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Source of and potential bio-indicator for the heavy metal pollution in Ny-Ålesund, Arctic

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Abstract Three kinds of tundra plant samples including Dicranum angustum (*a type of boreal bryophyte*), *Puccinellia phryganodes (a type of fringy plant)*, Salix polaris (a type of vascular plant) and surface soil were samples in 200 at Ny-Ålesund of the Arctic. The levels of eight heavy metal elements (Hg, Ph, Cd, Cu, Zn, Ni, Fe and Mn) and three metal-like elements (As, Se, Sr) in the plant and soil samples of the areas within previous coal mining activities are significantly higher than those of other areas. The relative accumulation of these elements in these tundra plant samples is consistent with the one in the soil samples, especially in the areas affected by previous coal-mining activities. Thus, the pollution is apparently from local coal mining activity. *Dicranum angustum* has the highest concentrations among those elements, and it can be a good bio-indicator for heavy metal pollution in Ny-Ålesund. Though Ny-Ålesund is less polluted by heavy metal than nearby Northern European human living areas, but much more than the tundras of the Alaska, Greenland and the Antarctic.

Key words Arctic; Ny-Ålesund; tundra plants; heavy metals; pollution gradient

1 Introduction

The Svalbard Archipelago may be the most polluted area of the Arctic[1]. Since the Industrial Revolution, the levels of heavy metals, such as Hg and Cd, have been significantly increased in the livers of the animals of the west coast, such as polar bears, seals and sea birds[2-5]. The marine animals living in the Kara Sea and the Barrents Sea, however, are not affected by these heavy metals' pollution[6]. The Svalbard has also experienced the process of acid sedimentation; in the snow and ice core samples, the acidity has increased by 90% to PH 5.0, accompanied by the increase of sulphate content[7].

Gulinska *et al.* (2003)[8] analyzed the soil samples from the Spitsbergen Isle of the Svalbard, and reported that the pollution of heavy metals was originated from local area. The Svalbard has a large reserve of coal, and coal mining started in the early 20th century[9]. The high level of heavy metals in the sea animals and other environmental damages could be caused by coal mining and other related anthropogenic activities.

Ny-Ålesund (N78°55′, E11°56′) is located in the Svalbard Archipelago. In this paper, the concentrations of heavy metals such as Hg, Cd and S in the soils and plants of the

areas with and without previous coal mining activities in Ny-Ålesund, the influence of coal mining on tundra vegetation was analysed and the potential of using plants as bio-indicator for heavy metal contamination was examined, and compared the heavy metal pollution level in the Svalbard was compared with those in other areas.

2 Backgrounds of the investigated sites

The Svalbard Archipelago is located between the Barrents Sea and the Kara Sea, it has a total area of 62700 km^2. It is 1750 km away from the Arctic point, and one of the most northernest places on the earth inhabited by human beings. The Svalbard Archipelago consists of the Spitsbergen Island, the Nordauslandet, the Edgeoya, and dozens small islands. There are numerous mountains, and the highest Newton Mountain has an elevation of 1730 m above sea level. 60% of the Svalbard Archipelago is covered by glaciers. Ever frozen earth layers is up to 500 m thick, and even in summer only the surface 2~3 m layers are melt. Due to the effect of the passing warm waters of the northern Atlantic, the Svalbard Archipelago has foggy and oceanic climate, it has an annual mean temperature of -4℃, and it is much warmer than other areas of the Arctic. In addition to coal, the Svalbard Archipelago also has a large reserve of phosphorite.

Ny-Ålesund is situated at 78°55′N, 11°56′E, 100 kilometers away from Longyearben (the capital of the Svalbard). The coal mine, explored by the WangWan corporation of Norway, was closed in 1960's because of a tragedy accident. Afterwards, many countries have set Arctic research stations there, and China set up the Huanghe Station on July the 28th, 2004.

3 Samples collection and analysis

The 12 sampling sites of this study (labeled as H0~H11) (Fig. 1b) were set up, starting from the bottom of the Zeppelinfjellet Hill, behind Chinese Huanghe Station, across the coal-mining areas (abandoned now), along the slope, and towards the seaside (Fig. 1). In the sampling area, there is a north-eastern faultage 80 meters above sea level. Above the faultage is the Cambrian-Ordovician stratum and below it is the Tertiary stratum. The horizontal and vertical spans of the sampling areas are 1, 414 m and 131 m, respectively (Fig. 1b).

