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Speciation Analysis of Cadmium in Dust Fall About Northern China Towns

MIN WANG[1,*], YUE-QUAN DENG[1], FA-QIN DONG[1], XIAO-CHUN HE[1], QUN-WEI DAI[2], SHI-YONG SUN[2], YUN-BI HUANG[2], JUN TANG[2], WU CHEN[2], LI-ZHU LIU[2] and YING-XUE GENG[2]

[1]School of Materials, Southwest University of Science and Technology, Mianyang 621010, Sichuan Province, P.R. China
[2]School of Environment and Resource, Southwest University of Science and Technology, Mianyang 621010, Sichuan Province, P.R. China

*Corresponding author: Tel: +86 15508026362, E-mail: wmfxhx@163.com

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In this article, the determination of the speciation of cadmium in dustfall about Northern China towns with reliable analytical method is reported. The distribution of total Cd varies in different regions, among which Duoba town of Qinghai Province tops it with the Cd amount of 5.3921 μg/g. And that of Shuangta town, Hebei Province is 2.0256 μg/g and the rest distribution are rather low, with the distribution 0.6-1.5 μg/g. Seeing from the Cd's average content level, these speciations' percentage are as follows: exchangeable form of 0.1484 μg/g, carbonates of 0.2283 μg/g, organic combination of 0.1750 μg/g and residual of 0.9179 μg/g. Besides, mainly form is residual and of low Fe-Mn oxides.

Key Words: Dust fall, Cadmium, Speciation analysis, Northern China town.

INTRODUCTION

Air pollution is increasingly serious that airborne particulate matter has been absorbing a great deal of inorganic pollutants and organic pollutants, which pose a significant health hazard once being absorbed into the body. Thus, the analysis of the toxic substances in the airborne particulate matter has become a research focus. Dust fall is a display of the accumulation of the settlement of atmospheric particulates in quite a long time period, representing the particle accumulation and its average situation in its region. According to the reports about the determination of cadmium, usually, the total concentration measurement is done through cadmium salvation by hydrochloric acid, nitric acid, hydrofluoric acid, perchloric acid in sequence, then determination by ICP-MS, ICP-OES method[1-3]. Meanwhile, reported by the rare speciation analysis, the special analysis methods to the environmental samples such as soil, sludge and the alike which is similar to airborne particle are mainly Tessier method, Forstner method, BCR method, *etc*.[4-9]. Among them, Tessier method is the common method now which can divide the element into 5 states, including Cd of exchangeable state, carbonates, Fe-Mn oxides combination state, organic combination state and residual state. Among them, Cd of exchangeable state leached with the highest toxicity activity once being in the neutral condition. While, carbonates and organic combination state distributes in the extraction conditions when pH = 5 and pH = 2 with the higher toxicity activity, which is similar to acidic conditions afforded by stomach acid. Compared to the former four states, residual state is with the lowest toxicity. Therefore, the determination of cadmium in each form plays a significant role in judging the element toxicity. This paper has presented Tessier method to determine the speciation of Cd in dustfall. We have determined Cd speciation of dustfall sample in these areas and discussed its distribution characteristics.

EXPERIMENTAL

1 mol/L $MgCl_2$ solution, 1 mol/L CH_3COONa-CH_3COOH Buffer solution, 0.04 mol/L $NH_2OH{\cdot}HCl$ solution, 0.02 mol/L HNO_3 solution, 30 % of H_2O_2, 3.2 moL/L CH_3COONH_4 solution, hydrochloric acid, hydrofluoric acid and perchloric acid, the reagents used which are all guaranteed reagents and solution is all prepared with triple distilled water. Sampling point distributions labeling map is shown as Fig. 1.

To select the indoor area with long-term dust while without clean for a long time as the sampling point, such as the warehouse, bottom-tank of the double-decked doors and windows, floors that no people live on for quite a long time; to collect dustfall sample by brush sweeping and select those can pass through 200 mesh sieve hole and preserve at -4 ºC refrigerator.

