PRELIMINARY SURVEY OF FLUORINE CONTENT IN SOIL AND PLANTS AROUND WUDA COALFIELD, INNER MONGOLIA, CHINA

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ABSTRACT: A total of 69 soil samples and 80 *Bassia dasyphylla* (sandwort) leaf and stem samples from Gobi desert land in the Wuda coalfield, Inner Mongolia, were analyzed. The results show that the average fluorine content in the soil of the coalfield area, the periphery of the coalfield area, and the Wuda urban area was 1250, 757, and 552 µg/g, respectively, which is higher than the background value. This suggests that the coal seam fire burning there, leads directly to fluorine pollution within a limited area. The average fluorine content in the leaves and stems of *Bassia dasyphylla* sampled immediately around the sites of the ongoing coal fire was 532 and 388 µg/g, respectively, while the concentration in leaf and stem samples collected in areas remote from the fire, but within the field, was 146 and 107 µg/g, respectively. This implies that this historic coal fire, which has been burning for the past 50 years, is responsible for a general deposition of fluorine in the local area. This result suggests that coal seam fires may also be a novel source of fluorine pollution in some urban areas. The scenario of urban areas being adjacent to coal seam fires is not limited to Wuda but is relatively common in northern China, and elsewhere. Whether or not there are other cities currently under the influence of coal seam fires merits further investigation.

Keywords: *Bassia dasyphylla*; Fluorine pollution; Inner Mongolia; Soil; Underground coal fire; Wuda, Wuhai.

INTRODUCTION

Coal seam fires can be triggered by an exothermic oxidation reaction of coal with oxygen when coal seams have long-term exposure to air.[1-5] When the heat generated from the oxidation reaction within the coal seam reaches ignition temperature, the result is self-ignition.[1,6] In geological terms, coal seam fires are intrinsic natural events, a notion that is supported by the presence of coal fires in the USA,[7] Tajikistan,[8] and China.[9] However, coal seam fires have increased tremendously since the industrial revolution due to large-scale coal mining, which exacerbates exposure of the coal seam.[5] Coal seam fires have been reported around the world, are considered a global catastrophe, and are most serious in industrialized and coal-rich countries.[5, 10]

China is the largest producer and consumer of coal globally, and currently has the most serious coal fires. They are mainly distributed along the northern coal belt of China.[11] At the beginning of the 21st century, the coal fire area, observed remotely by satellite infrared detectors, has spread over a wide area: 4800 km stretching from Heilongjiang Province in the east to Xinjiang Uygur Autonomous Region in the west. The overall population density in this region is low because most of the terrain is arid, semi-arid dryland, or desert.[5,9,12] Due to the rich coal and other natural resources there, many medium to small cities arose with the rise of the coal mining

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industry. Generally speaking, these densely populated coal-based cities are in the vicinity of large coal mines, many of which have suffered, or currently are suffering, from coal fires.[13] Therefore, it is very important to study the potential environmental impact of coal fires on local residents, especially the impacts on the living environment in populated areas.

High fluoride levels can cause negative effects on environmental and human health. For humans, these effects may include dental fluorosis, skeletal fluorosis, intellectual impairment of the exposed population, and other health hazards.[14] Fluorides can be emitted from industries that use high temperature processing, such as for the production of steel, aluminum, glass, china, phosphate fertilizer, and brick, as well as from coal burning.[15,16] As the largest coal consumer, fluorine pollution caused by coal-burning is the main fluorine source in China. Toxic substances in coal and coal mining by-products, including fluoride, trace elements, HF, SO_2, and particulate matter, are released into the aquatic and atmospheric environment due to combustion. It was reported that coal combustion accounted for ca. 10% of the total atmospheric fluorine emission in the United States.[17]In northern China, a total of 66,398.5 t of fluorine has been emitted due to combustion of 8 Gt of coal.[18]

Coal fires in the Wuda coalfield of Inner Mongolia are the largest coal fire in China and have been burning for 50 years (Figure 3A).[9] Studies on emissions (e.g., CO_2, CO, VOCs, PAHs, SO_2, etc.[19,20]) from this coal seam fire have been reported in recent years, in studies mainly focused on modeling the carbon emission inventory of coal seam fires. Results of our previous studies demonstrated that a high portion of the mercury in coal can be released into the environment from coal seam fires, based on *in situ*, real-time measurement.[13] However, little is known about fluorine emission from underground coal fires and the health impact this might have on adjacent populated areas. Considering that there are many cities in northern China that are adjacent to a coal fire, this study focused on a typical coal-based city near a major coalfield with a fire history of 50 years.The surface area of the coal field is very disturbed, and plants that might be typical of such areas are rare (Figure 2A). This paper gives the fluorine content of soil and plants in the coal fire area and the nearby populated area in order to reflect the fluorine pollution caused by coal fires. It is worth mentioning that the surface area of the coal field is extreme Gobi desert, and that plants are rare except for *Bassia dasyphylla*, which is a pioneer plant in the desert areas of northern China. For this reason, *B. dasyphylla* was the main plant used in the fluorine pollution research. According to our observations, it is also common in Inner Mongolia Dongsheng, Ningxia Rujigou, Xinjiang Hami, and other coalfields.

