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# Evaluation of various mercury forms in the urban road runoff sediments

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**ABSTRACT**

Mercury (Hg) contamination urban areas is a very important issue in environmental research studies. Current study was aimed to determine the Hg content and its distribution characteristics, and to ascertain the speciation of Hg in urban surface sediment. This study also discussed the driving factors of Hg content and its speciation. Road runoff and surface sediment samples collected from different districts in Nanjing, China were analyzed for different forms of Hg. These samples were analyzed using a Cold Vapor Atomic Absorption Spectroscopy (CVAAS). The results indicated that the total mercury (THg) content in the soil of study districts in Nanjing was in range of 35.2–4.99 × $10^3$ μg/kg and the mean value (323 μg/kg) was much higher than the normal values. The THg content shows clear differences for various functional zones, e.g. Electronic business district (1.15 × $10^3$ μg/kg) > Comprehensive business district (274 μg/kg) > Residential district (266 μg/kg) > Cultural and educational district (119 μg/kg) > Traffic district (105 μg/kg) > Natural district (60.8 μg/kg) > Industrial district (53.5 μg/kg). The speciation of Hg in surface sediment was as follows: F1-soluble mercury (Hg-sol) (2.21%), F2-exchangeable mercury (Hg-ex) (2.21%), F3-reactive mercury (Hg-re) (3.53%), F4-mercury oxide (Hg-oxide) (47.9%), and F5-residual mercury (Hg-resid) (44.2%). The correlation analysis shows that THg significantly correlated with F4 and F5. Furthermore, results reveal that the surface sediments in Nanjing are alkaline, therefore THg and Hg-resid were higher in lower pH. Overall, the rainfall events have various effects on THg content on the surface sediment from different districts in Nanjing. The characteristics of rainfall event may alter the speciation of Hg in surface sediment.

*Keywords:* Mercury speciation; Urban road runoff; Road surface sediment; Rainfall events; Pollution

## 1. Introduction

Mercury (Hg) is a highly toxic pollutant and found in environment both in organic and inorganic forms [1,2], and also harmful to human health [3]. The main sources of Hg can be categorized into natural and human sources. The natural source includes volcanic, forest fire, soil and water Hg release [3], whereas human source include traffic activities, ore smelting, garbage incineration, fossil fuel combustion and, etc. [4]. It is widely accepted that the global human source releases 2,100 tons of Hg per year to the atmosphere, while China alone releases 500–700 tons annually [5]. This is a result of fast urbanization and industrialization, and has led to Hg pollution becoming a critical environmental issue, and therefore, needs immediate and effective control measures.

Mercury can transport in atmosphere for a long distance, then deposit on road surfaces via dry and wet deposition. The particles deposited on the road surfaces are usually called "street dust" or "road area dust", whose size is less than 830 μm [6]. The dust particles are those air

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particles whose diameter is larger than 10 μm. Air particles include both solids and liquid matter except water. In general, dust is made up of coal dust, fine dust, the secondary dust. Therefore, Hg content in the topsoil and dust, especially in the dust, is an important index of the recent status of the environment and levels of pollution [7]. Urban surface sediment often contains high heavy metal pollutants [8]. On the one hand, the atmospheric fly ash, road surface cleaning or other external force to cities of the adjacent area migration aggravate the heavy metal element accumulated in the human body through the human skin contact, breathing, intake and, etc. It might be because of the precipitation erosion into the soil, water and other ecological system with different speciation. This is a direct threat to the health and safety of the water environment [9]. Chemical speciation determines their toxicity, and requires environmental mobility and bioavailability [10]. Up to now, many researchers conducted studies on fractionation of metals in street sediment and soil samples, by using a slightly modified three-step sequential extraction procedure proposed by the Community Bureau of Reference (BCR) for analysis of sediments [11]. For a long time, the research was mainly concentrated in the area of other heavy metal pollutants in surface sediment, source analysis, influence factors, grain size characteristics, the cumulative effect and pollution evaluation and, etc. [12–14], but few on the Hg pollution in the urban surface sediment. In recent years, the environmental studies has focused on the Asian developing countries, where the fast development of industrial and mineral areas has been causing release of Hg far greater than the European and American countries [15]. Among them, studies on mainland China including Beijing shows that the Hg content in surface soil and dust in many places has exceeded the Chinese national secondary soil standard of 1 mg/kg. This is more than the upper limit value of the basic human health safeguard [16,17]. The Hg content from different districts varied significantly due to the different land use pattern and the influence of human activities [18,19]. Soil, which acts as both source and sink of Hg, is an important reservoir in its biogeochemical cycling, and therefore, Hg level in soil is a significant environmental issue. Cities are urban areas with a high population density, intensive anthropogenic activities and a great number of sources of Hg, laying a considerable influence on human health [18]. In addition, as the major transfer process, rainfall has strong effect on the contamination of Hg in the urban surface sediment atmosphere input, and ground and surface runoff output are also of great importance [19].

The earlier studies mainly focused on the Hg content in dust, water or in atmosphere. Therefore, current study aimed to analyze the various Hg content in different land use districts in one of the most developed areas of China. The main objectives of the present study are as follows: (1) to determine the Hg content and its distribution characteristics; (2) to ascertain the speciation of Hg in urban surface sediment; and (3) to discuss the driving factors of Hg content and its speciation.

## 2. Materials and methods

### 2.1. Study area

Nanjing city (118°22′ and 119°14′ E, 31°14′ and 32°37′N), has subtropical monsoon climate, where average annual temperature is 15.4°C and annual average precipitation is 1106.5 mm. The study area was divided into different sites (districts) based on regional and industrial characteristics, land types, traffic load and human activities as presented in Fig. 1 and Table 1.