Firstly, put 0.5000 g of dustfall sample from each sampling point into the Teflon crucible. Mean while, make a blank sample. Mix 10 mL HF soaking for 2 h, place it on the electric hot plate and solute it to small volume by low temperature, add the conc. HCl of 5 mL, Concentrated HNO_3 of 5 mL and

TABLE-1
TESSIER METHOD OF DUSTFALL DETERMINING EXPERIMENT (μg/g)

	1	2	3	4	5	Average Value	Average percentage	RSD (%)
Exchangeable state	nd	0.0007	nd	nd	nd	0.0001	0.0223	200.00
Carbonates	0.0010	nd	0.0003	nd	0.0033	0.0009	0.1522	138.21
Fe-Mn Oxides Combination	nd	nd	nd	nd	nd	nd	nd	nd
Organic Combination	0.0168	0.0232	0.0308	0.0180	0.0462	0.0270	4.588	39.99
Residual	0.5580	0.5823	0.5580	0.5513	0.5498	0.5599	95.2371	2.09
Total Content	0.5757	0.6061	0.5890	0.5693	0.5992	0.5879		2.35

TABLE-2
MORPHOLOGICAL ANALYSIS OF Cd IN DUST FALL OF NORTHERN CHINA TOWNS (μg/g)

	(1)	(2)	(3)	(4)	(5)	(6)	(7)	(8)	(9)	Average value
Exchangeable state	0.0405	0.0288	0.0826	0.0032	0.1140	0.5538	0.4963	0.0167	nd	0.1484
Percentage	6.87	3.75	7.25	0.30	6.54	35.79	9.78	2.20	nd	8.05
Carbonates	0.0757	0.0718	0.1612	0.0393	0.0537	0.1531	1.4065	0.0893	0.0045	0.2283
Percentage	12.83	9.36	14.14	3.73	3.08	9.89	27.73	11.81	0.76	10.37
Fe-Mn oxides combination	0.0163	nd	0.1612	nd	nd	nd	0.0114	nd	nd	0.0210
Percentage	2.77	nd	0.57	nd	nd	nd	0.22	nd	nd	0.40
Organic combination	0.0344	0.0460	0.0507	0.1552	0.0461	0.0470	1.0767	0.0820	0.0374	0.1750
Percentage	5.84	6.01	4.45	14.72	2.65	3.04	21.23	10.86	6.29	8.34
Residual	0.4231	0.6201	0.8383	0.8566	1.5286	0.7936	2.0811	0.5676	0.5526	0.9179
Percentage	71.70	80.88	73.58	81.25	87.73	51.28	41.03	75.13	92.94	72.84
Added amount	0.5901	0.7667	1.1393	1.0542	1.7424	1.5475	5.0720	0.7555	0.5945	1.4735
Actual measured total amount	0.6590	0.7570	0.9228	1.2541	2.0256	1.4900	5.3921	0.8245	0.6138	1.5488

concentrated $HClO_4$ solution sample of 2 mL. Then, while the sample continuously diluted to transparent, heat it again till the white smoke removed, then dissolve the salt in the crucible by using the concentration of 50 % aqua regia, make the solution to a 50 mL volumetric flask and ready for ICP-AES determinations.

(1) Qiaodong District of Zhangjiakou City, Hebei Province; (2) Suburb of Yongning County in Ningxia Province; (3) Yanhu District, Yuncheng City, Shanxi Province; (4) Maiji Town of Tianshui City, Gansu Province; (5) Mount Shuangta Town of Shuangluan District, Hebei Province; (6) Western Suberb of Shijiazhuang City; (7) Duoba Town of Huangzhong County, Qinghai Province; (8) Suberb of Jingning County of Gansu Province; (9) Surberb of Tuoketuo County in Inner Mongolia Autonomous Region

Fig. 1. Sampling point distributions labeling map

Notes: Since sampling point number from drawing no. 2 to no. 6 are the same as the drawing no. 1, they will not be marked again.

Prepare accurately 2 g dustfall sample from each sampling point, making a blank sample as well. Then, put both samples and the blank sample into quartz conical flask of 100 mL with cover carefully for the step by step extraction operation of different speciation of Cd[6]. Exchangeable Cd carbonates Cd, Fe-Mn oxides combination Cd, organic combination Cd and residual Cd follow Tessier method. Sample solutions above are all determined by ICP-AES method.

RESULTS AND DISCUSSION

Take dustfall samples from Tuoketuo County, Inner Mongolia Autonomous region for experiment method including reproducibility (Table-1).

Table-1 shows Fe-Mn oxides combination in the dust fall has not been tested at all. Besides, few exchangeable state and carbonates has been tested and the dustfall is mainly existed in residual, account for 95 % with the total content of approximately 0.60 μg/g.

View by reproducibility, while the total content and residual in sample are much higher, the exchangeable state, carbonates, Fe-Mn oxides combination in the sample are extremely low, most of which have not been tested or even they can not be determined for RSD is rather large. And for the total content and residual in sample are much higher, RSD measured is at approximately 2 % with better measurement accuracy. Besides, RSD of the organic combination reached 40 % as its lower content. Therefore, the measuring accuracy depends on the content of cadmium each speciation.