Dicranum augustum (labeled as M-P), pucinellia phryganodes (F-P), and salix polaris (V-P) (Fig. 2) have extensive presence in Ny-Ålesund. These three plants were collected at each sampling site, and labeled as H0-M-P~H11-M-P, H0-F-P~H11-F-P, and H0-V-P~H11-V-P respectively. Puccinellia phryganodes was not present at the sampling sites H3, H7 and H10. Soil samples were also collected at each site and labeled as H0-S~H11-S. Additionally, these three plants samples (labeled as M-P, F-P, and V-P) and one soil sample (labeled as C-S) were collected as background references from east side of the airport in Ny-Ålesund, far away from the coal mine. One coal sample (labeled as H9-S) was collected in the mining area. All samples were refrigerated prior to analysis.

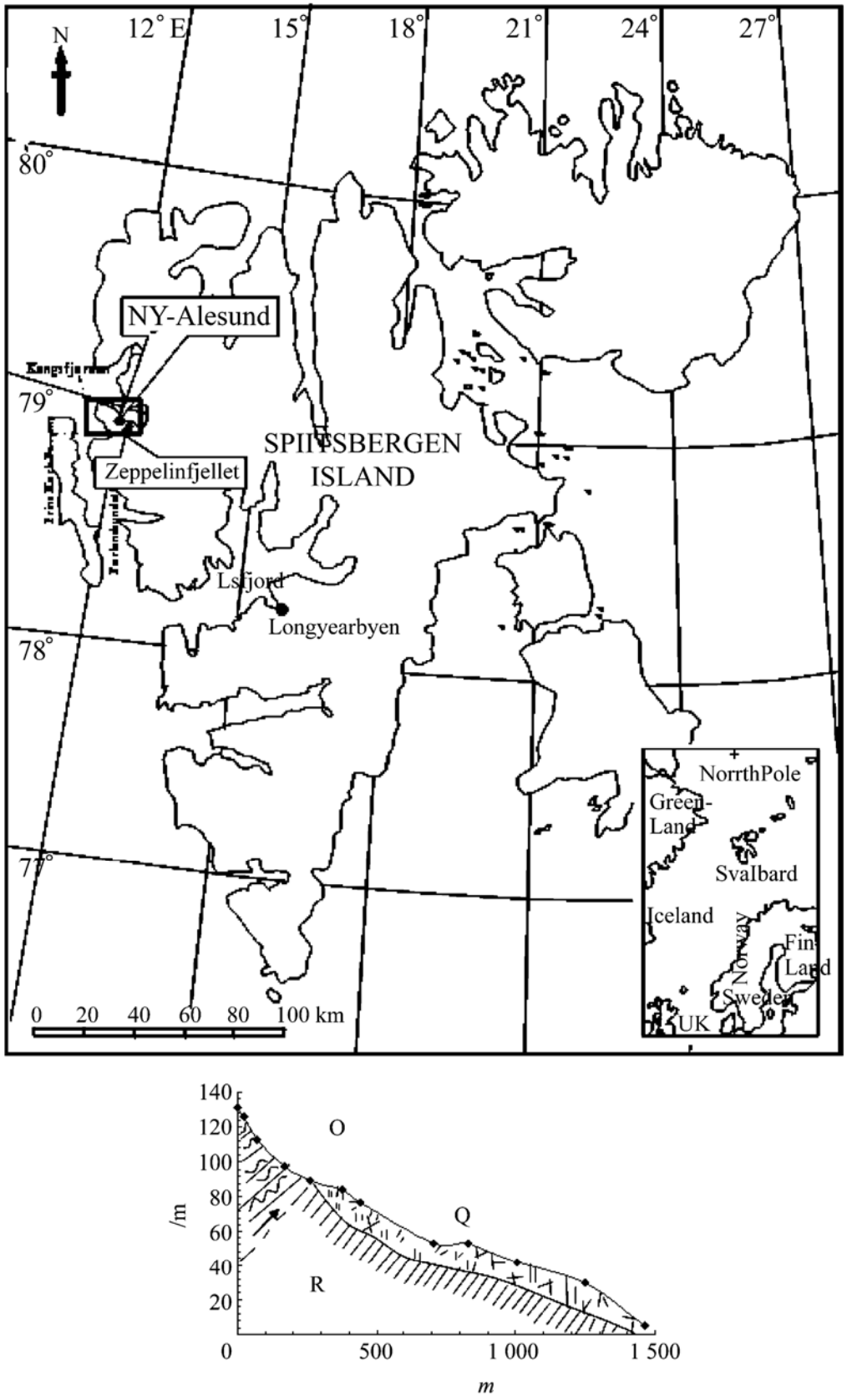

Fig 1 Map for Ny-Ålesund area, Arctic(a) and sampling location for the profile(b).

Before chemical analyses, plant samples were first washed in ultrapure water (MilliQ water) for 3-5 times to remove any adsorbed and external contaminants, air-dried in a clean laboratory, and homogenized. The cleaned and dried plant samples were cut into pieces, powdered and dissolved in high purity grade nitric acid, hydrochloric acid, and perchloric

acid. The soil samples were air-dried, sieved with standard 70 mesh dm^{-2}, powdered, and then dissolved in high purity grade nitric acid, hydrochloric acid, and perchloric acid.

Dicranum angustum Puccinellia phryganodes Salix polaris

Fig. 2 The three kinds of tundra plants most extensive in Ny-Ålesund, Arctic

Concentrations of Hg, Se and As were measured by atomic fluorescence spectrometry (AFS-2202a, Beijing Vital Co., China) with a detection limit (3 S.D. of the blank values) of 0.2 ng/g. The contents of Pb, Ni and Cd were determined by Graphite Furnace Atomic Absorption spectrometry. Abundance of P was determined by ultraviolet visible spectrophotometry (UV-VIS-8500, Nanjing, China). For details of these analytical methods, see Sun *et al.