MATERIALS AND METHODS

Study site: Wuda is located in the south-central part of Inner Mongolia in North China (Figure. 1). It is bordered by the Gobi Desert in the west, the Helan Shan Mountains in the southwest, is adjacent to the Ningxia Hui Autonomous Region, and the Yellow River crosses through from south to north at its eastern edge.[13,21] The area of Wuda District is about 220 km^2. Jiang et al. and Kuenzer et al. found the climate is characterized by a strongly continental, arid climate with a generally stony desertified terrain.[21,22] A prevailing northwesterly wind is observed in this area, with an annual average wind speed of 4.8 m/sec and the area has an average of 32 gale days per year.[13,23] The Wuda coalfield is located northwest of the Wuda District, has an area of 35 km^2, and is sited 5 km west of Wuda City. It is rich in Carboniferous-Permian coal with over 16 minable seams and a reserve of 660 million tons. It mainly produces bituminous coal with a high sulfur content.[13]

The large-scale industrial mining in Wuda coalfield dates back to 1958, along with the establishment of several gangue hills and reports of intermittent gangue hill fires.[13, 24] The first coal seam fire in this area was found in 1961, and the number of fires had expanded to 6 by 1978. This number of coal zones reached 26 by the end of 2004.[13] From 2006 to 2008, an unreasonable surface excavation method lead to an accelerated spreading of the coal fire[13,21,25] and resulted in extreme desertification of the surface of the entire coal field. Even the western edge of the coalfield was gradually engulfed by the desert (Figure 3B). Since 2009, the government had paid much attention to the control of the coal fire in Wuda and most of the flames visible at the surface have disappeared, but there still exists some risk of spreading.[21]

This study focused on two areas: (i) Area A is made up of the Wuda Coalfield and the peripheral area, (ii) Area B is the urban area of the Wuda district (39º30’21”N, 106º43’11”E). The site of Wuhaihu Island (39º31’12”N, 106º44’24’E) was chosen as a control area. The relative positions of A, B, and the control area are shown in Figure 1.

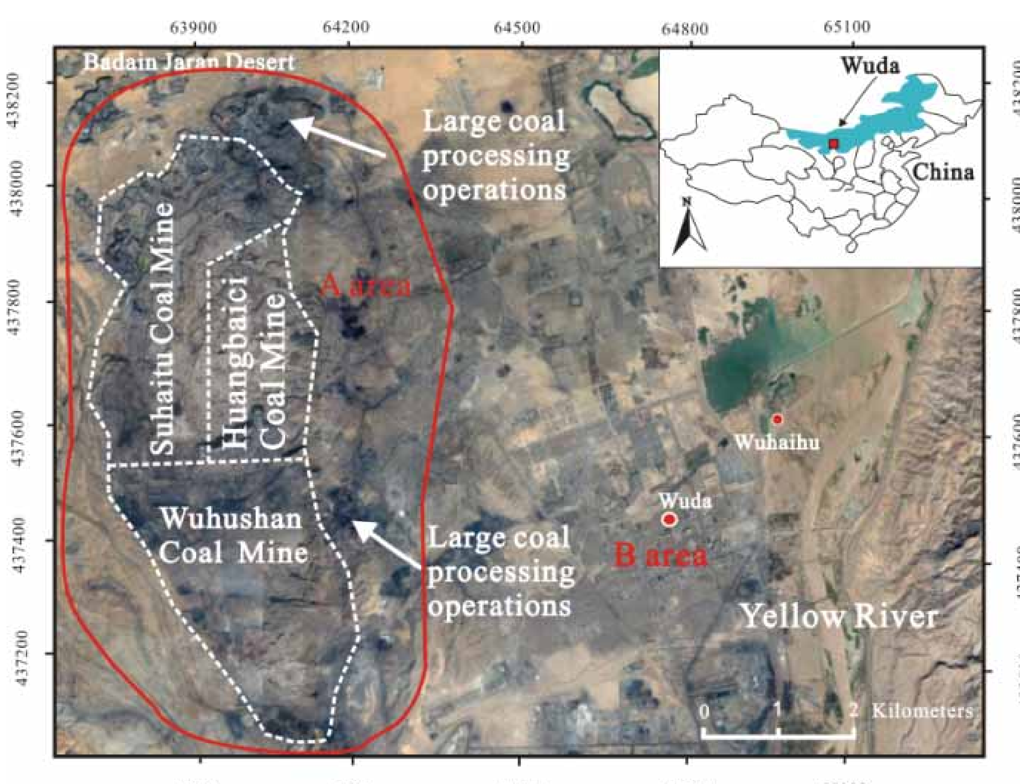
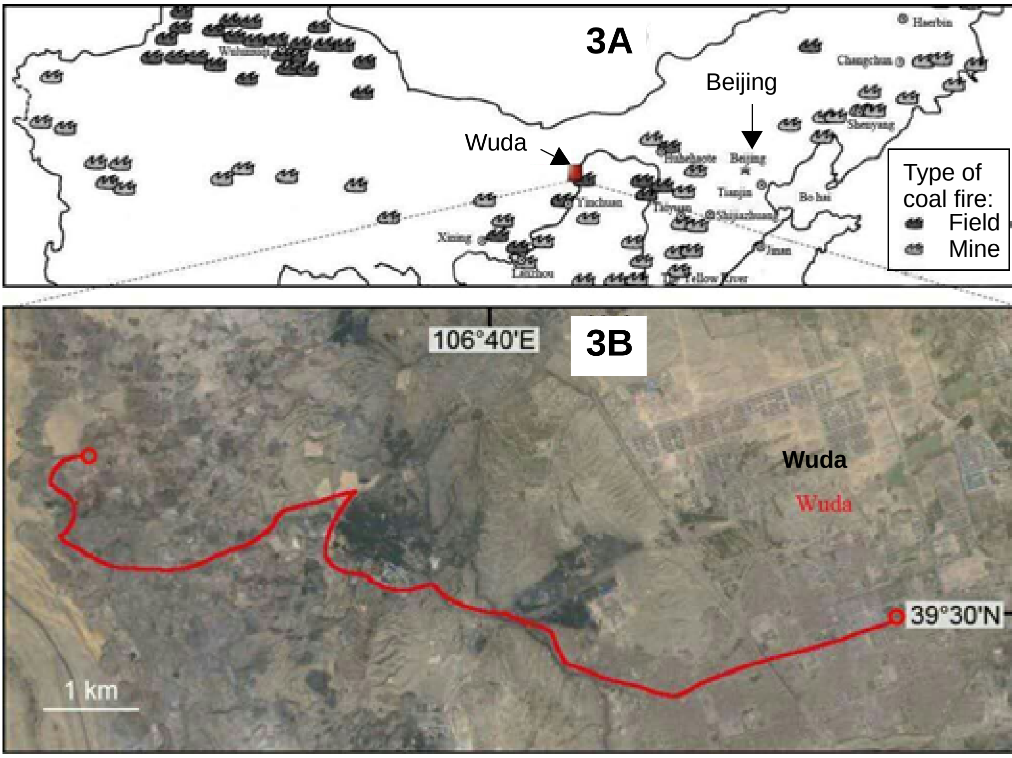