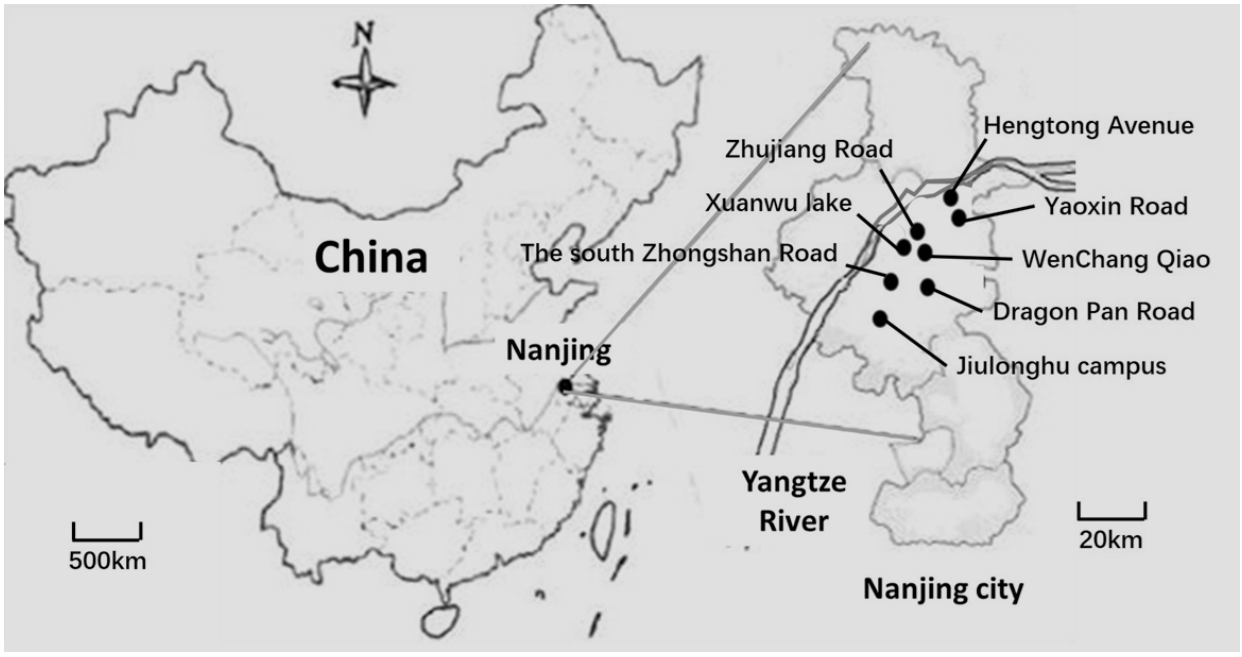


Fig. 1. Location map of sampling sites.

Table 1
Description of the sampling sites from different districts in Nanjing city

| Classification | No. | Site | Note | Possible emission source |
|---|---|---|---|---|
| Natural district | 1–3 | Xuanwu lake scenic spot | No traffic, large communities | Atmospheric settlement |
| Cultural and educational district | 4–6 | Jiulonghu campus of southeast university | School campus | Atmospheric settlement, Thermal power plant which located within two Km |
| Residential district | 7–9 | WenchangQiao accommodation area of Southeast University | Students and staff dormitory | Atmospheric settlement |
| Electronic business district | 10–12 | Zhujiang road | Mainly in electronic products | Atmospheric settlement, electronic product |
| Comprehensive business district | 13–15 | South zhongshan road | Xinjiekou commercial center district | Atmospheric settlement,dense crowd, vehicle |
| Traffic district | 16–18 | Dragon Pan road | Near the tunnel portal | Vehicle, atmospheric settlement |
| Industrial district-1 | 19–21 | Hengtong avenue | New port development zone, industrial enterprise mainly conclude photoelectric, machinery and petroleum gas etc., less traffic impact | Factory, atmospheric settlement |
| Industrial district-2 | 22–24 | Yaoxin road | New port development zone | Factory, atmospheric settlement |

### 2.2. Samples

The surface sediment samples were collected from the identified districts from March to September 2016. Three parallel samples were collected at each field campaign. Sampling intervals in different districts were controlled within 48 h. Samplings were carried out in a dry period, with plastic brush and dustpan acquisition to collect dust samples from around 1m² areas [20]. All the collected samples were stored in sealed polyethylene bags, labeled and immediately transported to the laboratory. They were then sieved using stainless steel tweezers through, 830 μm mesh to remove waste material and large particles such as animal and plant residues, large gravel particles and etc. The sieved samples were mix thoroughly prior to utilize for further experimental purpose. For the subsequent analysis, quantity of above 2 g samples was used in each experimental process.

### 2.3. Analytical procedures

The pH was measured in a 1:2.5 mixture (sample: distilled water) following the procedure described in earlier study [21]. The speciation of Hg in surface sediment was as follows: F1-soluble mercury (Hg-sol), F2-exchangeable mercury (Hg-ex), F3-reactive mercury (Hg-re), F4-mercury oxide (Hg-oxide), and F5-residual mercury (Hg-resid). The various Hg content forms was determined by CVAAS with Hydra II C mercury detector (John McQuatters, Mercury Product Specialist, Teledyne Leeman Labs, Hudson, NH). The Speciation analysis was carried out with the help of sequential extraction procedure, according to the procedure recommended by Standards, Measurements and Testing Program of the European Union (SM&T– formerly BCR) [22]. The improved BCR sequential extraction procedure [23] is briefly given in supportive Table 1 (ST1). Dust samples were subjected to a series of extraction steps to obtain F1 to F5 which represent water soluble Hg (Hg-sol), exchangeable Hg (Hg-ex), reducible Hg (Hg-re), oxidiable Hg (Hg-ox) and remaining Hg (Hg-resid). A standard reference GSB-04 (geochemical standard reference liquid sample in China) was used for precision and accuracy. Samples were prepared carefully prior to detection of the difference between the certified values of Hg and the measured values of Hg as the difference should be within 5% limit [21]. All chemicals were of reagent grade and distilled water was used for sample preparation. All the glass containers utilized in the experiments were soaked in 5% v/v nitric acid for at least 24 h and then rinsed with distilled water to ensure there was no cross-contamination.

## 3. Results and discussion

### 3.1. Total mercury content

The statistical results for Hg contents in the surface sediment of Nanjing are shown in Supportive Table 2 (ST2). The Hg content in surface sediment of Nanjing ranged from 35.2 μg/kg to 4.99 × $10^3$ μg/kg, with an average of 323 μg/kg. This is higher than Nanjing soil background value (123 μg/kg) [24] and achieves the secondary soil standard (300 μg/kg) [25]. Compared to other similar research, Hg content in surface sediment of Nanjing is lower than those of Baoji, Xian and Guangzhou, but higher than the Ottawa and Luanda. The differences may be caused by the research time, region, other