* (2001)[10]. For quality control purpose, certified reference materials (CRMs, supplied by National Research Center for CRM's of China, Beijing) were used as internal standards in proportion of 10% of total analyzed samples. The analytical values for the major elements and trace elements are within ±0.5% and ±5% of the certified ones, respectively.

Total sulfur was analyzed by KI volume method after combustion in SRJK-2 high temperature furnace[11]. Potassium Dichromate Volumetric method was used to measure the Total Organic Carbon (TOC) content with a duplicate error of 0.05%.

4 Results and discussion

4.1 Element levels of the soils

Table 1 lists the determined levels of TOC (total organic carbon), S and five heavy metals in the coal samples from the previous coal mining site and in the soil samples near the airport. The levels of S, TOC, Se, Sr, Hg and Cd in the coal sample are 3~39 times higher than those in the soil samples; the concentrations of Cu, Ni, Pb, Mn, Fe_2O_3 and As are 2~3 times lower; and there is no significant difference for Zn and P.

12 soil samples from the Tertiary coal layers at the lower part of Zeppelinfjellet Hill were analysed, and the results are plotted in Fig. 3. The levels of S, TOC, Se, Sr, Hg and Cd are strikingly higher than those in other areas; and the levels of Cu, Ni, Pb, Zn, Mn, Fe and As are lower. These substantial differences are very likely related with previous coal mining activities; and they are consistent with the observation that the levels of S, TOC, Se and Sr in coal are higher than those in the background soil (Table 1).

Table 1 Contents of TOC(total organic carbon), S and five heavy metals (g/g) in the coal and background soil (C-S) samples from Ny-Ålesund

	S/%	TOC/%	Se/ ppm	Sr/ ppm	Hg/ ppm	Cd/ ppm	Zn/ ppm
Coal	1. 374	81. 18	2. 73	242	0. 144	0. 68	81. 9
Soil	0. 038	2. 08	0. 38	80	0. 038	0. 15	69. 4
	Cu/ ppm	Ni/ ppm	P/ ppm	Pb/ ppm	Mn/ ppm	Fe_2O_3 / ppm	As/ ppm
Coal	12. 7	18. 3	513	7. 3	115	0. 72	3. 85
Soil	23. 4	44. 4	618	13. 7	451	3. 69	5. 3

