

Article

Wet Deposition of Trace Metals at a Typical Urban Site in Southwestern China: Fluxes, Sources and Contributions to Aquatic Environments

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Abstract: In this study, we quantified the atmospheric wet deposition (AWD) of 13 trace metals (TMs) and estimated their potential effects on the surface water of the Three Gorges Reservoir in China. Precipitation was collected in Wanzhou in southwestern China from March 2015 to February 2016. The concentrations and fluxes of the 13 TMs were in the ranges of 0.16–9.44 $\mu\text{g L}^{-1}$ and 0.18–10.22 $\text{mg m}^{-2} \text{yr}^{-1}$, respectively, in the order $\text{Al} > \text{Zn} > \text{Fe} > \text{Ba} > \text{Pb} > \text{Mn} > \text{Ti} > \text{Cd} > \text{Cu} > \text{As} > \text{V} > \text{Ni} \approx \text{Cr}$. Using principal component analysis, it was found that Al, Ba, Cu, Fe, Mn and Zn were mainly derived from a mixture of soil and road dust, As, Cd, Cr, Pb and Ti primarily originated from the local industries, and Ni and V were related to diesel and gasoline combustion, including both vehicle exhaust emissions and ship emissions from the nearby Yangtze River. The estimated TM inputs to the Three Gorges Reservoir were 11.1, 11.0, 5.7, 5.3, 4.5, 2.7, 2.5, 1.5, 1.0, 0.7, 0.5, 0.2, and 0.2 t yr^{-1} for Al, Zn, Fe, Ba, Pb, Mn, Ti, Cd, Cu, As, V, Ni and Cr, respectively. The AWD TM fluxes in Wanzhou were lower than those in metropolises and their inputs were limited for surface water of the Three Gorges Reservoir. However, Cd was strongly enriched in precipitation and rainstorms greatly increased the surface water concentrations of Cd and Pb. Therefore, the behavior of Cd and Pb in southwestern mountain areas of China, including emission, transport, transformation, and their ecological effects, should be given more attention in future studies.

Keywords: wet deposition; trace metals; Wanzhou; metal sources; ecological effects; Three Gorges Reservoir

1. Introduction

Air pollutants whether inorganic or organic will eventually return to the surface ecosystems through atmospheric dry and wet deposition [1,2]. Trace metals (TMs) in atmosphere, especially heavy metals, have attracted much attention owing to their great toxicity and non-degradability. Atmospheric TM deposition is a key process in the biogeochemical cycles of these elements [3]. Their deposition rates are usually low in clean natural environments, which are infrequently affected by human activities, whereas rapid urbanization and industrialization have accelerated deposition rates in suburban and urban regions [4,5]. Atmospheric deposition is an essential source of TMs in terrestrial and aquatic

ecosystems; however, excessive inputs lead to their accumulation, with potential harm to human health [6]. TMs in the atmosphere mainly originate from anthropogenic activities, e.g., fossil fuel combustion, road dust, smelting, construction dust, biomass burning, and waste incineration, and easily concentrate in atmospheric fine particles [7]. These particles transport TMs to remote regions, including as far as the Arctic, via atmospheric circulations [8–10]. Compared with dry deposition, by which TMs can directly remove from atmosphere with airborne particles, atmospheric wet deposition (AWD) through precipitation is considered to be the major pathway for removal of TMs from the atmosphere [11]; therefore, it is of great significance to quantify their fluxes, identify their sources, and assess their potential effects on ecosystems and human health.

About 10 years ago, atmospheric deposition studies had mainly focused on the acid rain causing ions (NO_3^- and SO_4^{2-}), due to the great harm caused by acid deposition [12,13]. With increasing human health concerns and the improvement of technology for detecting TMs, researchers have begun to pay attention to atmospheric TM deposition. Previous studies on TMs in precipitation have been carried out in Europe [3] and North America [14]. Data reports on heavy metals in precipitation have been released annually since 1976 in Europe [15]. In North America, the Mercury Deposition Network began measuring total mercury in precipitation in 1996, and it now has more than 100 sites [16]. Over the past decade, China has made great progress in the study of AWD of TMs, both on local and regional scales.