Table-2 shows the number of the added content in each form of the sample is in line with the total content obtained and measured, which proves Tessier method of dust fall determining experiment is reliable.

Analysis to the Cd form in dust fall about 9 villages and towns of northern China and the result is shown as Table-2.

Table-2 showed that there are huge differences between Cd's speciation distribution with different sampling point. On the whole, Cd's Fe-Mn oxides combination in all sampling point are few, six simples among which have not been tested. Averagely, residual account for the mainly percentage composition of the forms with 0.9179 μg/g, other speciation being second including exchangeable Cd of 0.1484 μg/g, 0.2283 μg/g carbonates, 0.1750 μg/g organic composition. Besides, the total content of Cd diversified from each point, among which Duoba County, Qinghai Province topped with the Cd total content of 5.3921 μg/g, Shuangta town, Chengde city, Hebei Province 2.0256 μg/g, Western Suberbs, Shijiazhuang city 2.0256 μg/g and Maiji town, Gansu Province 1.2541 μg/g ranked second. And the rest points are with much lower Cd distribution between 0.6-1 μg/g. Consequently, the region the sampling point located at concerns the total content of Cd distribution. Such as Duoba county, Qinghai Province with the high Cd concentration for its closing to metallurgy and chemical industrial zone which brings serious industrial pollution as well as being a thoroughfare with much dust. Situation in the sampling points which near to big city is same, including Shuangta town, Chengde city, Hebei Province, Western Suberbs, Shijiazhuang city and Maiji town, Gansu Province. Other points which are far away from large and medium-sized cities and thoroughfares with the low pollution enjoy the low Cd concentration.

Condition of exchangeable Cd in the dust fall in China northern villages and towns has been shown in Fig. 2A. Fig. 2Aa showed that the exchangeable Cd in Western Suberbs, Shijiazhuang City with 0.5538 μg/g and Duoba town, Huangzhong county, Qinghai Province with 0.4963 μg/g are the highest, followed by that of Qiaodong district of Zhangjiakou City, Hebei Province, Yanhu district, Yuncheng City, Shanxi Province, Shuangta town, Chengde city. Besides, the exchangeable Cd in some other sampling points are rather few such as Suburb of Yongning County in Ningxia Province, Maiji town of Tianshui city, Gansu Province and Suburb of Jingning County in Gansu Province and that of surberb of Tuoketuo County in Inner Mongolia Autonomous Region has not be tested. While Fig. 2Ab concluded that the Western Suberb of Shijiangzhuang city has the highest percentage of Cd, followed by Qiaodong cistrict of Zhangjiakou city, Hebei Province, Yanhu District, Yuncheng city, Shanxi Province, Shuangta town, Chengde city, Duoba town, Huangzhong County, Qinghai Province. And percentage of Cd in these points ranked the lowest including Maiji town of Tianshui city, Gansu Province, Suburb of Jingning County in Gansu Province and Tuoketuo County in Inner Mongolia Autonomous Region. Exchangeable form refers to a chemical form that metal, especially the soluble salts absorbing in clay, humus and other components which is sensible to environment change and will be released in the neutral condition with highest toxicity activity[10]. It can be seen that the percentage component of exchangeable Cd in pollutants from large and medium-sized cities and the industrial zone is much higher than other sampling points, otherwise the lower.