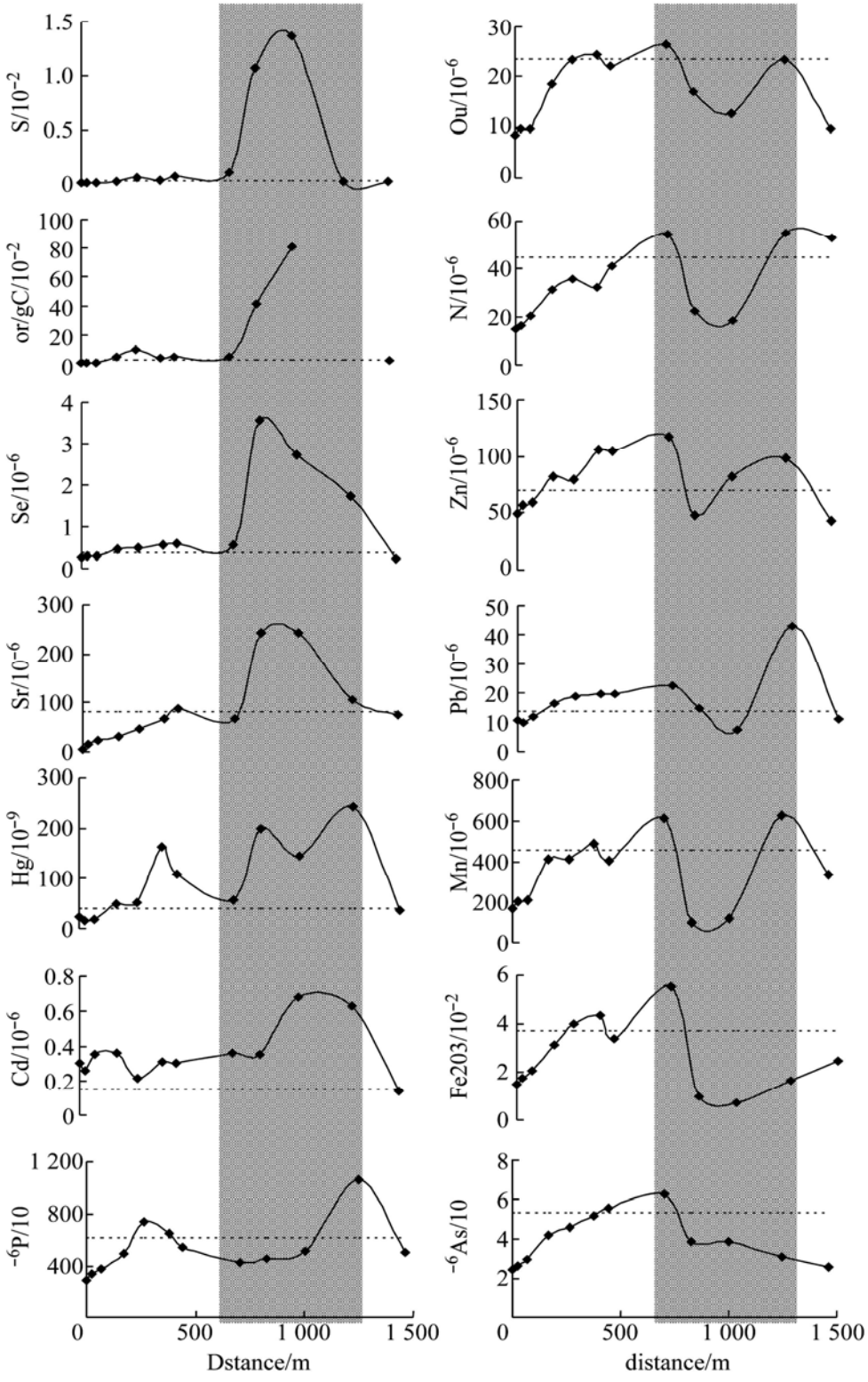

Fig 3 The variety of the elements concentration(g/g) of soil on the profile (dashed line presented the concentration of background soil(C-S)).