In North China Wan et al. showed that heavy metals have gradually increased in the atmosphere since the 1980s, and the rate of increase rate reached a maximum in the 1990s [17]. However, the rate slowed down and was even negative in the 2000s, although the level of TMs in the atmosphere was still high. Pan et al. found that AWD fluxes of TMs in North China were orders of magnitude higher than those in other regions, e.g., Hong Kong and the Yellow Sea in China, and the TM inputs to agricultural soils by atmospheric deposition were 10–78% of the anthropogenic input [4]. Recently, Xing et al. reported that in Jiaozhou Bay, eastern China, the average contribution of AWD to surface water concentrations of TMs was between 1.1% and 12.3%, and heavy rain greatly increased TM concentrations in the surface water [18]. With regard to AWD of TMs in remote regions, Tripathee et al. found that many TMs (Cr, Co., Ni, Cu, Zn, Cd and Pb) were significantly enriched in precipitation in central Himalayan regions owing to the long-range transport of these elements [19]. Zhu et al. revealed that wet heavy-metal deposition was significantly correlated with the level of industrial development, traffic volume, and energy consumption [8]. These studies were mainly concentrated in ecologically sensitive regions, such as large and medium cities, coastal waters, inland lakes, and remote ecosystems.

There are many valleys and mountains in southwestern China, which has a humid and cloudy climate. The Three Gorges Reservoir (TGR) region is located at the junction of Sichuan Basin and the middle and lower reaches of the Yangtze River and acts an ecological barrier in the middle and lower reaches of the Yangtze River. It is the focus of ecological environment protection in the west of China. The mountains, valleys, and large reservoir in southwestern China constitute a sensitive and fragile ecological environment, which will be profoundly impacted by atmospheric TM deposition. With the transfer of Chinese industries to the western region, the southwest will be subject to greater environmental pressure. In fact, atmospheric deposition has already been recognized as an important factor leading to heavy metal pollution of soils and waters in southwestern China, especially in the TGR region [20–22]. To the best of our knowledge, however, the contribution of atmospheric deposition to the total amounts of heavy metals in this region has not been quantified so far.

In this study, we collected precipitation over one year in urban Wanzhou, which is located in the hinterland of the TGR, 327 km from downtown Chongqing and 283 km from the Three Gorges Dam, and analyzed the concentrations of 13 TMs in the daily precipitation. The main goals of this study were to quantify the AWD TM fluxes and analyze the TM sources at a typical site in the TGR region, and to assess the AWD input of TMs and their potential contribution to the surface water of the TGR.

2. Methods

2.1. Sampling Site

Wanzhou is situated on the eastern edge of the Sichuan Basin and in the hinterland of the TGR region, southwestern China, with an urban population of about 1 million. It has a subtropical monsoon and wet climate with four distinct seasons and the terrain is mainly mountainous and hilly. The annual average temperature and rainfall are ~ 18.6 °C and ~ 1200 mm, respectively. Owing to the mountainous topography, Wanzhou is within the region of lowest wind speed over China [23].

The sampling site (Figure 1) was the Atmospheric Environment Comprehensive Observation Station located on the rooftop of a nine-story teaching building on the campus of Chongqing Three Gorges University. A weather station (Lufft, Philbach, WS500-UMB, Germany) was equipped to obtain meteorological data, including wind speed and direction, temperature, air pressure, and relative humidity. The surrounding environment of the site is mainly residential and cultural areas, with no pollution sources. The sampling site is about 600 m from the Yangtze River, and there is an urban arterial road about 100 m to the east. Therefore, the sampling site is representative of the urban environment of Wanzhou.

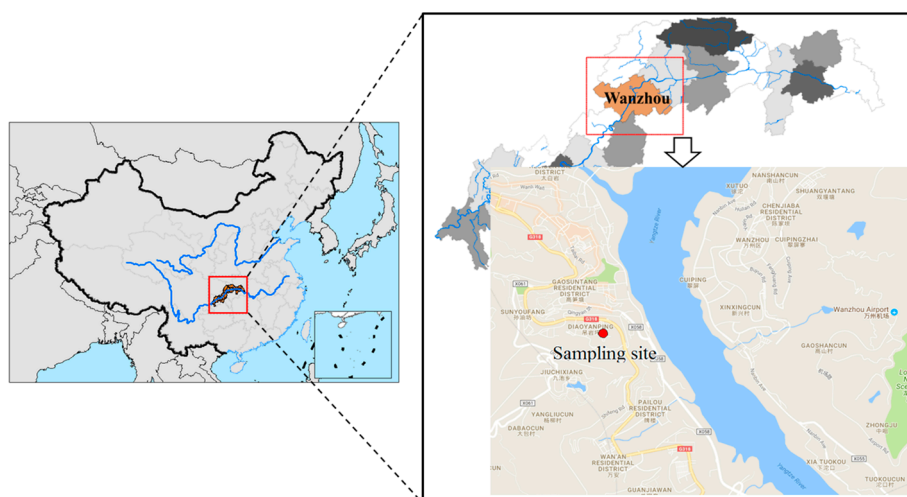


Figure 1. Location of sampling site in urban Wanzhou, China.