Table 2
$I_{geo}$ and its classification of mercury from surface dust in Nanjing city

| Areas | Mean conc. (μg·kg$^{-1}$) | $I_{geo}$ | Range of $I_{geo}$ | Class | Pollution level |
|---|---|---|---|---|---|
| Natural district | 60.8 | –1.60 | –2.39 ~ –0.99 | I | Practically unpolluted |
| Cultural and educational district | 120 | –0.62 | –1.78 ~ 0.89 | I | Practically unpolluted |
| Residential district | 267 | 0.53 | –0.80 ~ 1.10 | II | Unpolluted to moderately polluted |
| Electronic business district | $1.15 \times 10^3$ | 2.63 | –0.41 ~ 4.76 | IV | Moderately polluted |
| Comprehensive business district | 274 | 0.57 | –0.48 ~ 1.29 | II | Unpolluted to moderately polluted |
| Traffic district | 106 | –0.80 | –1.40 ~ –0.87 | I | Practically unpolluted |
| Industrial district[1] | 57.1 | –1.69 | –2.86 ~ –2.66 | I | Practically unpolluted |
| Industrial district[2] | 53.5 | –1.79 | –2.64 ~ –2.52 | I | Practically unpolluted |
| Baotou, China [31] | 64.9 | 0.58 | –0.64 ~ 2.36 | – | – |
| Slovakia [38] | 12.2 | 5.02 | 1.35 ~ 9.98 | – | – |

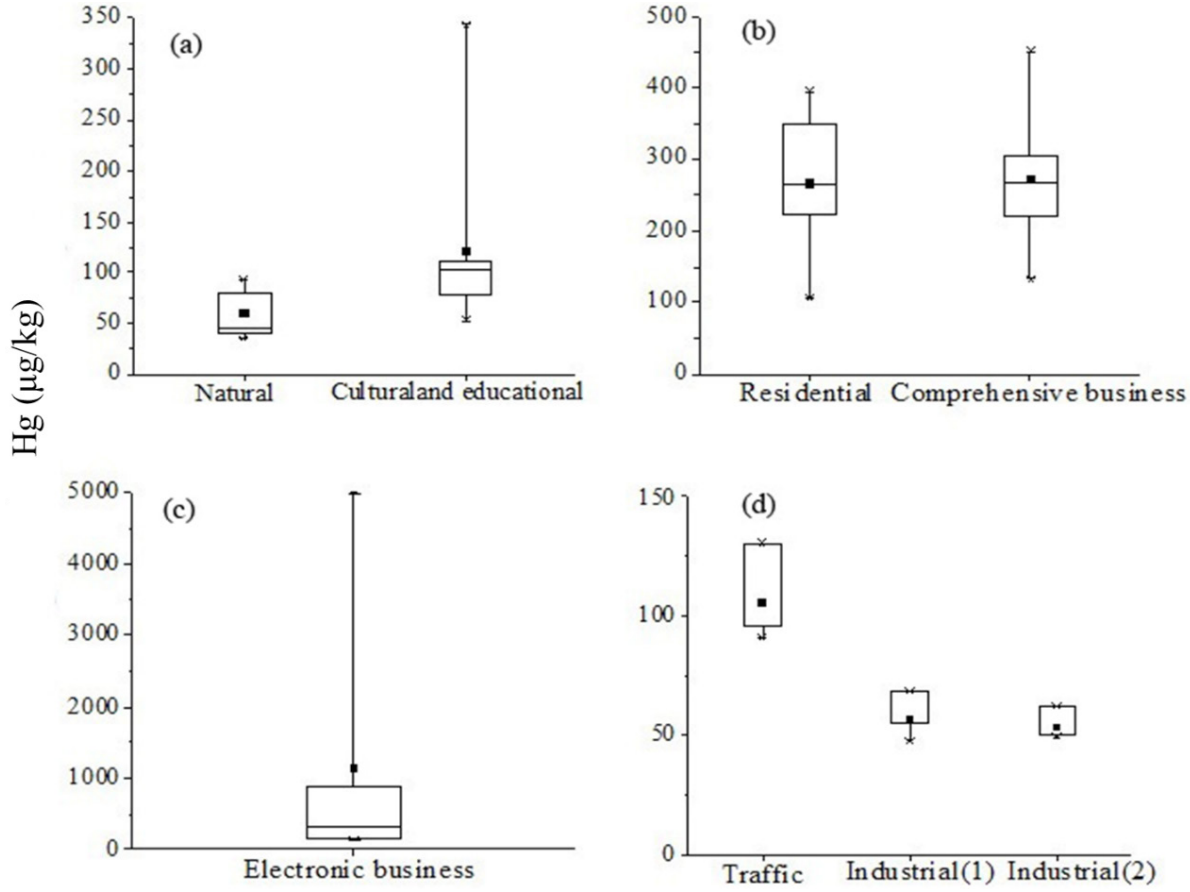


Fig. 2. Content of total mercury in surface dust in different study areas.

climatic factors and etc. [19,26,27]. Fig. 2 shows the THg content in surface sediment from different functional areas. It is clear from Fig. 2 that the middle of the rope box in the value on behalf of THg, the small square is for the average THg (25–75%) data area, and box of flat level represents the THg distribution situation. The boxes of the top and the bottom of the vertical lines represent the maximum and the minimum values.

The THg in surface sediment from the studied districts, varied greatly. The sequence of mean THg content is: Electronic business district > Comprehensive business district > Residential district > Cultural and educational district > Traffic district > Natural district > Industrial district. The highest mean content of the electronic business district is $1.15 \times 10^3$ μg/kg, the minimum mean content of the industrial district is 53.5 μg/kg. The highest range of THg content

in the electronic business district may be relevant to its land use and human activities.

### 3.2. Assessment of mercury contamination

The levels of Hg contamination in the surface sediment were characterized by the geo accumulation index ($I_{geo}$). The geo accumulation index is given [28] by:

$$I_{geo} = \log_2\left(\frac{Cn}{1.5 \times Bn}\right) \quad (1)$$

where *Cn* is the measured element content, and *Bn* is the geochemical background element content.

Analysis of the sampled data reveal that electronic business district is moderately polluted, where Hg range was also highest. On the other hand, the natural, traffic and industrial districts are practically unpolluted as shown in Table 2. It is worth mentioning that the significantly lower Hg content of surface sediment sample was observed in industrial district (≤50 μg/kg). This may be due to the fact that factories in the industrial area barely release Hg.

### 3.3. Speciation of mercury and its bioavailability

The speciation of Hg from surface sediment in Nanjing is shown in supportive Table 3 (ST3). Hg-ox and Hg-resid are the main components of Hg, whose percentage is more than 90%. This is to illustrate Hg from surface sediment in Nanjing is mainly adherent to the organic material and natural sandstone particles and the weathering soil. Each fraction of Hg content from different areas varied greatly. Among them Hg-ox in Electronic business district is much higher than the others (589 μg/kg). This may be due to the leakage of Hg from electronic products in this district.