Figure 1. Satellite image of the study area.

The landscape of some parts of Area A is shown in Figure 2. Based on the status of the coal fire, Area A can be approximately categorized into two parts: a central area and a peripheral area. The central area contains the Wuhushan coal mine, the Suhaitu coal mine, and the Huangbaici coal mine (Figure 1). Its ground surface is thick limestone and the underlying coal seam has been ignited, which results in heavy smog near the surface (Figure 2B). Surface vents and cracks (Figure 2C), with or without fumes, are scattered within the central area, along with several small-scale sites with open flames (Figure 2D). In the peripheral area, there are many different types of flattened surfaces with no vents, cracks, or open flame sites, but lots of smoke can be observed rising from the land surface (Figures 2E, 2F, and 2G). Some of the ground surface of this area has recently been leveled to use for the storage of raw coal for the coal washing plant, which had come into operation by the time of our study. In addition, there are three large coal processing operations and some coal-based industries, such as a power plant, nearby.

Figures 2A–2G. Surface landscapes of the area undergoing coal fire in the Wuda coal field, Wuhai.[25] 2A: typical plants in the coal field; 2B: heavy smog near the surface; 2C: surface vent or crack; 2D: open flames; 2E, 2F, and 2G: smoke arising from the land surface.

Area B is the urban area of Wuda District with a human population of 130,000 and it is crowded with district administrative offices, schools, factories, coal mine offices, parks, and residential areas. There are also several coal-fired power plants located to the south (downwind) of the Wuda urban area. A recent study shows that the urban area of Wuda is under direct influence (downwind) of hazardous gases from the coal fire area due to local meteorological conditions.[26] The urban area of Wuda, rather than the whole Wuda District and Wuhai City, is the original settlement for the coal mine workers. Therefore, the urban area of Wuda is suspected of having endured the accumulated influence of coal seam fires for over 50 years.



Figures 3A and 3B. 3A: Distribution of coal fire zones in north China (from Zhang et al.[9]); 3B: Desertified topology of the Wuda coal field, Wuhai, Inner Mongolia (from Google Earth); Red line = road where the specimens of *B. dasyphylla* (sandwort) leaves and stems were collected (from Liang et al.[25]).

Soil sample collection: In Area A, the Wuda Coalfield and the peripheral area, 69 soil samples were collected. In the central part of Area A, due to the complexity resulting from the terrain and the coal fire, soil samples were not collected close to vents, cracks, or flames. From Area B, the Wuda urban area, 22 soil samples were collected. In addition, 12 samples were collected from the control area (Wuhaihu Island). This island formed by artificial accumulation, is adjacent to the Yellow River, and is almost without industrial pollution.

Sample collection was achieved using a grid method in accordance with the Chinese National Standards (DB21T 1289-2004). At each sampling site, a composite soil sample composed of three subsamples to 20-cm-depth was collected using a stainless steel spade. The locations of all samples were determined by GPS, and the environmental conditions for each sample were recorded. All samples were sealed in polyethylene bags. In the laboratory, soil samples were air dried, gently crushed to disaggregate larger clumps, and sieved through a 2 mm sieve to remove stones, coarse materials, and other debris. The samples were then ground in an agate mortar, and sieved using a <100 size mesh, for chemical analysis.

Plant collection: The WY series of samples of *Bassia dasyphylla* were taken from the outer edge of the coal fire in the center of Area A. The plants were often covered with soot. The branches and leaves of *B. dasyphylla* were cut, and three parallel samples were collected.

The WR sample series of *B. dasyphylla* was collected along the coalfield road, starting northwest of the coalfield (39º30’15”N, 106º36’52”E) and ending at the southeastern corner (39º29’31”N, 106º41’07”E) (Figure 3B). The sampling points along the highway are far away from the field zone, so the growth and environment of the *B. dasyphylla* collected in this area were not directly affected by smoke from the coal fire. The BG series of (mixed plant) samples was collected in Wuda People’s Park (Wuda urban area: Area B) (39º29’59”N, 106º43’10”E).

The samples were washed three times with pure water and three times with high-purity water, placed on a clean bench for 48 hr, and then crushed for use. For comparison, some of the samples were not washed but simply air-dried and then pulverized for analysis.

Determination of total fluorine in soil: Total fluorine in the soil was determined by the combustion-hydrolysis fluoride ion-selective electrode method in accordance with the Chinese National Standards (GB4633-1997) (Figure 4). The electrode used was a composite fluorine ion electrode (Mode: perfectION™) which was provided by the METTLER TOLEDO company located in Switzerland. This was coupled to an electrometer also provided by the METTLER TOLEDO company. Standard solutions (0.1–5 mg/L) were prepared from a stock solution (100 mg/L) of standard reference materials provided by the National Institute of Metrology, China. For quality control, standard reference materials (GBW07403 [soil, China], GBW07406 [soil, China]) were randomly analyzed with each batch of coal samples. In all our fluorine analyses, the relative standard deviations were less than 10%.