2.2. Sampling and Analysis

Precipitation was collected using an autosampler (APS-3A, Changsha Xianglan Scientific Instrument Co. Ltd., Changsha, China) equipped with a multi-channel valve and portable refrigerator. When precipitation occurs, the cover of the sampler automatically opens for sample collection and the precipitation sample flows into a 1000 mL pre-cleaned silica gel bottle through a Teflon channel. The collected sample is automatically stored in the refrigerator and the channel is automatically replaced until 9 a.m. the next day. The cover is closed to prevent dust from entering the rain bucket when no precipitation occurs. After collection, each sample was filtered through a 0.45 μm pore diameter membrane filter, and then kept in a refrigerator at 4 °C for subsequent testing. In total, 109 precipitation samples were collected during the period from March 2015 to February 2016. However, 12 samples were too small to measure TM concentrations; the precipitation amount from these missing samples accounted for 1.6% of the total precipitation amount.

Mass concentrations of 13 TMs (Al, As, Ba, Cd, Cr, Cu, Fe, Mn, Pb, Ni, Ti, Zn and V) were measured using inductively coupled plasma optical emission spectrometry (Optima7000, PerkinElmer Company, Waltham, MA, USA). A multi-element mixed standard solution was purchased from the National Standard Material Net in China, and its mass concentration was 100 $\mu\text{g mL}^{-1}$. A series of

standard working solutions were diluted with ultra-pure water (resistivity > 18.25 MΩ cm) to give final concentrations of 0, 50, 100, 200 and 500 µg L⁻¹. The r² of calibration curve for all measured elements were over 0.999, and the detection limits were 0.20, 0.06, 0.03, 0.01, 0.03, 0.01, 0.25, 0.1, 0.05, 0.33, 0.24, 0.45 and 0.26 for Al, As, Ba, Cd, Cr, Cu, Fe, Mn, Pb, Ni, Ti, Zn and V, respectively. When the concentration was below the detection limit, half of the detection limit was taken for calculation. Quality control was carried out using a National Standard reference solution. The results showed that precisions for all determined trace metals were in the range between 2% and 5%, and the recovery of the elements was between ~90% and 110%.

2.3. Data Analysis

The volume-weighted mean (VWM) concentrations and wet deposition fluxes were calculated using Equations (1) and (2) respectively:

$$C_{VWM} = \frac{\sum_{i=1}^n (C_i \times P_i)}{\sum_{i=1}^n P_i} \quad (1)$$

$$F_{w(x)} = C_{VWM} \times P_t \times 0.001 \quad (2)$$

where C_{VWM} (µg L⁻¹) is the VWM concentration, C_i (µg L⁻¹) is the TM concentration in the i th rainfall, P_i (mm) is the i th rainfall amount, $F_{w(x)}$ (mg m⁻² yr⁻¹) is the annual wet deposition amount of element x , and P_t (mm) is the annual precipitation amount.

A box model developed by Heimbürger et al. was used to estimate the impact of total AWD on the surface water of the TGR [24]. The ratios ($\Delta C/C$) between the increase of TM concentrations in the surface water (ΔC) and dissolved TM concentrations in surface water (C) were used to estimate the enrichment or depletion of TMs, and the parameters of this model were calculated as follows:

$$t_R = \frac{V}{R} \quad (3)$$

$$\Delta C = \frac{(F_{TM} \times t_R)}{Z} \quad (4)$$

where t_R (day) is the residence time of surface waters in the TGR, calculated as 1.75 for this study, which is approximately equal to two days; therefore, we used 2 as the t_R value in subsequent calculations. V (m³) is the volume of surface water for the TGR, which was obtained by multiplying the water surface area (1.084×10^9 m²) [25] by the mixed layer depth (~2 m) [26]. R (m³ yr⁻¹) is the multi-year average runoff of the TGR (4.5×10^{11} m³ yr⁻¹) [27]. F_{TM} (µg m⁻² d⁻¹) is wet deposition of a given TM. Z (m) is the depth of the homogeneous mixed layer, which is usually equal to the depth of thermocline [24]; the thermocline depth of the TGR varied between 3.5 m and 7.0 m [26], and 3.5 m was used for calculations in this study.

The formula used to calculate the total amount of each TM entering the TGR is:

$$M = F \times S \quad (5)$$

where M is the annual TM input to the TGR through wet deposition, F (t km⁻²) is the wet deposition flux of the TM, and S (km²) is the water surface area of the TGR.

3. Results and Discussion

3.1. TM Characteristics in AWD

3.1.1. Concentrations and Fluxes

The concentrations and fluxes of the measured TMs from AWD are shown in Table 1. It can be seen that there were great variations in the magnitude of concentrations and fluxes of different TMs.

