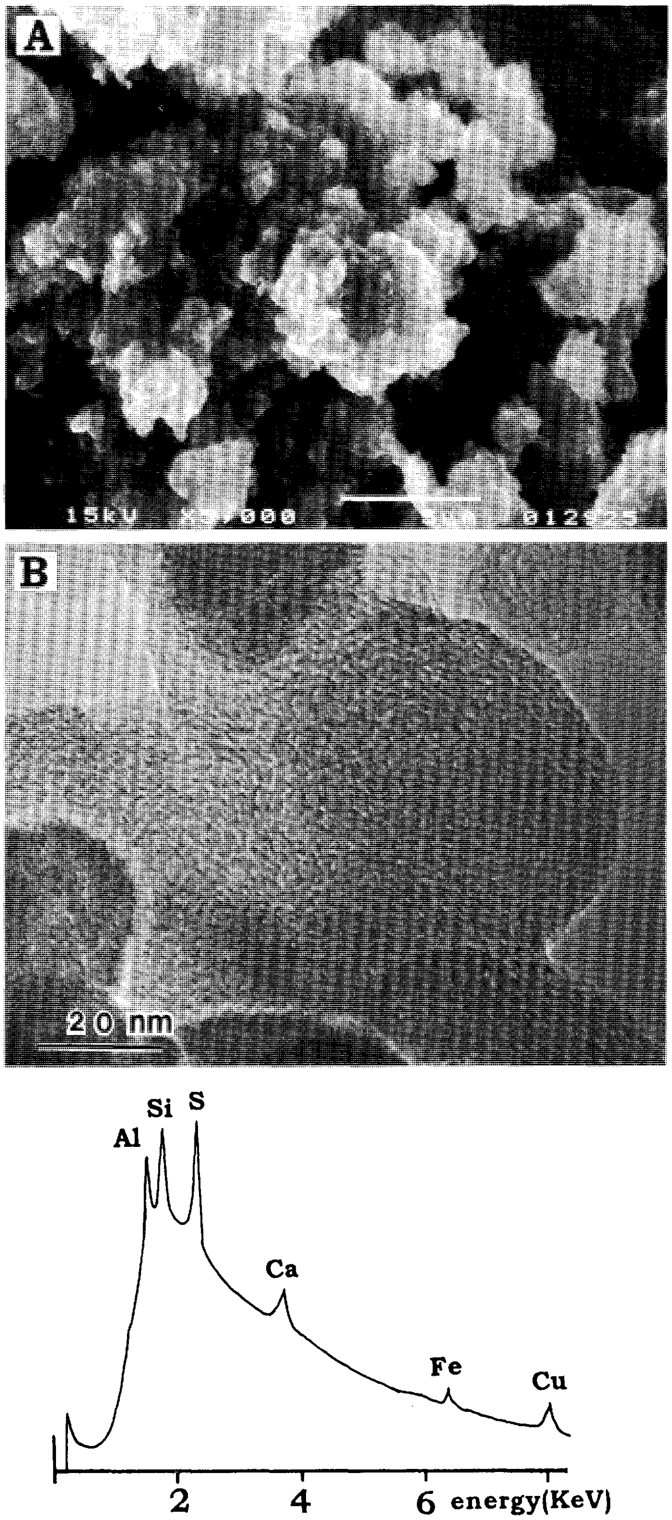

Fig. 8. Scanning and transmission electron micrographs and the energy dispersive X-ray analysis of exhaust emissions derived from the diesel engine, showing submicrometer carbonaceous soots (A) and the diameters of soots ranging between 50-100 nm(B). A high background with S peak were detected by EDX.

SEM-EDX analyses and TEM observation. Result showed that the exhaust particles consist mainly of carbonaceous soots with submicrometer (Fig. 8 A). Considerable amounts of S constituents were also detected by EDX analysis, displaying a high background with S peak, suggesting that large amounts of S constituents were coated as a thin layer on the surface of the soots (Fig. 8). Table 2 gives a chemical composition of exhaust emissions from diesel engines (Hildemann et al. 1993). Major composition is contributed by elemental carbon and organic carbon. S and Cl also showed significant concentrations. Both have a good agreement. Figure 8B shows the transmission electron micrograph of carbonaceous soots with diameters ranging between 50-100 nm. High Resolution TEM (HRTEM) showed spherical and hemispherical finger-print like structure, suggesting poorly crystallized carbon grains. As shown in Fig. 6A, submicrometer S-rich particles covered on the breath holes are very similar to the exhaust emissions of diesel engine shown in Fig. 8A. This result indicated that lårge amounts of S constitu-

Table 3. Compositional characterization of particles in the narcissus after water washing by EDX (wt %)

Types	Analytical point	Mg	Al	Si	P	S	Cl	K	Ca	Ti	Mn	Fe	Background
Road dust	1	4.67	12.30	7.59	-	-	-	2.16	0.3	28.21	7.78	26.98	low
	2	-	25.03	60.46	-	-	-	8.07	3.27	1.35	-	1.80	low
	3	-	23.69	29.23	2.03	11.43	-	16.03	3.73	-	-	3.87	low
	4	-	18.97	36.36	2.73	14.26	-	19.64	3.76	2.38	-	1.91	low
Narcissus leave	5	4.97	1.43	1.93	12.17	7.98	5.97	55.28	10.26	-	-	-	high
	6	4.28	0.87	3.22	14.73	8.06	10.38	47.64	10.82	-	-	-	high
Particles around breath holes	7	7.05	16.11	21.20	3.98	12.54	2.66	18.73	4.12	3.63	-	10.07	high
	8	3.54	16.01	27.01	-	34.32	1.11	12.82	3.37	0.48	-	1.33	high

ents detected in breath holes of polluted narcissus were resulted from the exhaust emissions of diesel engine.