The chemical fractionation patterns of Hg in the surface sediment are presented in Fig. 3. Although the Hg content in different districts was distinctly different, the chemical fractionation patterns of hg are of certain degree of similarity. The predominant fraction is F4 and F5, which is at least

Table 3
Pearson's correlation matrix in different districts in Nanjing urban area

| | | THg | F1 | F2 | F3 | F4 |
|---|---|---|---|---|---|---|
| Natural district | F1 | 0.441 | | | | |
| | F2 | 0.276 | 0.935[2] | | | |
| | F3 | 0.180 | 0.918[2] | 0.977[2] | | |
| | F4 | 0.730[1] | −0.074 | −0.279 | −0.386 | |
| | F5 | 0.529 | 0.0078 | 0.0014 | −0.0219 | 0.0849 |
| Cultural and educational district | F1 | −0.0559 | | | | |
| | F2 | 0.516 | −0.318 | | | |
| | F3 | 0.834[2] | −0.253 | 0.721[1] | | |
| | F4 | 0.971[2] | −0.285 | 0.573 | 0.840[2] | |
| | F5 | −0.0969 | 0.754[2] | −0.752[1] | −0.373 | −0.284 |
| Residential district | F1 | 0.244 | | | | |
| | F2 | −0.142 | 0.209 | | | |
| | F3 | −0.0426 | 0.429 | 0.229 | | |
| | F4 | 0.769[1] | 0.371 | 0.0124 | −0.245 | |
| | F5 | 0.537 | −0.217 | −0.408 | 0.124 | −0.069 |
| Industrial district | F1 | 0.874[1] | | | | |
| | F2 | −0.0791 | −0.319 | | | |
| | F3 | −0.868[1] | −0.937[2] | 0.069 | | |
| | F4 | 0.920[2] | 0.957[2] | −0.411 | −0.892[1] | |
| | F5 | 0.716 | 0.635 | −0.190 | −0.742[1] | 0.729 |
| Electronic business district | F1 | −0.0308 | | | | |
| | F2 | 0.772[1] | −0.343 | | | |
| | F3 | 0.502 | 0.0492 | 0.514 | | |
| | F4 | 0.986[2] | −0.0491 | 0.721[1] | 0.373 | |
| | F5 | 0.984[2] | −0.0684 | 0.817[2] | 0.609[1] | 0.943 |
| Comprehensive business district | F1 | 0.485 | | | | |
| | F2 | −0.352 | −0.155 | | | |
| | F3 | 0.160 | −0.164 | 0.490 | | |
| | F4 | 0.385 | 0.112 | −0.583[1] | −0.0725 | |
| | F5 | 0.857[2] | 0.374 | −0.146 | 0.09 | −0.123 |

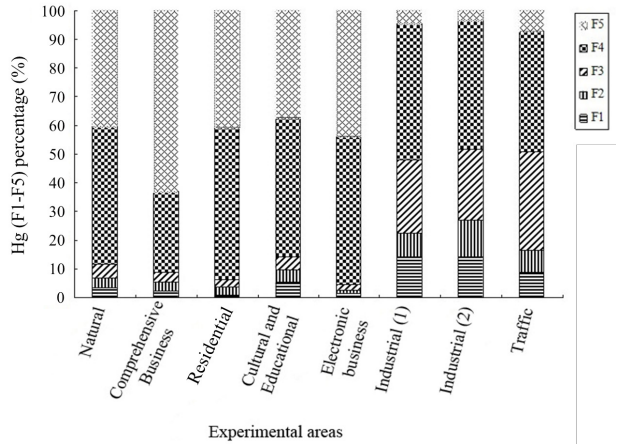


Fig. 3. Chemical fractionation patterns of mercury (F1–F5) in the surface dust samples.

more than 85%; for industrial district and traffic district. The predominant fraction is F3 and F4, which is at least more than 75%. As is described in the extraction step, F1 and F2 are weakly combined with dust and therefore easy to release in the environment; F2 and F3 can react with other chemical material in air, water or soil to generate soluble in water compounds into the environment; F5 is relatively stable and not easy to migrate and transform with smaller but lasting environmental impact [29]. Therefore, the bioavailability of Hg depends on F2 and the mobility of Hg depend on the sum of F1, F2, F3 and F4 [30]. Bioavailability of Hg from surface sediment in Nanjing is not strong. Because of the chemical fractionation, the Hg content in industrial district and traffic district is more active and useful for plants and animals.

### 3.4. Impact of each chemical fractionation patterns of mercury

The Pearson's correlation matrix of each chemical fractionation patterns of Hg shown in Table 3. THg are most significantly correlated with F4. In electronic business district, Pearson's correlation matrix between THg and F4 is 0.986. That is to explain F4 plays a vital role in the distribution of Hg from surface sediment in Nanjing. The influence of each chemical fractionation patterns of Hg is different. In natural district F1 are significantly correlated with F2 and F3, the Pearson's correlation matrix is 0.935 and 0.918; in natural district and cultural and educational district, the correlation matrix between F2 and F3 can reach up to 0.721. The higher correlation matrix shows that the two speciation of Hg can promote them in the distribution of Hg, and the difference may be produced by the differences of properties of dust, which need more relative research.

### 3.5. Influence factors

#### 3.5.1. Function areas

The highest THg content was observed in the electronic business district, where the THg reached $4.99 \times 10^3$ and $2.51 \times 10^3$ μg/kg, respectively, which is much higher than the mean THg. The two abnormal content increases the level of Hg pollution in this district compared to the study area as shown in (S4). As described in Fig. 2, it is highly possible that this areas exists the leakage threat of Hg from the electronic products by human or other activities. Compared to the comprehensive business district of both trading center with short distance, the traffic and human activities in comprehensive business district are more serious and complex. Because THg in electronic business district was higher than this in the comprehensive business district, it is proved that traffic is the main factor, which is consistent with the other studies in China [18,31]. The difference of the speciation of Hg in these two areas is the percentage of F4 and F5. In the electronic business district particles mostly chelated by Hg and all kinds of organic matter is higher as shown in Fig. 4. According to the field investigation, comprehensive business district is mostly constituted of superstores are better in the planning of the street and market that is wide and new, but electronic business district that is mostly composed with small open electronic business and restaurants is relatively narrow. Therefore, it is possible that dust can easier react with the matter produced in the electronic business district. For the residential district that is only influenced by human activities and close to the electronic business district, THg (267 μg/kg) is close to the comprehensive business district (274 μg/kg), but the speciation is similar with the electronic business district. Human activities and the environmental factors are quite important in the distribution of Hg. The environment of natural district is relatively steady so its content stayed at a low level. The Hg in the industrial district was also in a lower level. This national level industrial district in Nanjing was built in 1992 with electronic manufacturing industries e.g. Sharp, Nc Equipment, Gas companies, etc.