Determination of fluorine in plants: Total fluorine in plants was determined by oxygen flask combustion (OFC) using the catalyst fluoride ion-selective electrode method.[27] 0.03 g of powdered coal, 0.01 g of catalyst (WO_3), and 0.005 g of co-catalyst (Sn) were precisely weighed, mixed, and transferred to a 40×40 mm ash-free filter paper (Advantec, 5C). A schematic of the procedure is given in steps 1–6 in Figure 4. After being folded into a cylindrical shape, each paper with a sample was inserted into the platinum cage attached to the flask plug. Then the fuse was ignited, and the samples were combusted in a 500 mL oxygen-filled quartz flask with 5 mL of water. After combustion, the flask was shaken for 2 min and then allowed to stand for 1 hr. The resulting absorbent was then filtered and the pH adjusted to 5–7. TISAB solution (5 mL) was added, and the volume of the solution was made up to 25 mL. After shaking, the solution was left to stand for more than 30 min, and the fluoride ions in the solution were then measured with a composite fluorine ion electrode as mentioned above.

The accuracy of the measurements was assessed using the addition method in samples. Recoveries of addition samples were 95.48% and the method repeatability was tested by analyzing five replicates of one coal sample. The coefficient of variation in the coal replicates was 2.26%.

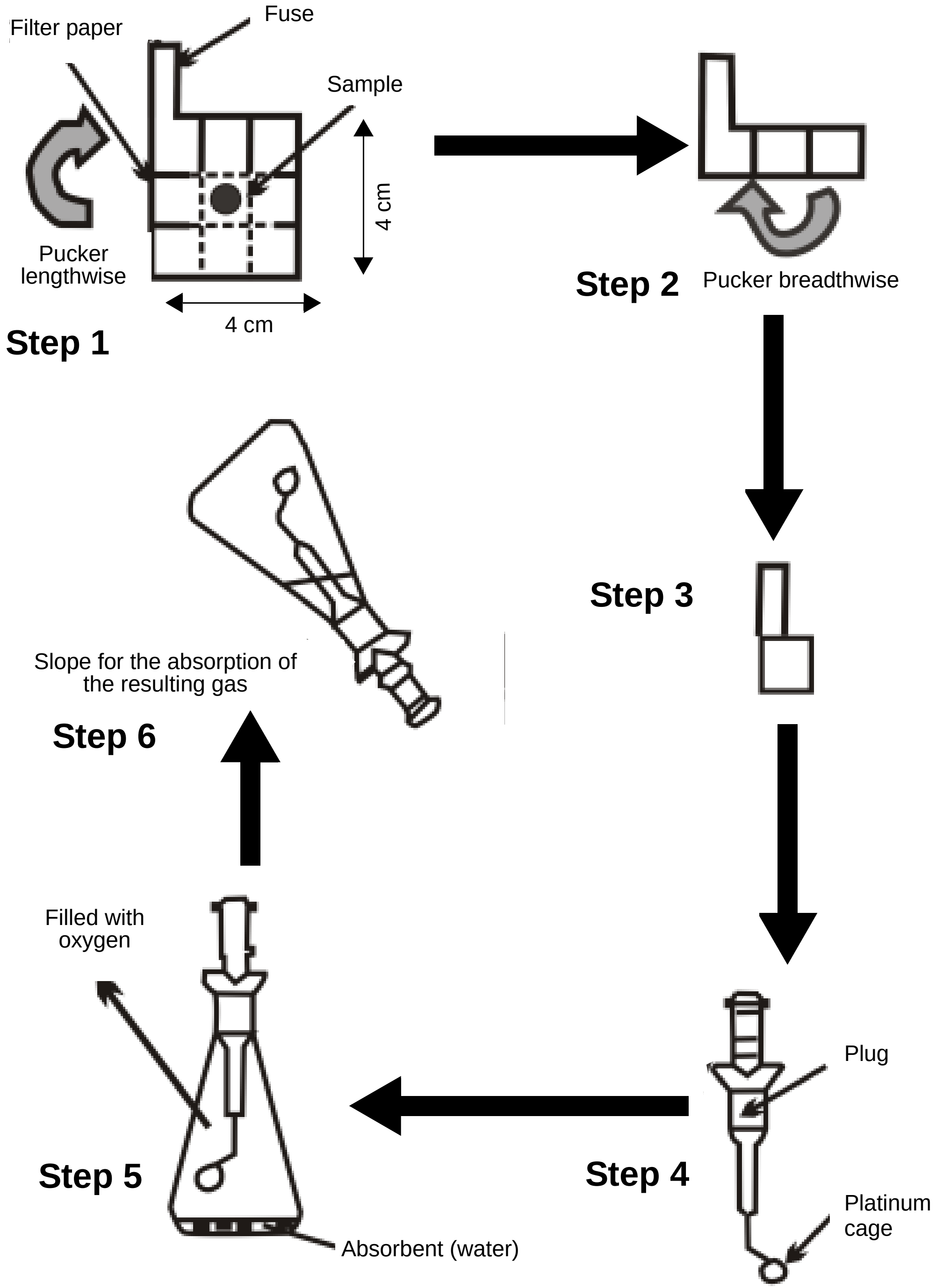


Figure 4. Procedure of the oxygen flask combustion (OFC) method. Steps 1–6: After being folded into a cylindrical shape, each 40×40 mm ash-free filter paper with a sample was inserted into the platinum cage attached to the flask plug. The fuse was then ignited, and the samples were combusted in a 500 mL oxygen-filled quartz flask with 5 mL of water. After combustion, the flask was shaken for 2 min and allowed to stand for 1 hr before further processing and the measurement of the F level in the absorbent.