The concentrations of Hg, Sr, P, Cu, Ni, Pb, Zn, Mn, Fe_2O_3 and As in the non-coal mining area increase as the altitude decreases, and that is likely caused by weathering, transporting and leaching of these mobile elements. During sample collecting, it was noticed that soil particles become finer as the altitude decreases. The levels of S, TOC, Se, and Cd do not have such pattern. Closer to the seashore, the variations of element levels become complicated due to the impact of sea water and human activities.

The concentration of Hg and Pb peaked near the sampling point H11 of frequent human activities at the edge of the previous mining area, suggesting a significant contribution from human activities. The concentration of Hg is dramatically reduced near ocean (H2), likely caused by dilution of sea water vapor.

In summary, the high levels of Hg, Cd and S in the local soil samples are very likely caused by previous coal-mining activities in this area.

4.2 Relative enrichment of heavy metals and S in three tundra plants

Table 2 lists the determined concentrations of 10 heavy metal elements (Fe, Zn, Cu, Ni, Pb, As, Se, Cd, Hg) in the three tundra plants (M-P, F-P, V-P) and shows that these three plants have a substantially different and selective absorption of heavy metals and S. For convenience of comparison, relative ratios were calculated, M-P/V-P and F-P/V-P, of an element's concentration in plant M-P and F-P over that in V-P.

Table 2 Mean concentrations and coefficient of variation (CV) of 10 heavy metals in the tundra plants M-P, F-P, and V-P

Concentration/ppm		Fe	Zn	Mn	Cu	Ni	Pb	Se	As	Cd	Hg
M-P	Mean	5171.67	184.6	111.05	9.08	13.75	8.34	1.11	1.14	0.51	0.078
	Range	1240~12840	77.2~310	54.9~178	2.8~20.0	6.4~28.5	2.02~22.9	0.25~4.03	0.29~3.65	0.22~0.92	0.037~0.185
CV/%		69.58	36.65	38.54	59.07	53.41	64.81	92.19	81.14	37.01	56.71
F-P	Mean	1140.38	98.04	123.85	4.06	4.33	2.05	0.49	0.31	0.40	0.035
	Range	235~1920	40.7~243	55~208	1.56~6.69	1.9~9.2	0.48~4.27	0.18~2.34	0.13~0.45	0.1~1.02	0.018~0.050
CV/%		46.31	53.48	39.22	33.54	46.47	55.03	126.4	32.73	71.37	45.49
V-P	Mean	951.08	53.12	45.41	2.22	2.76	1.57	0.29	0.23	0.29	0.021
	Range	432~2640	30.8~167	19.3~127	0.76~4.22	1.2~4.5	0.73~3.64	0.13~1.32	0.13~0.36	0.13~0.6	0.012~0.042
CV/%		61.31	66.30	65.31	50.99	37.54	62.15	111.9	28.54	54.12	35.31

As shown in Fig. 4, the concentrations of nine heavy metal elements (Fe, Zn, Cu, Ni, Pb, Se, As, Cd, Hg), Mn and S in the three plants have the order: M-P > F-P > V-P, M-P = F-P > V-P and M-P = F-P < V-P, respectively. Overall, the concentrations of heavy metals in M-P are substantially higher than those in F-P and V-P. The levels of Hg, Se, Cu and Zn in M-P are twice those in F-P and 4 times those in V-P; the concentrations of Pb and As in M-P are 5-6 times those in F-P and V-P; the contents of Fe and Ni in M-P are twice those in F-P and 5-6 times those in V-P.