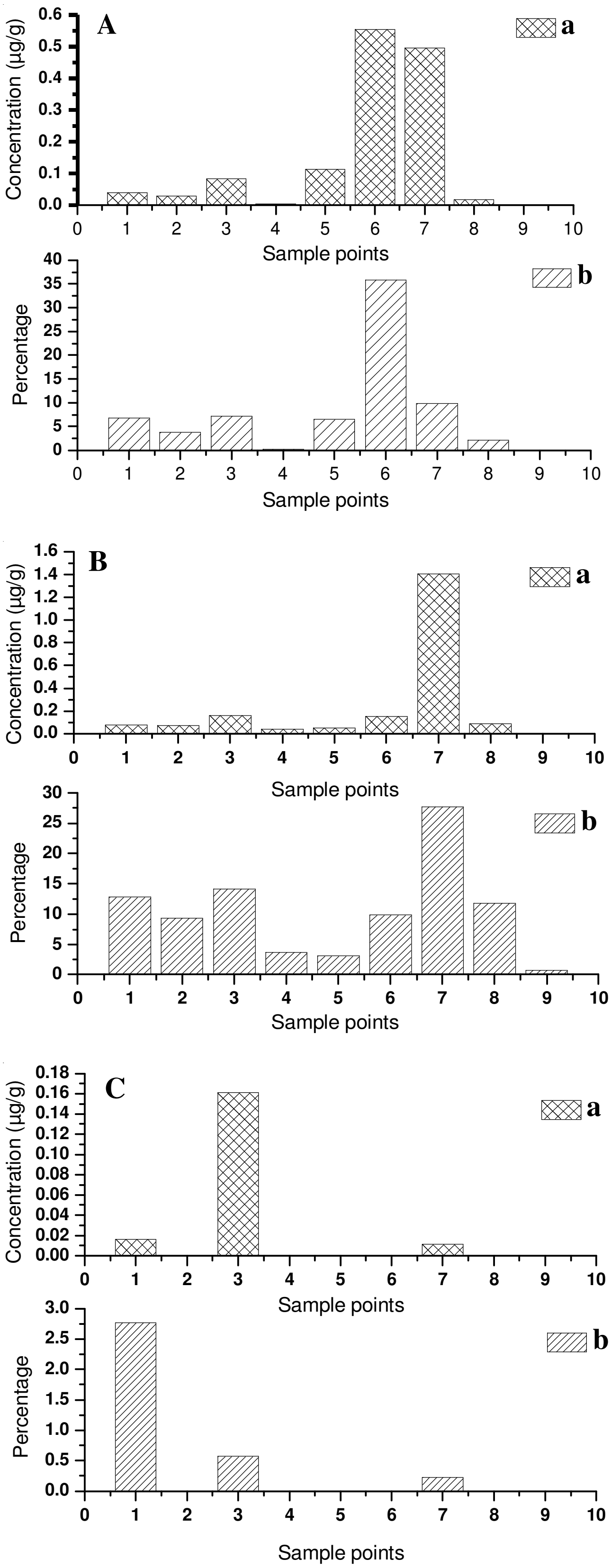
The presence of cadmium carbonate in the dust fall about China northern villages and towns are shown in Fig. 2B. Fig. 2Ba showed that the Cd carbonates in Duoba town, Qinghai Province ranked first reaching 1.4 μg/g, followed by Yanhu district, Yuncheng city, Shanxi Province and western Superb of Shijiazhuang city. Besides, carbonates in other sampling point are rather low and no carbonates tested in Superb of Tuoketuo County, Inner Mongolia Autonomous region. While seen from Fig. 2Bb, Duoba County of Qinghai Province has the highest percentage of carbonates which accounts for 27.7 %, followed by Qiaodong district of Zhangjiakou city with 12.8 %, Suburb of Yongning County in Ningxia Province with 9.3 %, Yanhu district, Yuncheng city, Shanxi Province with 14.1 %, western Suberbs, Shijiazhuang city with 9.8 % and Jingning County in Gansu Province with 11.8 %. Besides, percentage of carbonates in these points are few including Maiji Town of Tianshui city, Gansu Province with 3.7 %, Mount Shuangta town, Shuangta district, Chengde city with 3.08 % and Tuoketuo County, Inner Mongolia Autonomous region with 0.76 %. Since carbonates are sensible to pH, it is to be released in the acidic conditions.

Condition of Cd Fe-Mn oxides in the dust fall about China northern villages and towns are shown in the Fig. 2C which showed that the content of Cd Fe-Mn oxides in the dust fall in these areas were all rather low, among which only Qiaodong district of Zhangjiakou city having Fe-Mn oxides percentage of 2.7 % with concentration of 0.16 μg/g, Yuncheng city, Shanxi Province 0.56 % with concentration of 0.016 μg/g and Duoba town, Qinghai Province 0.22 % with concentration of 0.011 μg/g.

Condition of organic combination in the dust fall about China northern villages and towns are shown in Fig. 2D. Fig. 2Da showed that the organic combination in Duoba town, Qinghai Province ranked first reaching 1.07 μg/g, followed by Maiji town, Tianshui city, Gansu Province with 1.07 μg/g and that of other points are rather low. While seen from Fig. Db, the organic combination percentage in Duoba town, Qinghai Province was the highest of 21.22 %, followed by Maiji town, Tianshui city, Gansu Province with 14.7 % and the superb of Jingning County, Gansu Province of 10.85 %. And that of eastern district, Zhangjiakou city, Superb of Yongning County, Ningxia Province, Superb of Tuoketuo County, Inner Mongolia Autonomous region was respectively of 5.8 %, 6.0%, 6.2%, other sampling points rather low. Thoroughfare as Duoba town of Qinghai Province is, much organic Cd has been found here because of the heavy organic pollutant by the vehicle exhaust and large coal consumption by the local people. Besides, a tourism hotspot and buddhist sanctuary with many temples and high-volume vehicle as Maiji Town, Tianshui city of Gansu Province is, much organic Cd has also been found here because of much fly ash brought by the vehicle exhaust and incense, wax and paper money burning. Thus, organic and sulfide bounded is quite affected by the different organic matter.