RESULTS

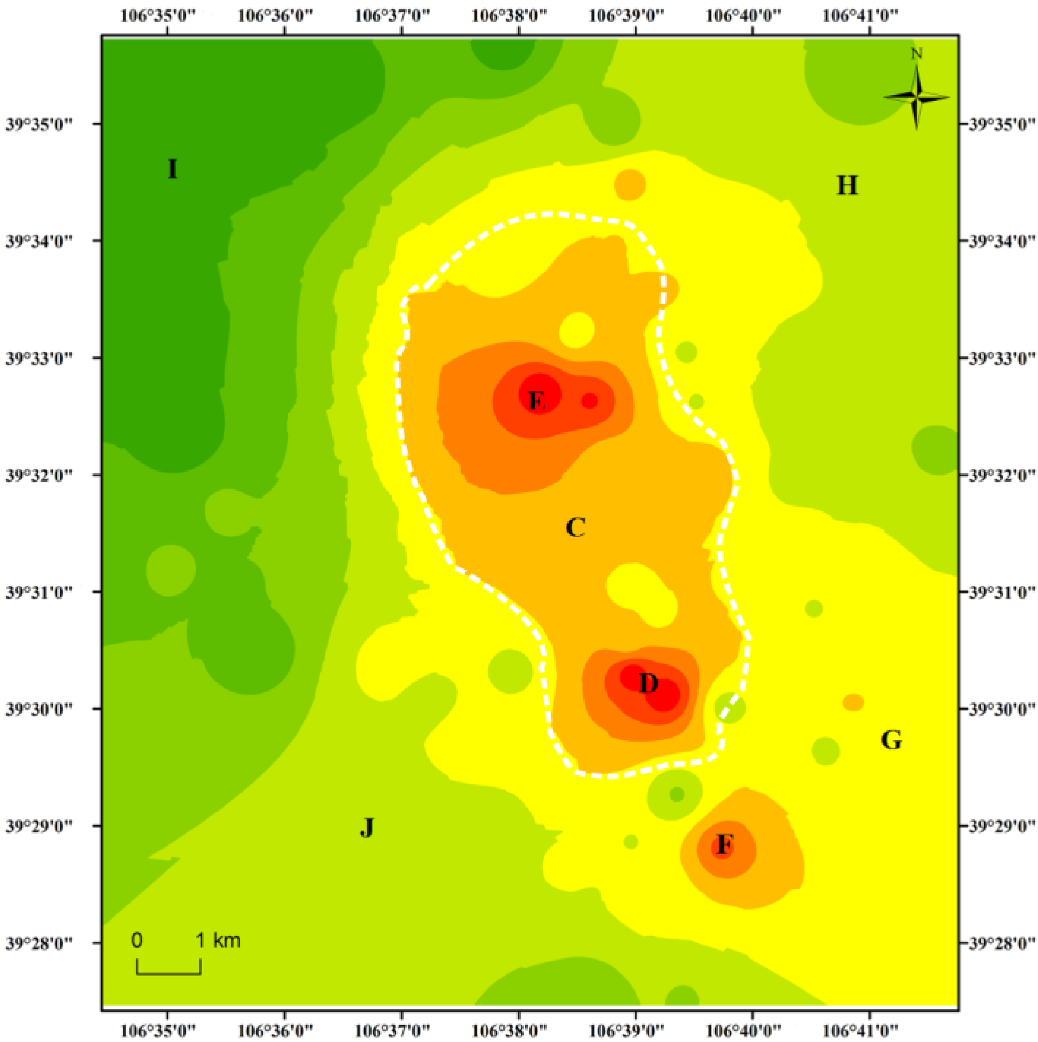
Fluorine distribution in the soil around the coalfield area: The total fluorine content of the soil of the central and peripheral coalfield areas is illustrated in Figure 5. The overall average fluorine content in the central area was 1250 µg/g (range: 983–1668 µg/g) and that in the peripheral area it was 757 µg/g (range: 235–1406 µg/g) (Table 1).

Table 1. Soil fluorine concentration in the study areas
(n= number of samples, RSD=relative standard deviation)

Locality	Mean (µg/g)	RSD	Min (µg/g)	Max (µg/g)	n
Sites around ongoing coal fires	1250	0.15	1003	1668	16
Sites away from the fires, but within the field	757	0.31	235	1406	53
Wuda urban area (area B)	552	0.36	196	1043	22
Wuhaihu Island (control)	240	0.17	186	293	10

The results show that the soil fluorine content in both areas was much higher than the background values (average 240 µg/g) (Table 1), and was about 4-times the background value for Inner Mongolia (285 µg/g).[28] Moreover, the average fluorine content was significantly higher than that around the Jiaozuo fluorides factory, China,[29] but slightly lower than that in the Jinhua fluorite ore area, China.[30] These results indicate diffusion and advection of the fluorine released from point sources to surrounding areas (advection=the transport of a substance by bulk motion; the transfer of heat or matter by the flow of a fluid, especially horizontally in the atmosphere or the sea).

Area A: central part: The spatial distribution of soil fluorine in this study was interpolated using the inverse distance weighting method in ArcGis, as shown in Figure 5. Figure 5 shows a vivid description of the soil fluorine in both the central and peripheral part of Area A. The white dotted line was roughly the boundary between the central area (C, D, and E) and the peripheral area (F, G, H, I, and J). The orange area (C) is not far from the area with vents and cracks from which smoking points could be observed. The fluorine content in this area reached 1142–1475 µg/g, suggesting intense coal seam smoldering beneath this area. This could be explained by the diffusion and advection of fumes with fluorine released from vent, cracks, or smoke points and then deposited in this area. The D area of the central part is close to a giant burning coal pillar that gives off strong fumes in the Wuhushan coal mine. This area (D) exhibited the highest soil-F content (1534–1668 µg/g) in the central part. The E area also exhibited a high level of total F content in the soil, and this could be attributed to the relatively low terrain of the (E) area, which promotes the deposition of fluorine. Generally, the soil fluorine content of the central area greatly exceeded the background value.