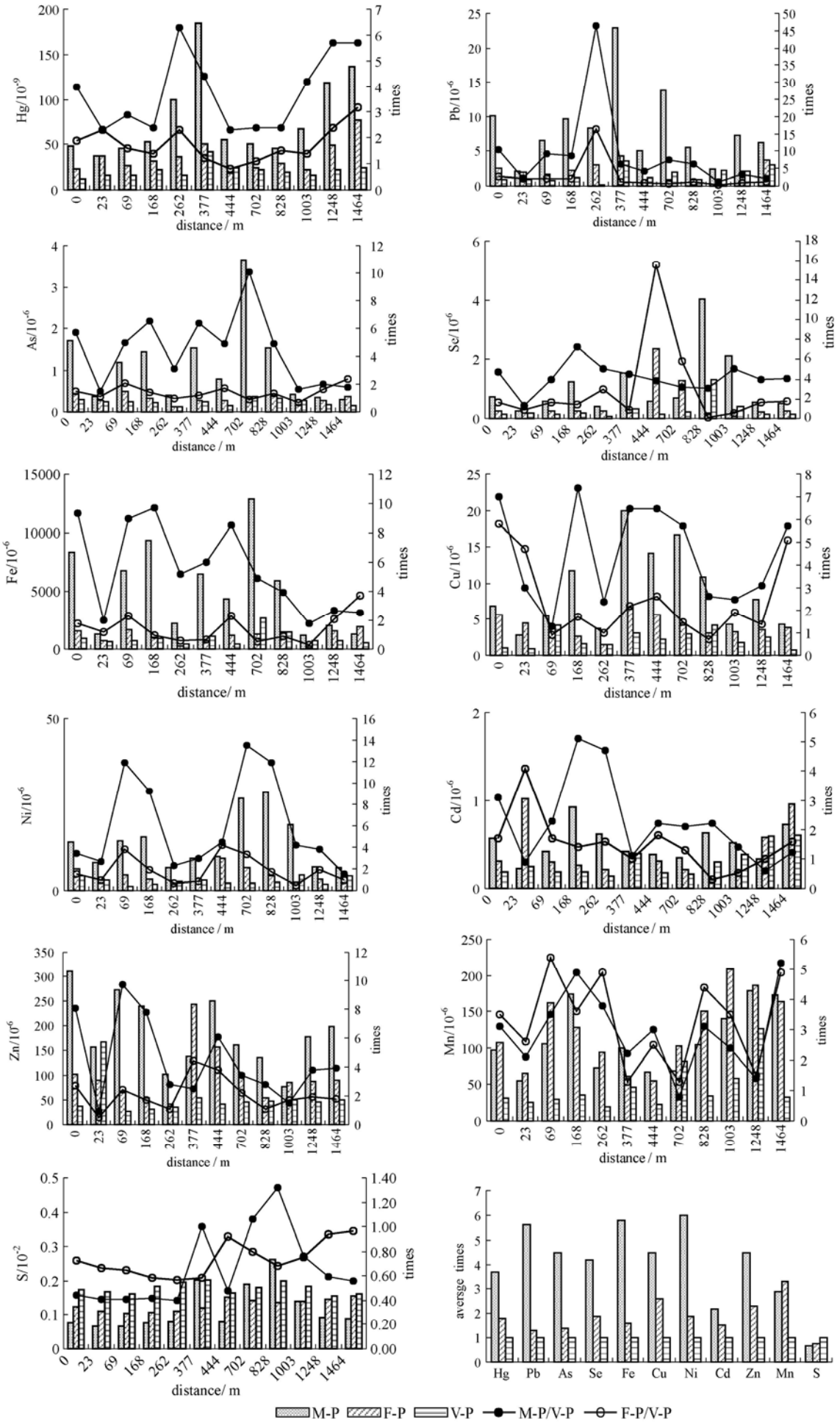

Fig 4 Comparing in absorbing sulphur and heavy metals among M-P, F-P, V-P.

These findings are consistent with previously published results. Maijia *et al.* (2004)[12] analyzed heavy metal levels in boreal bryophytes, lichens and vascular plants from Harjavalta Cu-Ni mine, and reported the relative accumulation of bio-elements (N, P, K, Mg, S, Ca) as vascular plants > bryophytes > lichens and of heavy metal elements (Fe, Zn, Mn, Cu, Ni, Cd, Pb) as brophytes > lichens > vascular plants.

Such heavy metal contaminations may have unfavorable impact on the growth and survival of plant. M-P. Holm *et al.* (2003)[13] studied acidic water in the coal mine of the Svalbard and reported that heavy metals and sulphate in the acid water may damage local tundra plants. Holte *et al.* (1996)[14] studied coal piles near the coast of Longyearben in the Svalbard and found that coal mine affected the survival and biodiversity of biological organisms in the gulf.