Al was the most abundant element with a VWM concentration of $9.44 \mu\text{g L}^{-1}$ and an AWD flux of $10.22 \text{ mg m}^{-2} \text{ yr}^{-1}$, while the rarest element was Cr with a VWM concentration of just $0.16 \mu\text{g L}^{-1}$ and an AWD flux of $0.18 \text{ mg m}^{-2} \text{ yr}^{-1}$. The order in terms of concentrations and fluxes of TMs was $\text{Al} > \text{Zn} > \text{Fe} > \text{Ba} > \text{Pb} > \text{Mn} > \text{Ti} > \text{Cd} > \text{Cu} > \text{As} > \text{V} > \text{Ni} \approx \text{Cr}$. Based on the magnitude of the concentrations, the elements were divided into two major groups: Al, Zn, Fe, Ba, Pb, Mn, Ti, and Cd with an average concentration between $1 \mu\text{g L}^{-1}$ and $10 \mu\text{g L}^{-1}$, and Cu, As, V, Ni and Cr with concentrations between $0.1 \mu\text{g L}^{-1}$ and $1 \mu\text{g L}^{-1}$.

Table 1. Concentrations and fluxes of trace metals in precipitation in Wanzhou, China, the units were $\mu\text{g L}^{-1}$ and $\text{mg m}^{-2} \text{ yr}^{-1}$, respectively.

Ele.	Min.	Max.	VWM Con.	SD	CV	Dep. Flux
Al	0.38	78.32	9.44	14.43	1.14	10.22
As	0.06	7.08	0.61	1.90	0.69	0.66
Ba	0.20	31.67	4.49	4.85	0.82	4.86
Cd	<DL	4.27	1.32	1.63	0.99	1.43
Cr	<DL	1.68	0.16	0.29	0.88	0.18
Cu	<DL	25.61	0.88	3.60	1.40	0.95
Fe	0.26	42.32	4.85	6.70	1.17	5.25
Mn	0.64	37.92	3.18	6.95	1.26	3.44
Ni	<DL	2.69	0.17	0.44	1.22	0.18
Pb	0.12	15.46	3.82	5.15	0.95	4.14
Ti	<DL	9.17	2.15	4.09	1.35	2.33
V	<DL	3.17	0.44	0.73	0.65	0.47
Zn	0.49	96.81	9.34	13.13	1.03	10.11

Note: <DL indicates below the detection limit.

The coefficients of variation (CV) in Table 1 showed that the TM concentrations varied significantly. The CV for Cu and Ti were the highest (1.40 and 1.35) and the CV for V was the lowest (0.65), which indicated that the Cu and Ti concentrations in precipitation were not stable and the V concentration was relatively stable, and that Cu and Ti may be influenced by human activities. Figure 2 shows the monthly variations of the TM VWM concentrations. Lower concentrations of both crustal-related and anthropogenic TMs usually appeared during the rainy months (June to October), while higher concentrations occurred in dry months (November to May). This seasonal pattern was likely due to the combined effect of seasonal changes in emissions and rain intensity. The seasonal variation of TM concentrations is discussed in detail in Section 3.1.2.

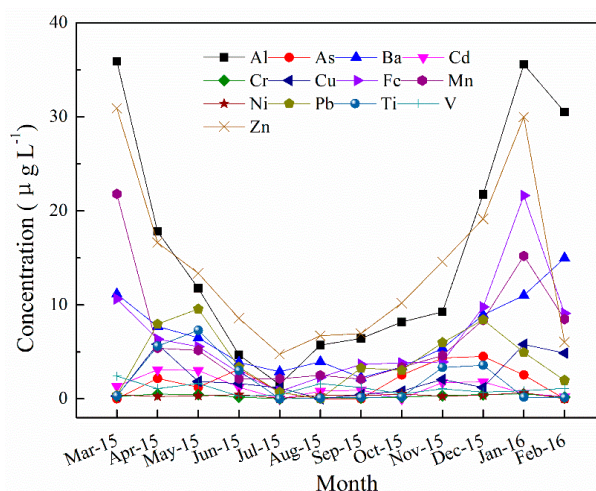


Figure 2. Monthly variations in the VWM concentrations of TMs in AWD in Wanzhou from March 2015 to February 2016.

Table 2. Comparison of concentrations ($\mu\text{g L}^{-1}$) and fluxes ($\text{mg m}^{-2} \text{yr}^{-1}$) of trace metals in precipitation in Wanzhou, China and other locations of the world.