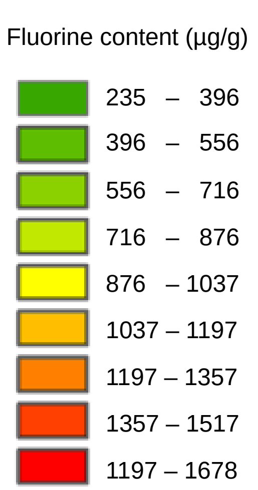


Figure 5. Distribution of soil fluorine content in area A (the Wuda Coalfield and the peripheral area).

Area A: peripheral part: In the peripheral part of Area A, the fluorine content exhibited a northwest-to-southeast gradient, as shown in Figure 5. The F-area at the southeast corner exhibited a high level of F in the topsoil (average 1406 µg/g), while the G, H, J, and I areas showed fluorine content ranges of 908–1088, 843–946, 631–806, and 235–573 µg/g, respectively. Admittedly, the common northwesterly wind would play an important role in determining the gradient along which the diffusion and advection would bring the fluorine from the central to the peripheral parts, and the northwesterly wind would concentrate them to the south. However, there is also consistency between the gradient and local industrial activities. The F-area is the locale of a coal washing plant that stops working intermittently. Long-term coal washing may lead to the direct discharge of coal washing residue to the ground, resulting in enrichment of the soil fluorine content. The yellow (G-area) in the southeastern corner is close to Wusitai Industrial Park and could be under the long-term influence of industrial activities. The high fluorine content of the yellow area surrounding the coalfield could be attributed to the influence of the coal fire or to randomly abandoned coal piles. The H-area in the north has low terrain and is downwind of coal fire areas and of two large, coal-fired power plants. The J-area is at the junction of the desert and coal mine, and the increase of F in the soil there may share the same source as for the H-area. The I-area in the northwest corner is adjacent to the Badain Jaran Desert. This location, combined with the common northwesterly wind, has allowed this area to remain uncontaminated to some degree. In the peripheral part of the A-area, the soil fluorine content was elevated to a certain degree and even the western desert was contaminated. Sometimes the whole sky in this study area was filled with smoke. Consider that there were four coal-washing plants in the peripheral area during our study, and no workers were observed wearing any kind of mask. The fluorine released from the fire zone, and from the surrounding area, pose a great threat to human health. In addition, this phenomenon is not unique in the coal field, given that there are many other facilities sharing similar conditions in this area.

Fluorine in the soil of the urban area: The spatial distribution of the total fluorine in the soil of the Wuda urban area (Area B) is illustrated in Figure 6. The overall average was 552 µg/g (range: 272–1043 µg/g), which is more than twice the background value (240 µg/g). It is evident that the urban area is fluorine-polluted. Clearly, the soil in R-area had the highest fluorine content (average 1043 µg/g), and the fluorine appeared to be distributed from a point source around the R-area. In general, the F concentration decreased to the southeast as the distance from the R-area increased. These studies show that the anthropogenic sources of soil fluorine in Shashi and Yuncheng are mainly the coal-fired plants and aluminum smelter, respectively.[31] The soil fluorine content may have a similar source. However, the substantial excess may be attributed to the underground coal fire, suggesting a potential fluorine resource for coal-based cities. One difference between a coal fire and a coal-fired power plant is that the latter exhausts emissions through a chimney while the coal fire emits fluorine at ground level. The latter situation brings more deposition and disturbance from the near-surface atmosphere to the local environment.