#### 3.5.2. pH

Current study reflects that the surface sediments in Nanjing are of alkaline nature. Specifically, the dust collected at cultural and educational district shows the higher pH value (8.4). On the other hand, the lowest pH of 7.7 was observed in Natural district (Fig. 4a). The difference to some degree may affect the distribution of Hg. Fig. 4b shows THg is higher mostly with lower pH. When pH was from 7.2 to 8.1, the mean THg content was 480 μg/kg; but while it was from 8.1 to 9.0, the mean THg content was 255 μg/kg. Fig. 4c reveals the same trend between pH and F5, which reflects the relationship of THg and F5. Fig. 4d shows there may be a tendency that the F1 content increases with the pH arising. When pH was from 7.2 to 8.1, the mean F1 content was 3.48 μg/kg; when it was from 8.1 to 9.0, the mean F1 content was 5.79 μg/kg. Generally speaking, Hg with carbonates and iron/manganese oxides is beneficial to enrich when pH gets higher [32,33]. However, in this study, there is no obvious order between pH and F2 or F3 or F4. Possible reason could be that the dust itself is alkaline, therefore the particles with carbonates and iron/manganese oxides may have been saturated, for which cannot form new Hg species F2 or F3.

#### 3.5.3. Rainfall

The impact of rainfall events on the THg content in surface sediment in different functional areas of Nanjing varied significantly (Table 4). Results reveal that reduction

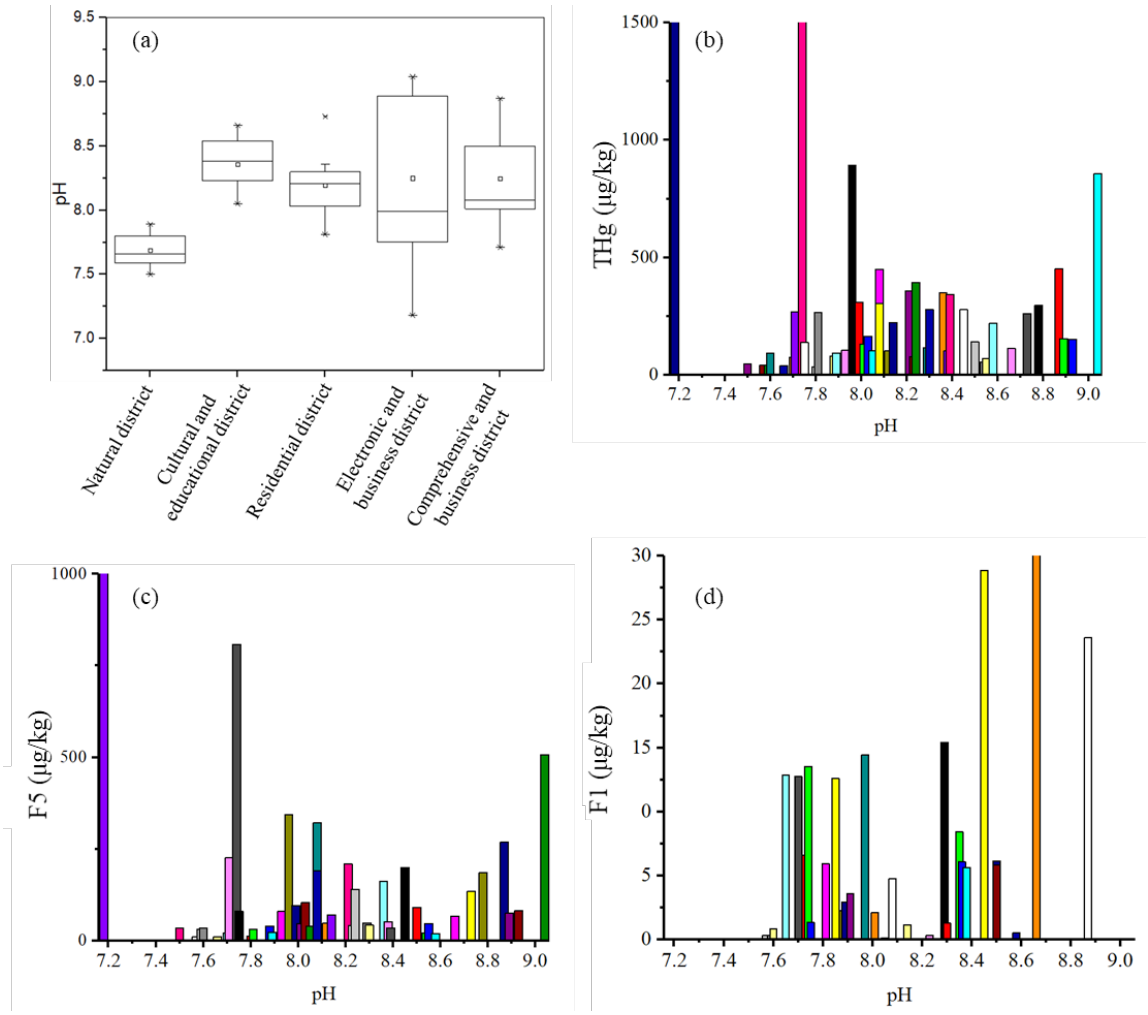


Fig. 4. (a) Surface dust pH level Vs Time and; (b–d) relationship between pH level and THg, F5, and F1 in different study sites.

Table 4
The change of the total mercury content before and after the rainfall events

| Areas | The first Rainfall event content (μg/kg) | | Reduction (%) | The second Rainfall event content (μg/kg) | | Reduction (%) |
|---|---|---|---|---|---|---|
| | Before | After | | Before | After | |
| Natural district | 41.0 | 35.2 | 14.0% | 92.8 | 39.4 | 57.5% |
| Cultural and educational district | 104 | 77.0 | 25.8% | 103 | 69.6 | 32.2% |
| Residential district | 279 | 223 | 19.8% | 358 | 165 | 54.0% |
| Electronic business district | 155 | 139 | 10.4% | $2.51 \times 10^3$ | 152 | 94.0% |
| Comprehensive business district | 219 | 132 | 39.7% | 450 | 140 | 68.9% |

percentage of THg in electronic business district were most significant, which was 10.4 and 94.0%, respectively. Higher adsorption of THg before the second rainfall event could be possible reason behind this trend. The rainfall events can cut the THg content of dust and rainfall type, depth, duration, intensity and characteristics of different functional areas for its cut effect and cause analysis is to be further discussion and research.