	Wanzhou		Chongqing, China [28]		Lijiang, China [29]		Northern China [4]	Mt. Qomolangma [30]		Izmir, Turkey [31]		Noshiro, Japan [32]	
	Urban 2015–2016		Urban 2011–2012		Urban 2012		Mixed 10 sites 2007–2010	Remote 2009–2010		Urban 2003–2004		Remote 2003–2005	
	VWM	Fluxes	VMW	Fluxes	Mean	Fluxes	Fluxes	VMW	Fluxes	Mean	Fluxes	VMW	Fluxes
Precipitation (mm)		1082.5		797.4		660.0	400.0–800.0		286.0				1730
Al	9.44	10.22			113.8	27.11	45.0–120.0	2.92	0.85				
Zn	9.34	10.11	95.64	76.26	7.62	3.64	22.0–90.0	0.47	0.13	186.4	45.40		
Fe	4.85	5.25	91.59	73.03	31.39	11.87	60.0–149.0	4.55	1.30				
Ba	4.49	4.86			3.44	0.84							
Pb	3.82	4.14	37.94	30.25	1.93	1.12	5.0–27.5	0.04	0.010	7.00	3.80	5.20	9.00
Mn	3.18	3.44	13.76	10.97	3.41	1.67	8.0–19.0	0.59	0.168			4.60	8.00
Ti	2.15	2.33			1.08	0.40							
Cd	1.32	1.43	0.55	0.44	0.08	0.04	0.18–0.31	0.005	0.002	3.10	1.30	0.17	0.30
Cu	0.88	0.95	16.31	13.00	0.59	0.24	1.8–3.8	0.06	0.017	19.70	10.00	1.40	2.30
As	0.61	0.66	5.65	4.50	0.42	0.25	1.0–2.1	0.04	0.012			0.68	1.20
V	0.44	0.47	1.98	1.58	1.51	0.26	0.4–0.9	0.02	0.007			0.45	0.78
Ni	0.17	0.18	2.79	2.22	0.24	0.09	0.5–2.0	0.15	0.042	7.40	4.90	0.50	0.86
Cr	0.16	0.18	3.63	2.90	0.31	0.14	0.3–0.7	0.06	0.016	17.20	5.80	0.24	0.41

The TM concentrations and fluxes found in this study were compared with those reported for other typical locations (Table 2). The TM concentrations and fluxes in the urban precipitation in this study were significantly higher than those at Mt. Qomolangma station (Everest), which is regarded as a remote background site [30]. However, the concentrations and deposition fluxes in this study were significantly lower than those found in metropolises, e.g., Northern China and Chongqing (Table 2). Compared with Lijiang, a mountainous tourist city in Yunnan Province, southwest China, it was found that the concentrations of the typical crustal elements Fe and Al in Lijiang were significantly higher than those found in this study for Wanzhou, while the concentration of Cd was much lower than that in Wanzhou, the concentration of Pb was about half of that in Wanzhou, and the concentration levels of the other TMs were very similar. However, the larger precipitation amount in Wanzhou resulted in greater wet deposition fluxes for most TMs, because wet deposition fluxes are positive correlated with precipitation amount [33]. It is noteworthy that the Cd concentration in this study was only lower than that in Izmir, Turkey, and the Cd flux was the largest of all the locations in Table 2.

The accumulation of heavy metals has been a major environmental problem in the TGR area, with Cd being particularly prominent [20,34–36], which could be attributed to the higher Cd values of the TGR soils and combustion of local coals rich in Cd [37,38]. Compared with locations outside of China, the concentrations of the TMs in this study (except for Cd) were slightly lower than those in Noshiro, a remote site on the west coast of Japan, where relatively higher concentrations are caused by long-distance transport of contaminants from the Asian continent. However, their concentrations and deposition fluxes were significantly lower than those in Izmir, Turkey. Thus, these results indicated that the AWD of TMs at the study site in Wanzhou were moderate compared with other sites.

3.1.2. Seasonal Variability

As shown in Figure 3, the seasonal variation in the concentrations and deposition fluxes of TMs was significant ($p < 0.01$). Although the variation trend was not the same for each element, overall, almost all elements showed higher concentrations in winter and autumn, while their fluxes were generally higher in summer and autumn. This seasonal variation was consistent with the seasonal distribution of precipitation, indicating that increased precipitation has a significant dilution effect on the TM concentration. In addition, some elements (Zn, Pb, Cu and Cr) showed the same trend as typical crustal elements (Al, Fe, Ba, Mn and Ti), i.e., they all exhibited relatively higher concentrations in spring, suggesting that they are likely to have a common source—the Earth's crust. This was confirmed by the highest wind speed of the four seasons occurring in spring (Figure 4), because windy weather increases the soil dust in air [23]. In contrast, As, V, and Ni had higher concentrations in autumn, which may be attributed to the increased anthropogenic emissions and low wind speed (0.76 m s^{-1}) during this season.