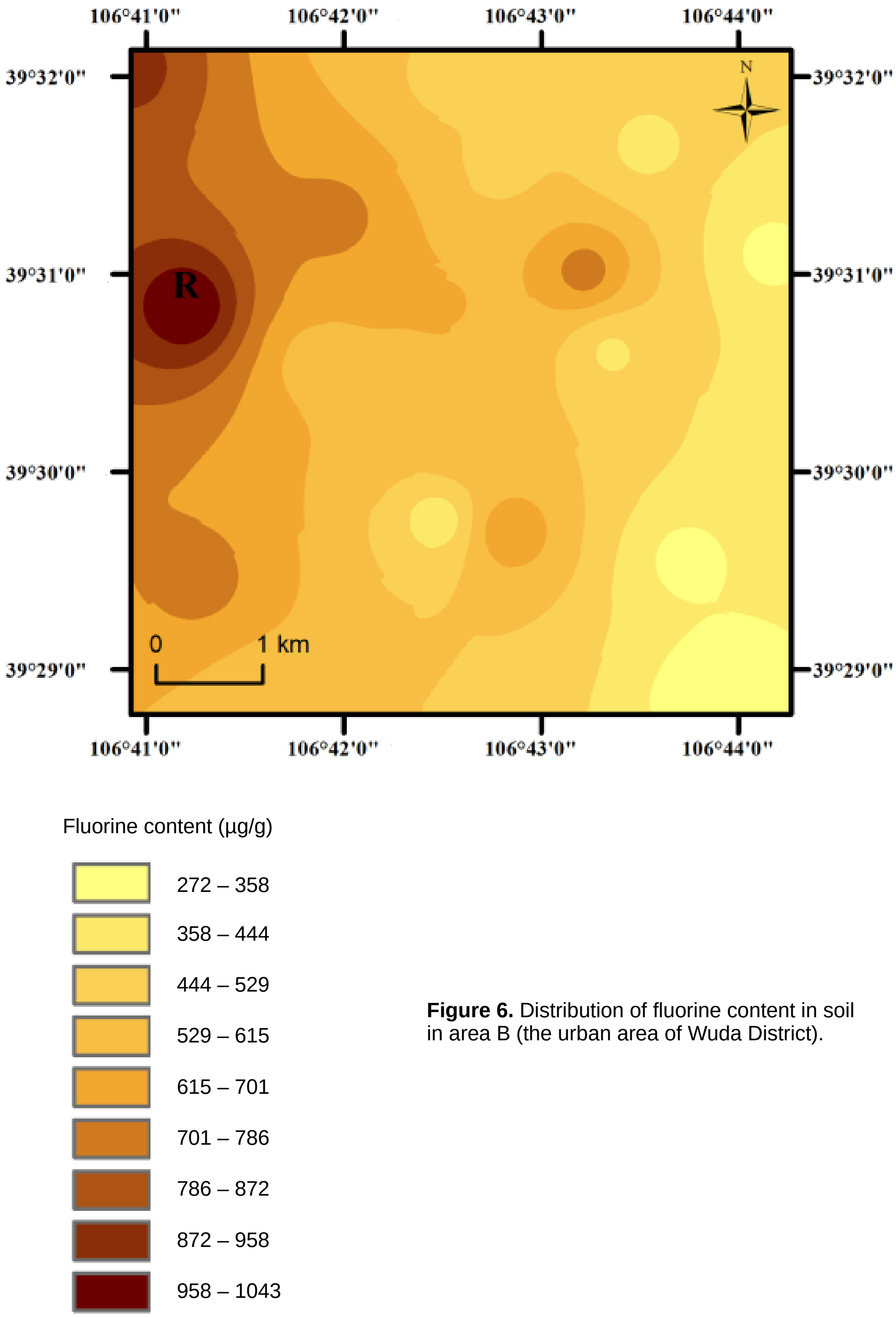


Figure 6. Distribution of fluorine content in soil in area B (the urban area of Wuda District).

The roughly northwest to southeast gradient of fluorine shown in Figure 6 supports the influence of the underground fire, given that the urban area is downwind from the fire zone. The high fluorine content in the middle may also be caused by industrial activity because a hot power plant was observed there. A recent study concerning SO_2 found that the Wuda urban area was under the long-term influence of the coal fire in the Wuda coal field.[26] Liang et al. also confirmed directly that the coal seam fire released mercury and could lead to an elevated level of gaseous mercury in the near-surface air in the Wuda urban area.[13] The case of an urban area adjacent to a coal seam fire is not limited to Wuda, but rather it is common in northern China. Whether there are other cities under the influence of coal fires requires further study.

Fluorine in plants: The plant leaf fluorine content in the WY series *B. dasyphylla* samples, under the influence of the coal fire, is shown in Table 2.

Table 2. Plant leaf fluorine concentration in the study areas. (n= number of samples, RSD=relative standard deviation, WY=the site around the ongoing coal fires in the Wuda coalfield, WR=away from the fires but within the Wuda coalfield, BG=far away from the Wuda coalfield)

Sample	Mean (µg/g)	RSD	Min (µg/g)	Max (µg/g)	n
WY series	532	0.20	327	641	11
WR series	146	0.45	65	343	29
BG series	76	0.41	28	129	10

The overall average fluorine content of leaves and stems was 532 and 388 µg/g, respectively. For reference, the F-content of the unwashed leaves and stems was 687 and 516 µg/g, respectively. These results are significantly higher than that in plants around low-pollution areas in Yuncheng, China (23.3–54.2 µg/g)[32] and Shashi, China (16–131 µg/g),[31] but close to that in plants around fluoride-ore areas such as aluminum smelters and fluorite mines.[30, 33] Aluminum smelters and fluorite ore areas are, among others, recognized fluorine sources. Thus, the higher fluorine content of the WY-series samples, compared to that in low-pollution areas, suggests that fluorine contamination is likely in regions near coal fire zones.

There are two ways in which plants absorb environmental substances: through the roots and through the foliage. Desert pioneer herbs have an outstanding ability to absorb water, and other things, from their environment. The fact that the leaf fluorine content (532 µg/g) is higher than that of the stems (388 µg/g) tends to indicate that plant fluorine pollution in the vicinity of the coal fire zone is caused not only by soil fluorine pollution but also by air fluorine pollution and that the latter may in fact predominate.

The fluorine content in the leaves of the WR-series samples from the coalfield area is listed in Table 2. The overall average fluorine content of leaves and stems was 146 and 108 µg/g, respectively, which was significantly higher than that found in the low-pollution area.[30] This tends to indicate that the roadways along the coalfield area used to represent the overall condition of the Wuda Coalfield could be fluorine-polluted. In addition, the average leaf fluorine content of the BG-series mixed plants was 76 μg/g (47–154 μg/g), which is still higher than that of the low-pollution area. This implies that the People's Park may also be fluorine polluted, which means that the Wuda urban area is also likely F-polluted. In fact, we would also have collected *B. dasyphylla* samples from this area but this species was not found in the field work, because artificial plants have replaced the natural ones, to the extent that there are no *B. dasyphylla* plants in the urban area.

Bio-indicators are used not only for prospecting, but also for environmental pollutant identification, investigation, monitoring, and evaluation.[33,34] Liang et al. used *B. dasyphylla* to indicate mercury pollution in the Wuda coalfield.[25] Therefore, *B. dasyphylla* could also be used to reflect fluorine pollution.