It should be noted that the first rainfall event had 63.8 mm rainfall before the precipitation of 2.5 h, with average precipitation intensity of 0.4 mm/min for 2.4 h. The second rainfall event had 28.9 mm rainfall, with average precipitation intensity of 0.2 mm/min, but following three days were continuous showers and cloudy weather conditions. Table 5 shows the change in the F4 and F5 that were the main dust components before and after the rainfall events.

Table 5
The change of F4 and F5 content before and after the rainfall events

| Areas | Speciation | The first Rainfall event content (μg/kg) | | Reduction percentage | The second Rainfall eventcontent (μg/kg) | | Reduction percentage |
|---|---|---|---|---|---|---|---|
| | | Before | After | | Before | After | |
| Natural district | F4 | 28.9 | 21.9 | 24.2% | 55.3 | 25.1 | 54.7% |
| | F5 | 10.3 | 13.1 | –27.7% | 35.0 | 11.3 | 67.6% |
| Cultural and | F4 | 60.2 | 33.3 | 44.7% | 44.3 | 12.9 | 70.8% |
| educational district | F5 | 39.5 | 41.9 | –6.08% | 52.3 | 47.2 | 9.84% |
| Residential district | F4 | 221 | 151 | 31.7% | 144 | 28.2 | 80.4% |
| | F5 | 43.2 | 70.9 | –64.4% | 210 | 104 | 50.5% |
| Electronic business district | F4 | 73.7 | 56.0 | 23.9% | $1.68 \times 10^3$ | 38.0 | 97.7% |
| | F5 | 75.2 | 81.0 | –7.73% | 808 | 82.7 | 89.8% |
| Comprehensive Business district | F4 | 188 | 80.5 | 57.2% | 116 | 23.2 | 80.0% |
| | F5 | 19.7 | 45.6 | –131% | 321 | 90.9 | 71.7% |

The first rainfall event had a different degree of decreasing effect on the F4 content in surface sediment from five areas, which is at least 23.9% in the electronic business district, but had the opposite effect on F5. The rainfall is mostly in acidic nature and change the pH of dust, which also influence the adsorption balance of Ferric-manganese oxidation state of Hg [34–39], and promote the release of Hg in F4. Whereas, F5 which is stable in long-term, it is possible that the first rainfall is not strong enough to go alone with runoff, which causes them deposited on both sides of street. Results reveal significant effect on F4 and F5 is apparent due to the characteristics of the rainfall.

## 4. Conclusions

Surface sediment samples collected from different selected districts in Nanjing show high Hg content that may have serious impact on the environment. The average THg content in surface sediment was 323 μg/kg, which is 2.6 times higher than normal value (123 μg/kg) of Nanjing soil. The difference of THg content was significant: Electronic business district > Comprehensive business district > Residential district > Cultural and educational district > Traffic district > Natural district > Industrial district. Contamination assessment based on the geo-accumulation index shows that the electronic business district is moderately polluted, while the natural, traffic and industrial districts are practically unpolluted. Application of the improved BCR sequential extraction procedure to surface sediment in Nanjing indicated that Hg-ox and Hg-resid are the main forms of Hg whose percentage are more than 90%. Results reveal that Hg forms in industrial and the traffic districts were more active and useful for plants and animals. Statistical analysis shows that THg was significantly correlated with Hg forms presented in F4 and F5. Overall, surface sediment in Nanjing shows alkaline nature and THg and Hg-resid content were mostly higher in lower pH level. Rainfall events over the surface sediment from different land uses in Nanjing have different contribution to THg content. Possible explanation could be that the different rainfall characteristics may alter the speciation of Hg in surface sediment.

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## References

[1] Q. Wu, S. Wang, G. Li, S. Liang, C.J. Lin, Y. Wang, S. Cai, K. Liu, J. Hao, Temporal trend and spatial distribution of speciated atmospheric mercury emissions in China during 1978–2014, Environ. Sci. Technol., 50(24) (2016) 13428–13435.
[2] I. Fricke, R. Götz, R. Schleyer, W. Püttmann, Analysis of sources and sinks of mercury in the urban water cycle of Frankfurt am Main, Germany, Water, 7 (2015) 6097–6116.
[3] L.M. Zhang, Z.Y. Wu, I. Cheng, L.P. Wright, M.L. Olson, D.A. Gay, M.R. Risch, S. Brooks, M.S. Castro, G.D. Conley, E.S. Edgerton, T.M. Holsen, M. Thomas, W. Luke, R. Tordon, P. Weiss-Penzias, The estimated six-year mercury dry deposition across North America, Environ. Sci. Technol., 50 (2016) 12864–12873.
[4] S. Chung, H.T. Chon, Assessment of the level of mercury contamination from some anthropogenic sources in Ulaanbaatar, Mongolia, J. Geochem. Explor., 147(Part B) (2014) 237–244.
[5] X.B. Feng, G.L. Qiu, X.W. Fu, T.Y. He, P. Li, S.F. Wang, Environmental mercury pollution. Progress Chem., 21 (2009) 436–457. (in Chinese).
[6] D. Peixuan, T. Hui, H. Yongming, Concept, research content and method of urban dust, Geo. Shanxi, 22(1) (2004) 73–79.
[7] G. Sun, Z. Li, X. Bi, Y. Chen, S. Lu, X. Yuan, Distribution, sources and health risk assessment of mercury in kindergarten dust, Atmospheric Environ., 73 (2013) 169–176.
[8] Z. Huan, W. Wenxiong, Bioavailability of mercury in sediments: a review, Environ. Chem., 30(1) (2011) 168–178.
[9] A. Christoforidis, N. Stamatis, Heavy metal contamination in street dust and roadside soil along the major national road in Kavala's region, Greece, J. Geoderma, 151 (2009) 257–263.
[10] I.A. Tazisong, Z.N. Senwo, M.I. Williams, Mercury speciation and effects on soil microbial activities, J. Environ. Sci. Health, Part A., 47(6) (2012) 854–862.
[11] S.M. Obeidat, I.F. Al-Momani, R.A. Othman, Partitioning of trace metals in sediments from the mediterranean coastal zone of Ajdabia to Benghazi, Libya: Case study, Jordan J. Chem., 11 (2016) 247–258.
[12] X. Hu, Y. Zhang, J. Luo, T. Wang, H. Lian, Z. Ding, Bioaccessibility and health risk of arsenic, mercury and other metals in