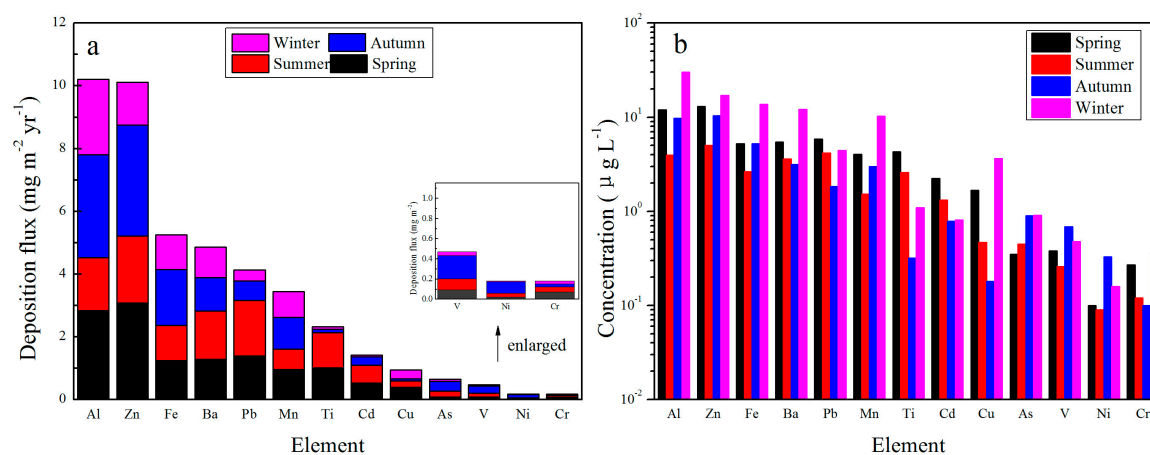


Figure 3. Seasonal variations in fluxes (a) and VWM concentrations (b) of TMs in AWD in Wanzhou.

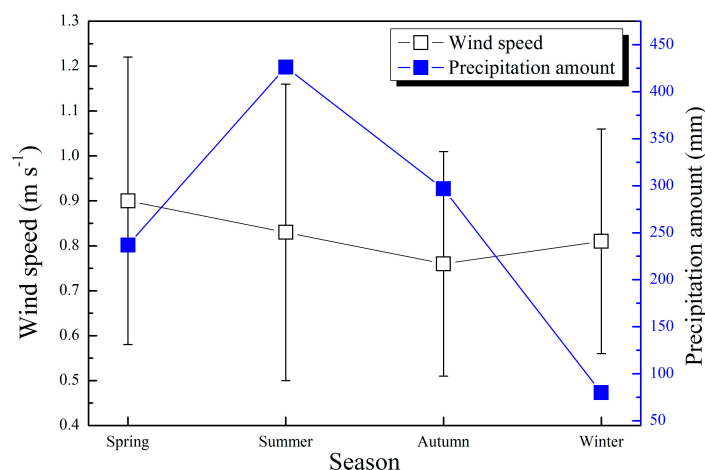


Figure 4. Seasonal variations of wind speed (calculated for daily values) and precipitation in Wanzhou during the study period.

3.2. Principal Component Analysis

Varimax rotated principal component analysis of the TM concentrations was carried out using SPSS software (IBM SPSS, Chicago, IL, USA). Three factors were extracted with eigenvalues >1, and the cumulative contribution rate of the three factors was 88.7%. The results are shown in Figure 5. Only load factors higher than 0.50 are discussed in this study.

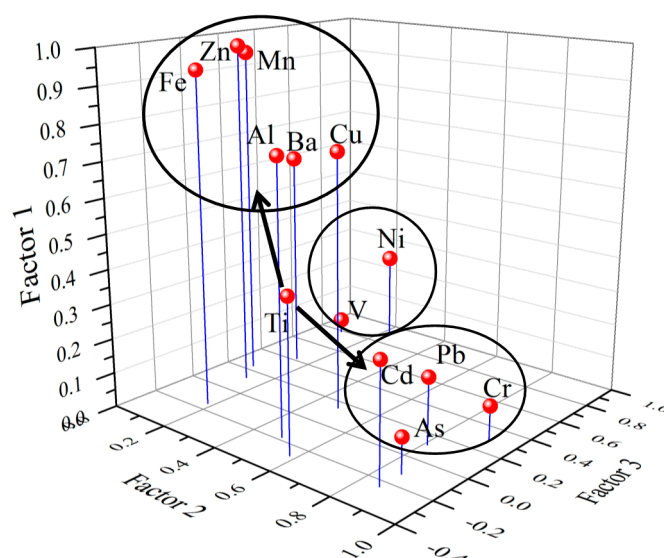


Figure 5. Varimax rotated principal component analysis results for trace metals in precipitation samples collected in urban Wanzhou, between March 2015 and February 2016. Data used for plotting in this figure are factor loadings which represent correlation of variables.