Existed in the lattice of silicate, clay, original mineral and secondary mineral, residual metal ions are fixed in the dust fall with stability and not easy to be migrated and release. Thus, the higher content of the residual, the lower toxicity the dust fall will be. Otherwise, the toxicity will be higher. The more component of the other form in dust fall, the higher toxicity the dust fall will be with. Seen from Fig. 2E condition of residual in the dust fall about China northern villages and towns, the residual in these points are rather low including Duoba town, Qinghai Province of only 41.03 % and western

Superb of Shijiazhuang city of 51.28 %. While, other forms with higher toxicity as well as large total amount of Cd can be found in these areas, which lead to much serious toxicity of dust all. Besides, the content of residual in other points are all more than 70 % while element total amount is fixed, leading its wholly lower Cd toxicity.



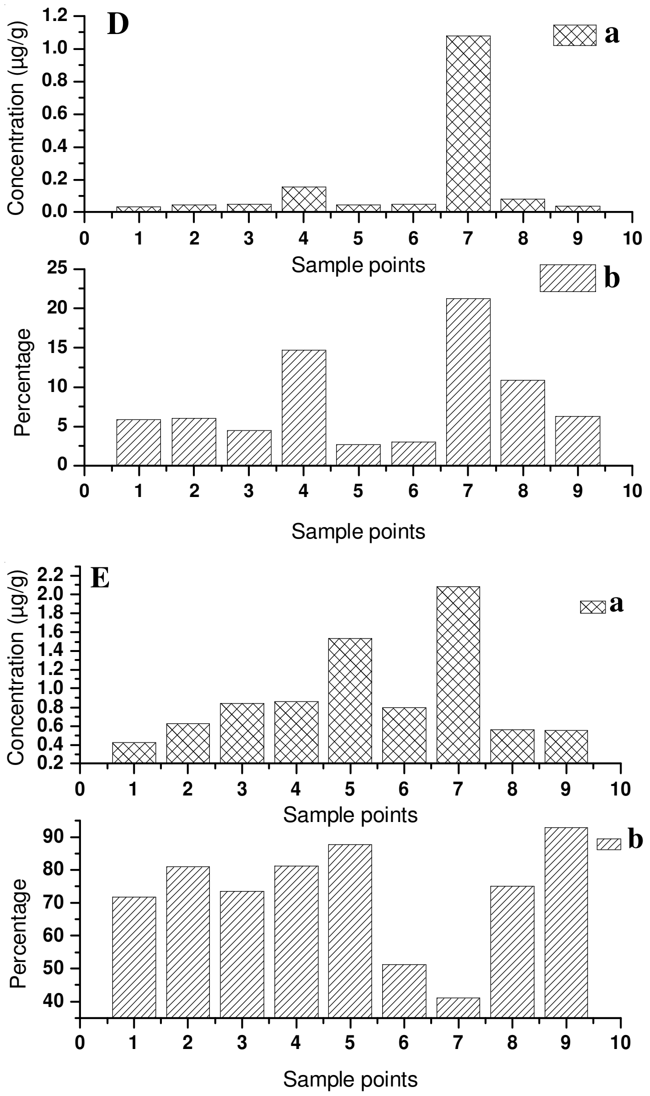


Fig. 2. Condition of Cd in the Dust fall in China Northern villages and towns; A) condition of exchangeable Cd; B) Condition of carbonates Cd; C) Condition of Cd Fe-Mn oxides; D) Condition of organic combination Cd; E) Condition of residual

Conclusion

This paper uses Tessier method to determine the Cd speciation in dust fall about northern China towns and the total content of each sampling is in line with the total content measured with reliable analytical method. The result shows:

Viewed from the location of points, near to the Qinghai metallurgy chemical industrial zone with serious industrial pollution and being the thoroughfare with a great deal of ash fly, Duoba town of Qinghai Province is with high Cd concentration. Same situation appears in these points including Shuangta Town, Chengde city, Hebei Province, western Superb of Shijiazhuang city, Maiji town, Tianshui city, Gansu Province. However, Cd concentration is low in those little polluted points which are far away from the large-medium sized city and thoroughfare such as Jingning city of Gansu Province and Tuoketuo County of Inner Mongolia Autonomous region. Besides, the total amount of toxic exchangeable form, carbonates, organic combination percentage varied with pollution level. The more serious the pollution is, the more content there will be, then much more serious toxicity.

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