4.3 Potential of mosses used as bio-indicators for heavy metal contamination and other environmental changes in Ny-Ålesund

Mosses and lichen have been widely used to monitor heavy metal accumulation and pollution in Norway, Canada, Finland, Poland, and other Northern European areas[15-20]. Bargagli *et al.* (1998)[21] studied the accumulation profiles of Hg, Cd and Pb in the mosses from ice-free Edmonson Point and Northern Victoria Land of the Antarctic. Szczepaniak and Biziuk (2003)[22] reported that mosses are better bio-indicator for heavy metal pollution of atmospheric precipitation than lichens.

In Fig. 5, the levels of heavy metals and S in the soil samples and in the plant M-P of the areas with previous coal mining activities. The concentrations of S, Hg, and Cd in M-P and the soils of the area with previous coal mining activities were compared with those of the area without coal mining are much higher than those of the areas without. The relative accumulation of heavy metal elements (Se, As, Cu, Ph, Fe, Ni, Zn, Mn) in M-P is consistent with the one in the soil samples, especially in the areas affected by coal-mining (Shadows in Fig. 5). The pollution from coal-mining is of short-distance and low altitude nature, and the plants apparently absorbed nutrition and correspondent pollution elements mainly from soil. Thus M-P could be a good bio-indicator for heavy metal pollution in Ny-Ålesund.

4.4 Heavy metal levels in Ny-Ålesund and other areas

In Table 3, heavy metal levels in Ny-Ålesund were compared with those in other areas. Overall, Ny-Ålesund was a less heavy metal polluted than nearby Northern European human living areas, but much more than the tundras of the Alaska, Greenland, and the Antarctic.

Reimann *et al.* (2001)[23] measured the heavy metal concentrations in mosses collected from nine different catchments in Finland, Russia and Norway. The median level of Cd is 0.129 ppm (0.035-0.267), of Hg 0.051 ppm (0.04-0.765), and of S is 960 ppm (613-2020). In the tundra of Greenland, the mosses have much lower level of Cd[24]. Cd and Hg are not detectable in mosses of the tundra in Alaska[21]. In this study, the mosses

in Ny-Ålesund, Svalbard, have higher levels of heavy metal. The level of Cd is 0.455 ppm