urban street dusts from a mega-city, Nanjing, China. Environ. Pollut., 159 (2011) 1215–1221.
[13] Z. Mingkui, W. Hao, Concentrations and chemical forms of potentially toxic metals in road-deposited sediments from different zones of Hangzhou, China. J. Environ. Sci., 21 (2009) 625–631.
[14] C. Jing, L. Min, L. Xianhua, Y. Jie, L. Xiao, W. Li, G. Lei, Heavy metal mass accumulation of urban surface sediment in Shanghai city, Environ. Sci., 29(12) (2008) 3484–3488.
[15] P. Li, X.B. Feng, G.L. Qiu, L.H. Shang, Z.G. Li, Mercury pollution in Asia: a review of the contaminated sites, J. Hazard. Mater., 168 (2009) 591–601.
[16] X. Zhang, K. Luo, X. Sun, J. Tan, Y. Lu, Mercury in the topsoil and dust of Beijing City, Sci. Total Environ., 368 (2006) 713–722.
[17] Y. Han, P. Du, J. Cao, E.S. Posmentier, Multivariate analysis of heavy metal contamination in urban dusts of Xian, Central China. Sci. Total Environ., 355 (2006) 176–186.
[18] X. Chen, X. Xia, S. Wu, F. Wang, X. Guo, Mercury in urban soils with various types of land use in Beijing, China, Environ. Pollut., 158 (2010) 48–54.
[19] N. Zheng, Q. Wang, Z. Liang, Heavy metals exposure of children from stairway and sidewalk dust in the smelting district, northeast of China, Atmos. Environ., 44 (2010) 3239–3245.
[20] Y. Ye, P. Xu, Y. Zhai, L. Chen. Pollution characteristics of highway pavement sediments, Chinese J. Environ. Engi., 7 (2013) 1196–1200. (in Chinese)
[21] O.A. Khashman, The investigation of metal concentrations in street dust samples in Aqaba city, Jordan. J. Environ. Geochem. Hlth., 29 (2007) 197–207.
[22] Z. Mester, C. Cremisini, E. Ghiara, R. Morabito, Comparison of two sequential extraction procedures for metal fractionation in sediment samples, Analyt. Chimi. Acta., 359 (1998) 133–142.
[23] S. Tokalioglu, Application of a three-stage sequential extraction procedure for the determination of extractable metal contents in highway soils, Turk. J. Chem., 27 (2003) 333–346.
[24] G. Shi, Z. Chen, C. Bi, Y. Li, J. Teng, L. Wang, S. Xu, Comprehensive assessment of toxic metals in urban and suburban street deposited sediments (SDSs) in the biggest metropolitan area of China, Environ. Pollut., 158 (2010) 694–703.
[25] NEPA (1995), GB 15618-1995 Environmental quality standard for soils. National Environmental Protection Agency, Beijing.
[26] X. Feng, S. Tang, L. Shang, H. Yan, J. Sommar, O. Lindqvist, Total gaseous mercury in the atmosphere of Guiyang, PR China. Sci. Total Environ., 304 (2003) 61–72.
[27] P.E. Rasmussen, K.S. Subramanian, B.J. Jessiman, Amult-ielement profile of house dust in relation to exterior dust and soils in the city of Ottawa, Canada. Sci. Total Environ., 267 (2001) 125–140.
[28] G. Müller. Index of geoaccumulation in sediments of the Rhine River, Geo. J., 2 (1969) 108–118.
[29] D. Zhenhu, L. Jin-ling, L. Liuqiang, L. Huin, W. Hao, H. Zhenzhen, Distribution of Hg in mangrove plants and correlation with Hg speciation in sediments, Environ. Sci., 9 (2010) 2235–2239.
[30] S. Tokalioglu, S. Kartal, Multivariate analysis of the data and speciation of heavy metals in street dust samples from the Organized Industrial District in Kayseri (Turkey), Atmos. Environ., 40 (2006) 2797–2805.
[31] X. Han, X. Lu, G. Qing, Y. Wu, Health risks and contamination levels of heavy metals in dusts from parks and squares of an industrial city in semi-arid area of China, Int. J. Environ. Res. Public Health, 14(8) (2017).
[32] Y.R. Liu, X. Lu, L. Zhao, J. An, J.Z. He, E.M. Pierce, A. Johs, B.H. Gu, Effects of cellular sorption on mercury bioavailability and methyl mercury production by desulfovibriodesulfuricans ND132, Environ. Sci. Technol., 50 (2016) 13335–13341.
[33] S.B. Nicolas, E. Preus, J. Katon, M. Hiltner, Selective extractions to assess the bio geo chemically relevant fractionation of inorganic mercury in sediments and soils, Analyt. Chimica Acta., 479 (2003) 233–248.
[34] H. Zhu, C. Chen, C. Xu, Q. Zhu, D. Huang, Effects of soil acidification and liming on the phytoavailability of cadmium in paddy soils of central subtropical China, Environ. Poll., 219(Supplement C) (2016) 99–106.
[35] T. Larssen, G.R. Carmichael, Acid rain and acidification in China: the importance of base cation deposition. Environ Poll., 110(1) (2000) 89–102.
[36] S.A.M.A.S. Eqani, A.K. Bhowmik, S. Qamar, S.T.A. Shah, M. Sohail, S.I. Mulla, M. Fasola, H.Q. Shen, Mercury contamination in deposited dust and its bioaccumulation patterns throughout Pakistan, Sci. Total Environ., 569–570 (Sup. C) (2016) 585–593.
[37] M. Rajaee, N.R. Long, P.E. Renne, N. Basu, Mercury exposure assessment and spatial distribution in a Ghanaian small-scale gold mining community, Int. J. Environ. Res. Public Health., 12(9) (2015).
[38] J. Árvay, L. Demková, M. Hauptvog, M. Michalko, D. Bajčan, R. Stanovič, J. Thomas, M. Hrstkova, P. Trebichalsky, Assessment of environmental and health risks in former polymetallic ore mining and smelting area, Slovakia: Spatial distribution and accumulation of mercury in four different ecosystems, Ecotoxicol. Environ. Safety, 144 (Sup. C) (2017) 236–244.
[39] Y. Lin, F. Fang, J. Wu, Z. Zhu, D. Zhang, M. Xu, Indoor and outdoor levels, sources, and health risk assessment of mercury in dusts from a coal-industry city of China, Human Ecol. Risk Assess. Int. J., 23(5) (2017) 1028–1040.