Discussion

Increase of S concentration in narcissus implies a serious pollution from exhaust emissions

Above results got by XRF and SEM-EDX microanalyses have clearly revealed that polluted narcissus changed not only color and shapes, but also chemical composition obviously. At least twice exhaust emission derived from the diesel engine car which parks the same spot everynight made narcissus to be polluted very frequently during a short period (2 months). S concentration increased about 6 times in comparison to normal narcissus (Table 1). According to Table 2, principal components from diesel exhaust emissions are elemental carbon (EC) and organic carbon (OC). Ratios of EC/SO_4^{2-} and OC/SO_4^{2-} are 184.1 and 148.2, respectively. It is possible that narcissus have polluted with much more elemental and organic carbons than SO_2 from exhaust emissions. Although carbon element could not be detected by the EDX in this study, it could be supported by submicrometer S-rich carbonaceous soots found in the breath holes of narcissus (Fig. 6A). Yokley et al. (1986) have indicated that exhaust emissions derived from diesel engine contain various polycyclic aromatic hydrocarbons (PAHs) which are present as particulate aerosols in the atmosphere. Among PAHs, benzo (a) pyren and nitropyren matter have a large percentage (Bulter and Crossley 1981; Williams et al. 1986). 32.6% of organic carbon (Table 2) could be mainly composed of these PAHs (Williams et al. 1986). Therefore, these compounds could have some impact on the growth of narcissus. Some trace components such as Ni, As and Cr, as shown in Table 2, also have a effect on the narcissus (Markert 1993).

Retention for pollutants by breath holes causes an abnormally physiological growth

Breath hole is an important organ of plant through which the breath and photosynthesis process are produced. Therefore, it is an important way for plant to exchange matter between inside plant and the atmosphere. SEM-EDX analysis have revealed that large amounts of submicrometer S-rich carbonaceous soots covered on the breath holes of narcissus. They could be retained through breath holes of narcissus. This retention is easily taken place during growth of narcissus with photocatalytic reaction or photo-induced reaction (Gibson et al. 1986). The presence of about 33% of water-insoluble S composition could support the possibility. According to Markert (1993), about 90% of the exhaust emissions are retained by plants and only 10% go to the lower horizon of soils. The retention of S constituent in leave of fir seedling has been reported (Izuta et al. 1993). If we consider the ratios of EC/SO_4^{2-} and OC/SO_4^{2-} in diesel exhaust emissions, 33% of S constituents resided after water washing suggest that much higher concentrations of elemental and organic carbons (184.1 and 148.2 times, respectively higher than S constituents) could be retained by the breath holes of narcissus. This was a very serious pollution for narcissus. When diesel exhaust emissions were retained through the breath holes or covered on the surface of narcissus, normal growth function of it could be damaged (Foy et al. 1978; Markert 1993; Fenn and Bytnerowicz 1993). This could a major factor causing polluted narcissus grow abnormally with no flower, deformed leave and changed color. Although only the influence of warm gases derived from the diesel engine could make narcissus change its color and shapes, above components from diesel exhaust emissions had a much more seriously physiological effect on the surface of narcissus than the influence of warm gases.

From above result, we have shown a case that narcissus has polluted frequently by exhaust emissions of diesel engine during a short period (2 months), which resulted in a damage of normal growth function of narcissus. This could be common in the environmental air pollution of ecosystem, although this result could be a special case of acute pollution of diesel exhaust emissions subjected by narcissus. Since high concentration of diesel exhaust emissions in the atmosphere has also been reported in several urban cities (Sagai et al. 1993), for plants and agricultural crops growing under the air pollution, especially alongside highway with heavy traffic load, what impact will take place when they are subjected by exhaust emissions during a relatively long period? It may become a serious problem of environmental air pollution of ecosystem. What should be done for us ? It is a time to give a special attention.

Conclusions

The electron microscopically study with the narcissus pollution during a short period as a case, revealed a serious problem of environmental air pollution. Major conclusions can be summarized as follows:

1. Narcissus leave polluted by exhaust emissions from a diesel engine was characterized by the change of color from green to yellow and black, the increase of S, and Na, Mg, Al, Si, K, Ca and Fe from the exhaust emissions and surrounding road dust.
2. S concentration increased about 6 times in polluted narcissus, suggesting a very serious pollution subjected by narcissus.
3. Electron microanalyses by SEM-EDX and TEM reveled the presence of partial water-insoluble S-rich carbonaneous soots in the breath holes of narcissus. This suggested that a part of exhaust emissions could be retained through breath holes by narcissus.
4. During the growth of narcissus, breath holes were polluted frequently by exhaust emissions, causing its normal growth function damaged acutely. This could be a major factor of narcissus growing abnormally with no flower, deformed leave and changed color.

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田崎和江・周　国平・馬飼野光治． 1996． ディーゼルエンジンの排気ガスによる植物への影響．地球科学，50，100～110

要　旨

ディーゼルエンジン車の排気ガスを一日2回直接受けたスイセンを採取し，XRF，SEM-EDX，TEMで観察および分析を行った．排気ガスに汚染されたスイセンの葉は黒色に変色し，気孔の内部及び周辺には，Sを含む多量の微粒子が被覆し，Al，Si，Cl，Ca，K，Fe の増加も認められた．これらの結果は，ディーゼルエンジンの排気ガスが植物の光合成などの生理作用に，短期間で大きく影響を及ぼすことを明らかにした．