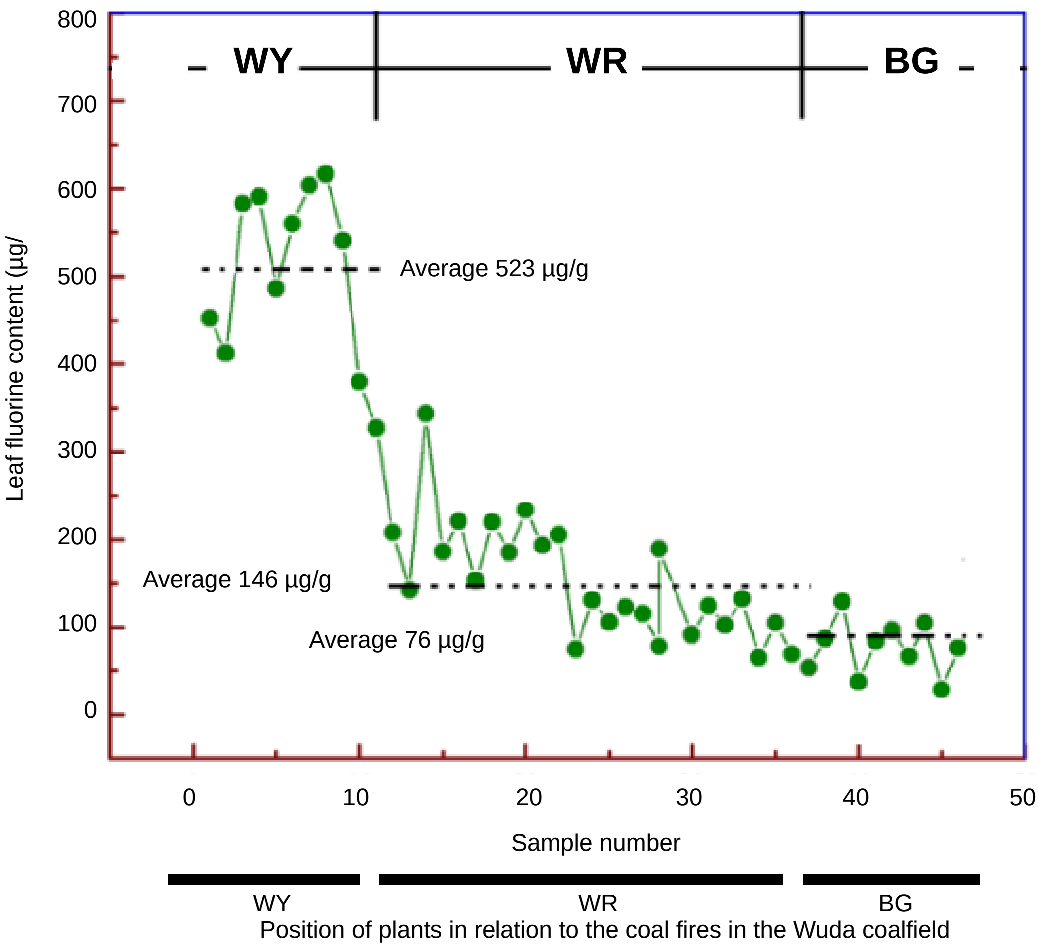


Figure 7. Graph of the leaf fluorine content in plants from the central part of the Wuda coal field to outside the Wuda coal field: WY: the site around the ongoing coal fires in the Wuda coalfield; WR: away from the fires but within the Wuda coalfield; BG: far away from the Wuda coal

In summary, the leaf fluorine of all the samples, plotted in Figure 7, can be used as a bio-indicator of the different levels of plant pollution in the different regions. More specifically, the pollution level of the Wuda urban area (represented by People's Park) could be close to that of the Yuncheng urban area and that of the Wuda coalfield (represented by the roadside samples (WR) was higher than of typical power plants. The contamination level near the coal fire zone (WY) would be second only to a typical fluorite factory. In addition, neither *B. dasyphylla* nor other plants could grow in the central part of the coalfield area because of the coal fire. It is clear that the airborne fluorine contamination in the central part of the coalfield area (WY) must exceed the surrounding peripheral area (WR) and is likely to reach the level typical of a fluorite mine.

CONCLUSIONS

It can be concluded that coal seam fires can release fluorine and lead to an elevated total fluorine level in soil and plants, both in the coalfield area and in the adjoining downwind urban areas. The total fluorine content of soil was 1250 µg/g in the center of the coalfield, and 757 µg/g on the periphery. The average fluorine content in the leaves and stems of *B. dasyphylla* sampled immediately around the sites of the ongoing coal fires were 532 and 388 µg/g, respectively. The F-content in the leaves and stems of *B. dasyphylla* collected at areas remote from the fire, but within the field, were 146 and 107 µg/g, respectively, implying that the historic coal fire, which has been burning for the past 50 years, may have resulted in a general deposition of fluorine. Considering that there are two coal washing factories in the peripheral area and many other facilities in the whole coalfield, which share similar conditions, this elevated fluorine level should raise concerns of occupational hazard. Furthermore, the soil fluorine content in the Wuda urban area reached 648 µg/g, much higher than the background value. The fluorine content of the mixed plants in the Wuda urban area was also higher than that of a low-pollution area. The Wuda urban area population of 130,000 is located downwind of the coal seam fires and has therefore received a long-term influence from these fires for over 50 years. This suggests that a coal seam fire may be a novel source of fluorine pollution in coalfields and adjacent urban areas. The scenario of an urban area being adjacent to a coal seam fire is not limited to Wuda, rather it is relatively common in northern China and elsewhere. Therefore, whether there are other cities currently under the influence of coal seam fires requires additional, comprehensive study.

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