As can be seen from Figure 5, the first factor (PC₁), which explained 53.6% of the total variance, was associated with Al (0.76), Ba (0.73), Cu (0.63), Fe (0.94), Mn (0.95), Ti (0.59) and Zn (0.98). Al, Ba, Fe and Mn are typical crustal elements, indicating that the crustal sources contributed substantially to those elements grouped in PC₁. Furthermore, high loads of Zn and Cu were observed in PC₁. These are indicator elements of road dust, because Zn and Cu are related to both vehicle exhaust emissions and the wear of brakes and tires [39]. As a result, PC₁ represents a mixture of sources—soil dust and traffic emissions.

Factor 2 (PC₂), which accounted for 23.3% the variance, was loaded with As (0.86), Cd (0.86), Cr (0.92), Pb (0.81), and Ti (0.58). As, Pb, Cr and Cd are typical elements that mainly originate from industries such as coal-fired power plants and the cement industry [40,41]. Thus, it is reasonable to deduce that the elements grouped in PC₂ are attributed to emissions from local industrial activities. The potential sources of these metals were further analyzed by combining the major pollution sources with wind (speed and direction) at the sampling site (Figure 6). As can be seen from Figure 6, the wind speed was relatively low, with an average wind speed of 0.84 m s⁻¹ during the study period, and mostly came from the east, southeast and south. The major pollution sources are distributed in the southeast; therefore, local sources, e.g., Shenghua power plant, cement plants, and chemical plants (Figure 6), may be responsible for the TMs of PC₂ in Wanzhou.

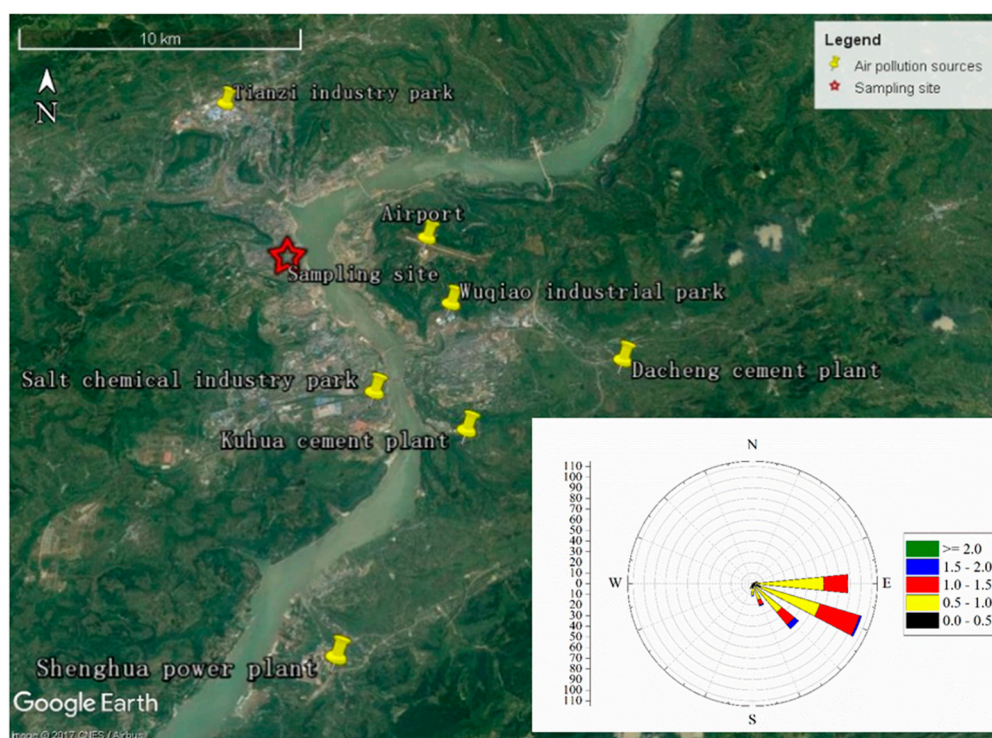


Figure 6. The main air pollution sources in Wanzhou. Inset: wind rose diagram for the study period.