**Supportive Tables**

Table S1
The improved BCR sequential extraction scheme

| Extraction step | Dust phase | Reactive/concentration/ pH | Methods |
|---|---|---|---|
| F1 Hg-sol | Water soluble | Distilled water: pH 7 | 25 mL distilled water was added to 1.00 g of dry dust sample in a 100 mL polypropylene tube. Shake 2 h (22±5°C); centrifuge at 3000 rpm for 20 min. |
| F2 Hg-ex | Exchangeable, water and acid soluble (e.g.,carbonates) | Acetic acid: $CH_3COOH$ (0.11 mol $L^{-1}$), pH 2.9 | Add 40 milliliters $CH_3COOH$. Shake 16 h (22±5°C); centrifuge at 3000 rpm for 20 min. |
| F3 Hg-re | Reducible (e.g., iron/manganese oxides) | Hydroxyl ammonium chloride: $NH_2OH{\cdot}HCl$ (0.1 mol $L^{-1}$) at pH 2 | Add 40 millilitres $NH_2OH{\cdot}HCl$. Shake 16 h (22±5°C); centrifuge at 3000 rpm for 20 min. |
| F4 Hg-ox | Oxidisable (e.g., organic substance and sulphides) | Hydrogen peroxide: $H_2O_2$ (8.8 mol $L^{-1}$), followed by ammonium acetate: $CH_3COONH_4$ (1.0 mol $L^{-1}$) at pH 2 | Add 10 milliliters $H_2O_2$. Digestion 1 h (22±5°C); add 1010 milliliters $H_2O_2$; digestion 1 h (85±2°C); add 50 milliliters $CH_3COONH_4$; shake 16 h (22±5°C); centrifuge at 3000 rpm for 20 min. |
| F5 Hg-resid | Remaining, non-silicate bound metals | Aqua regia: 3HCl + $HNO_3$ | Add 3 ml distilled water, 7.5 ml 6 mol/L HCl; 2.5 ml 14 mol/L$HNO_3$; standing 1 night; countercurrent boiling 2 h. |

Table S2
Content of Mercury in the urban surface dust in China and other countries (μg/kg)

| Place | Mean | Range | Time | Source |
|---|---|---|---|---|
| Nanjing | 323 | 35.2~4.99 × $10^3$ | 2016 spring, summer | Current study |
| Huainan | 72 | 91–235 | 2015 spring | [39] |
| Pakistan | 1120 | 30–6120 | 2016 | [36] |
| Kejetia, Ghana | 36 | 5–248 | 2010 | [37] |
| Guangzhou | 1470 | 13–3616 | 2013 spring | [24] |
| Nanjing | 120 | 50~340 | 2009 autumn | [12] |
| Baoji | 1110 | 480–2320 | 2006.2 | [32] |
| Xian | 638 | 108–5212 | 1998, 1999, 2001 | [17] |
| Beijing | 340 | 45~1378 | Winter | [16] |
| Shanghai | 140 | 10–530 | 2008 | [24] |
| Northeast of China | 1222 | 119–5212 | 2007 | [19] |
| Kavala'sregion, Greece | 100 | – | 2002.7~2003.6 | [9] |
| Ottawa | 29 | 4~188 | Winter | [27] |

Table S3
The speciation of mercury from surface dust in different areas in Nanjingcity(μg/kg)

| Extraction step | Statistics | Natural district | Cultural and educational district | Residential district | Electronic business district | Comprehensive business district | Traffic district | Industrial district (1) | Industrial district (2) |
|---|---|---|---|---|---|---|---|---|---|
| F1 | Range | 0–12.8 | 0–37.6 | 0–6.10 | 0–144 | 0–23.6 | 6.62–12.6 | 3.61–14.5 | 3.91–12.9 |
| | Mean | 2.16 | 6.56 | 1.61 | 17.6 | 6.65 | 9.22 | 8.06 | 7.54 |
| F2 | Range | 0–10.2 | 0–16.3 | 0–22.0 | 0–44.3 | 3.83–10.4 | 0–20.0 | 2.28–7.18 | 0–16.0 |
| | Mean | 2.00 | 4.87 | 8.60 | 12.5 | 8.34 | 8.13 | 4.69 | 6.95 |
| F3 | Range | 0–17.0 | 0–20.2 | 0–16.0 | 0–71.2 | 0–43.4 | 30.0–46.4 | 0–23.0 | 6.24–16.9 |
| | Mean | 2.78 | 5.47 | 6.02 | 24.1 | 8.78 | 36.2 | 14.7 | 13.1 |
| F4 | Range | 6.80–66.7 | 4.98–271 | 14.2–237 | 38.0–2.55 × $10^3$ | 22.1–188 | 25.3–61.1 | 17.5–43.8 | 12.0–36.8 |
| | Mean | 29.3 | 58.4 | 142 | 589 | 78.0 | 44.5 | 27.0 | 24.1 |
| F5 | Range | 10.3–40.3 | 21.9–67.6 | 30.3–210 | 75.2–2.34 × $10^3$ | 19.7–322 | 1.79–14.4 | 0.660–5.85 | 1.38–2.68 |
| | Mean | 24.5 | 44.7 | 109 | 502 | 172 | 7.61 | 2.66 | 1.82 |
| Total | Range | 17.0–147 | 26.9–412 | 44.5–493 | 113–5.14 × $10^3$ | 45.7–587 | 63.5–154 | 24.1–94.3 | 23.6–85.2 |
| | Mean | 60.8 | 120 | 267 | 1.15 × $10^3$ | 274 | 106 | 57.0 | 53.5 |

Table S4
The characteristics of different study areas in Nanjing city

| Areas | Traffic activities | Human activities | Regional characteristics |
|---|---|---|---|
| Natural district | Hardly none | Many | Natural Park |
| Cultural and educational district | Hardly none | General | School |
| Residential district | Hardly none | General | Living Community |
| Electronicbusiness district | General | Many | Electronic products stores |
| Comprehensive business district | Serious | Many | Commercial center |
| Traffic district | Serious | Rare | Tunnel portal |
| Industrial district (1) | Slight | Rare | Newly district in Northeast of Nanjing |
| Industrial district (2) | Slight | Rare | More traffic |