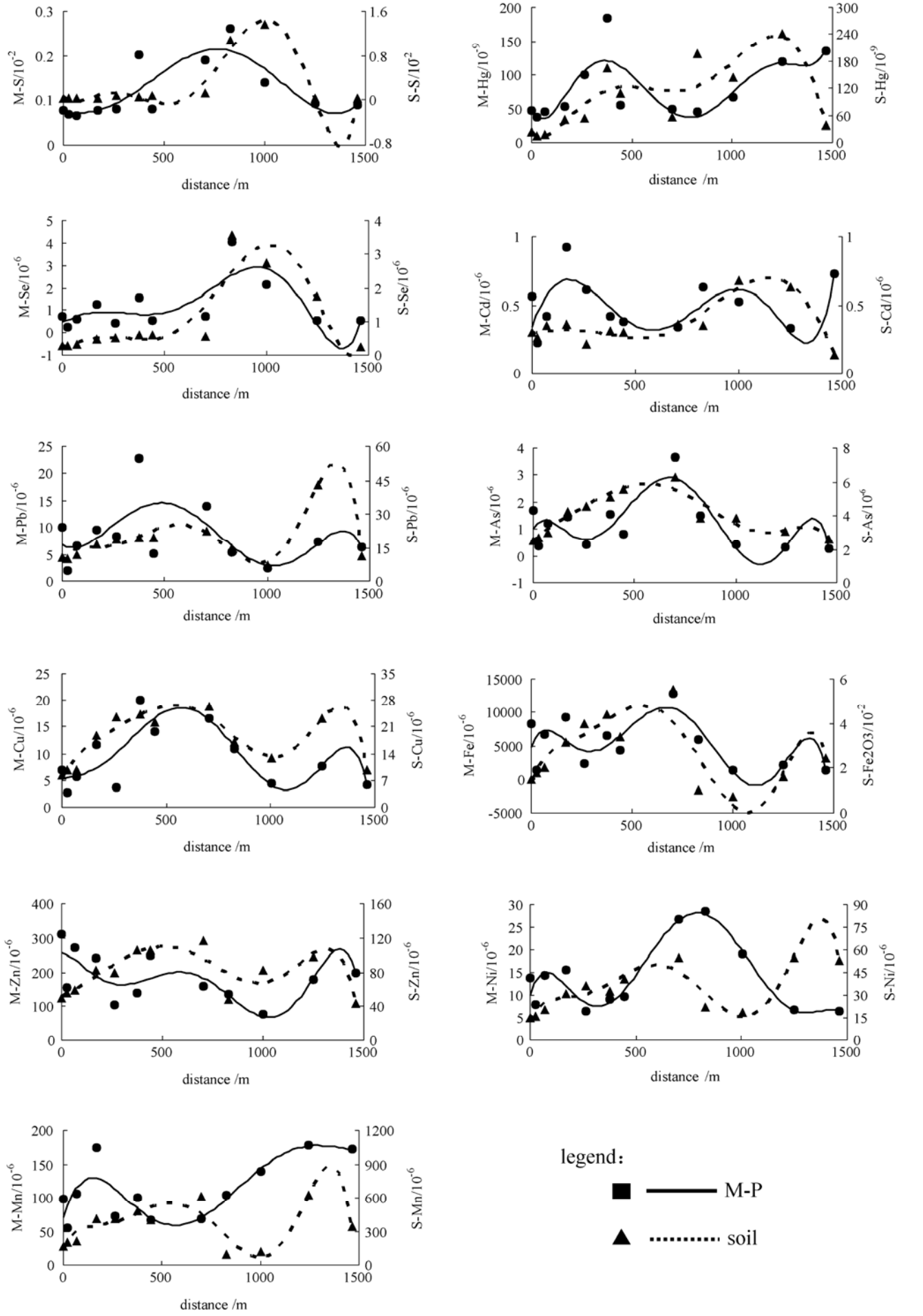

Fig. 5 Comparing in absorbing sulphur and heavy metals among M-P, F-P, V-P.

(0.33-0.63), of Hg is 0.070 ppm (0.045-0.119), and of S is 1710 ppm (920-2620). The higher levels of Hg, Cd and S in Ny-Ålesund are very likely caused by local previous coal mining activities.

Table 3 Concentrations of Cd, Hg and S in mosses from European countries around Arctic in 1995, Arctic, Antarctic, and Ny-Ålesund

Location		Moss species	Cd /ppm	Hg/ppm	S/ppm	Data source
European countries around Arctic			130~440	/	/	Grodzinska *et al.* (2001)[18]
Arctic	Greenland tundra	Hylocomium splendens	0.08~0.36	0.07~0.13	/	Pilegaard (1987)[24]
	Alaska tundra	H. splemdens	< DL	< DL	/	Wiersma *et al.* (1986)[25]
	Northern European countries in the Arctic	Pleurozium	0.035-0.267 0.129(Med)	0.04-0.765 0.051(Med)	613-202 0960(Med)	Reimann *et al.* (2001)[23]
	Barrents shore	Barents-Moss	0.032-0.536 0.132(Med)	< 0.04-0.765 0.055(Med)	610-2020 965(Med)	Reimann *et al.* (2001)[23]
Antarctic	King George Island	Andreaea regularis	< DL	< DL	/	Shen Xiansheng *et al.* (2001)[26]
	King George Island	Moss	0.063-0.162 0.10(Med)	0.017-0.14 0.075(Med)	/	Pu Jiabing *et al.* (1995)[27]
	Northern Victoria upland	Bryum pseudotriquetrum Sarconeurum glaciale	0.06-0.24 0.10(Med) 0.05-0.28 0.13(Med)	0.08-0.23 0.12(Med) 0.10-0.25 0.14(Med)	/	Bargagli *et al.* (1995)[21]
Ny-Ålesund		Dicranum angustum	0.33~0.63 0.455(Med)	0.045~0.119 0.070(Med)	920-2620 1710(Med)	This article

Note: DL, detection limit; /, not available; Med, median.

5 Conclusion

Ny-Ålesund has the worse pollution of Hg, Cd, and S in the Arctic, very likely caused by previous coal mining activities, and the pollution is worse than that in the Antarctic. The local tundra plant Dicranum Angustum has a substantial and selective enrichment of these heavy metals, and it can be used as a good bio-indicator for such heavy metal contamination.

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