Finally, the third factor (PC₃) accounted for 11.8% of the total variance, with high loads of Ni and V. Previous studies have suggested that Ni and V originate from diesel and gasoline oil combustion emissions [42,43], so this factor may represent transportation sources, e.g., vehicle exhaust emissions and ship emissions from the nearby Yangtze River. The average ratio V/Ni was 2.56, and nearly 50% of V/Ni ratios were in the range of the typical ship emissions ratio (2.5–4.0) [44], indicating that ship emissions near the Yangtze River had a great contribution to the sources of Ni and V in Wanzhou.

3.3. Potential Effects of Precipitation TMs on the TGR

AWD is considered to be an important pathway for the transport of pollutants into aquatic ecosystems [33]. By comparing VWM concentrations of the typical heavy metals in precipitation in Wanzhou with the average concentrations in the surface water of the TGR [21], it was found that Cd and Pb concentrations in precipitation were significantly higher than those in the surface water of the TGR, 1.32 µg L⁻¹ versus 0.20 µg L⁻¹ and 3.82 µg L⁻¹ versus 0.07 µg L⁻¹ for Cd and Pb, respectively.

The contributions of several typical heavy metals in AWD on the surface water of the TGR are presented in Table 3. The largest enrichment concentration (6.48 µg m⁻³) as well as the highest contribution (9.25%) to the surface TM concentrations were found for Pb. Although Cd was enriched

in precipitation, it contributed only 1.12% to the surface water concentration, which could be attributed to the relatively higher Cd concentration of surface water in the TGR reducing the contribution of wet deposition. The AWD contributions of three elements (As, Cr, and Ni) were lower than 0.1%, suggesting that these elements have almost no effect on the surface water. Compared with agricultural and industrial sources, the AWD contributions were very low, but substantial inputs from short-term heavy rains may strongly promote increases in surface concentrations of Cd and Pb. For instance, the contributions of Cd and Pb on 30 June 2015 with a rainfall amount of 56.2 mm increased to 6.47% and 55.42%, respectively, by comparing with the daily average contributions. In addition, the annual TM inputs into the TGR through AWD were estimated using Equation (5) as 11.1, 11.0, 5.7, 5.3, 4.5, 2.7, 2.5, 1.5, 1.0, 0.7, 0.5, 0.2, and 0.2 t for Al, Zn, Fe, Ba, Pb, Mn, Ti, Cd, Cu, As, V, Ni, and Cr, respectively.

Table 3. Enrichment effects of wet deposition on surface water trace metals (TM) concentrations of the Three Gorges Reservoir.

TMs	Enrichment Concentration (ΔC)/ $\mu\text{g m}^{-3}$	Average TM Concentrations of the TGR (C)/ $\mu\text{g m}^{-3}$	Contribution of Wet Deposition to Surface TM Concentrations ($\Delta C/C$)/%
As	1.03	2100	0.05
Cd	2.23	200	1.12
Cr	0.28	500	0.06
Ni	0.29	1300	0.02
Pb	6.48	70	9.25

4. Conclusions

The one year AWD of 13 TMs at an urban site (Wanzhou) was investigated in southern China. The AWD fluxes were 10.22, 10.11, 5.25, 4.86, 4.14, 3.44, 2.33, 1.43, 0.95, 0.66, 0.47, 0.18, and 0.18 $\text{mg m}^{-2} \text{yr}^{-1}$ for Al, Zn, Fe, Ba, Pb, Mn, Ti, Cd, Cu, As, V, Ni, and Cr, respectively. Compared with other locations, the moderate concentrations and deposition fluxes of the TMs indicated that the air quality was relatively good in Wanzhou. However, Cd was strongly enriched in precipitation and its concentration was higher than many other typical urban sites in China. The principal component analyses showed that Al, Ba, Cu, Fe, Mn, Ti, and Zn were mainly derived from a mixture of soil and road dust; As, Cd, Cr, and Pb primarily originated from the local industries; and Ni and V were associated with transportation sources. The AWD TM inputs were significantly lower than those from agricultural and industrial sources, while sudden rainstorms greatly increased the surface water concentrations of Pb and Cd, resulting in water pollution of the TGR. The inputs of TMs to the TGR were estimated to be 11.1, 11.0, 5.7, 5.3, 4.5, 2.7, 2.5, 1.5, 1.0, 0.7, 0.5, 0.2, and 0.2 t yr^{-1} for Al, Zn, Fe, Ba, Pb, Mn, Ti, Cd, Cu, As, V, Ni and Cr, respectively. However, it is inaccurate to estimate TM inputs to the TGR using data from only one sampling site for one year. Future studies should use multiple representative sampling points for long-term observations to better quantify the TM inputs by AWD.

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