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Atmospheric Mercury Concentrations in Guangzhou City, Measured by Spectroscopic Techniques

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Abstract: Atmospheric levels of atomic mercury pollution were measured using spectroscopic techniques in the city of Guangzhou, Guangdong Province, China. Assessments were mainly performed at ground level using a portable (vehicle mounted or hand carried) Zeeman modulation correlation spectrometer (Lumex RA-915M), and the results are given in easily comprehensible diagrams. Measurements were made with continuous recording in car traverses along major roads which cross the city, but also at selected spots, such as at a university campus with laboratory buildings. Further, pollution levels at different locations were recorded when walking through a major and a small hospital. While concentrations in the city in the range 3–10 ng/m^3 were typical, and strongly dependent on the traffic situation, very high concentrations (up to 1300 ng/m^3) were found at certain indoor hospital locations, again drawing attention to the fact that high mercury levels due to inadequate handling routines can remain undetected but could readily be eliminated by adequate measurements and subsequent sanitation.

Keywords: gaseous atomic mercury; concentration mapping; Zeeman modulation spectrometer; Guangzhou; indoor mercury mapping

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1. Introduction

The purpose of the present paper is to, in a pedagogical way, illustrate what levels of atmospheric mercury pollution a citizen of a major urban center may be exposed to along major roads, in park environments and at certain indoor locations. Further, we stress that adequate measurements can reveal "silent" pollution sources, e.g., in hospitals, which could easily be eliminated once the knowledge of an otherwise overlooked problem is available. We also point out the significance of techniques based on optical spectroscopy in real-time assessment of the levels of mercury, which as an atmospheric pollutant is present predominantly in atomic form.

Mercury is a serious heavy metal pollutant, which has attracted much attention [1–3]. Mercury emissions come from natural sources such as volcanoes and geothermal fields [4,5], and from anthropogenic sources such as chloralkali and incineration plants, mercury mining and mercury handling, as well as from fossil fuel combustion [6–10]. The latter source includes emissions from road vehicles (see [11–13]). The global anthropogenic mercury emission is dominated by coal burning (24%) and artisanal and small-scale gold mining (37%) [14]. Mercury in the environment can be transported over long distances through the atmosphere and by ocean currents, which leads to transboundary pollution and even to global environmental impact from local mercury releases [1,15,16].

Because of its special properties, such as being a conducting liquid with high density, mercury is widely used in many technical contexts (thermostats, batteries, pressure gauges, etc.) [17], and in various industries, notably in electrolytic production of sodium hydroxide NaOH [8,9]. Mercury compounds have also had applications in agriculture and in the medical field [2]. At present, mercury receives great attention from the international community because of its high toxicity, bioaccumulation and long-term retention [1]. Even trace amounts of mercury can harm human health [18,19]. Mercury exists in different forms in the environment, with methyl mercury as a particularly serious agent, which is responsible for many severe intoxication events [18–20]. Many countries have adopted the Minamata convention from 2013 [21], dealing with the reduction of mercury utilization. It is named after a Japanese fishing village hit in 1956 by widespread mercury intoxication of the population [20]. Since mercury pollution affects the atmosphere, soil and water, it is difficult to eradicate [1,2]. The best way is clearly to reduce or eliminate its release at the source.

Related to the rapid development of China, pollution problems have manifested and are now intensely combatted by authorities. This also includes mercury, which has been much studied [22–31]. The number of automobiles has risen sharply, and exhaust fumes contribute to mercury pollution problems [11–13].

It is known that hospitals and dentistry clinics are frequently subjected to elevated mercury levels, and medical staff as well as patients are therefore facing mercury pollution hazards [32–37]. This is also the case in China [38,39]. Hospitals are places where mercury-containing equipment is relatively concentrated, but hazards are easily overlooked. Mercury used in hospitals, represented by, e.g., mercury sphygmomanometers (instruments for measuring blood pressure) and mercury thermometers, is presently a non-negligible source of mercury pollution [40–42]. Such equipment has the advantages of low price, convenient maintenance, simple manufacturing, etc., and has been widely used in hospitals for a long time. Due to frequent use of mercury-containing products in hospitals, and occasional improper handling by some medical personnel, mercury leaks occur. The mercury is not always handled as the leak occurs, but it may be left as a "silent" source of mercury pollution, lasting for a long time.

Amalgam, a mercury alloy with silver, tin, zinc and copper, has for a long time been used worldwide in dentistry as a tooth filling material [33,34,37]. Mercury is thoroughly mixed with metal powder in a mechanical blender before use to form the amalgam. In this process, a small amount of mercury will evaporate. Clearly, because of the handling of the material and treatment residues, such dentistry clinics have traditionally been associated with high mercury levels. Amalgam is now, like mercury-containing fluorescent tube discharge light sources, being phased out at a high rate.

Unlike other pollutants, mercury is present in the atmosphere mainly as free atoms [16,43,44], which makes optical spectroscopic techniques especially suited for sensitive, real-time measurements (see, e.g., [45]). Mercury can be concentrated from the ambient air by amalgamation in exposed gold foils over some times, followed by rapid heating and detection of the released mercury cloud through atomic absorption or fluorescence spectroscopy. Atomic mercury can also be detected without pre-concentration using a Zeeman modulation optical correlation technique [46] and laser-spectroscopic techniques based on long-path optical absorption [47] or differential absorption lidar techniques [9,10,48].

In order to illuminate the presence and hazards of mercury in the urban environment, we have pursued a study in the Southern China city of Guangzhou, the third largest Chinese city. This is by no means a systematic study yielding time-averaged and representative data for mercury pollution, but it intends, in a pedagogical way, to illustrate what levels a citizen in a major city may be exposed to. Data in easily comprehensible diagrams show high indoor mercury concentrations in two hospitals, lower concentrations in studied university laboratories and moderately elevated concentrations in the ambient city air, as studied along major highways.

2. Study Design

2.1. Mercury Monitoring Instrumentation

For a 10-year period, our group has been developing environmental monitoring using optical spectroscopic techniques, in particular lidar applications, with extensive monitoring of atmospheric atomic mercury [49], including fumes from the Emperor Qin underground mausoleum in Xi'an [50]. As a complement, we have in the present study used a portable RA-915M atomic mercury analyzer supplied by Ohio Lumex Corp., which is also very suited for indoor measurements. Here, we present measurement results using this instrument, with a sampling strategy, which is clearly not representative for achieving time and spatially averaged mean values, but which serves a different purpose, as described in the introduction. Representative values for different regions, as acquired, e.g., from the global GMOS mercury monitoring network, are presented in [51,52].

The instrument used is based on differential Zeeman atomic absorption spectrometry using high-frequency modulation of light polarization [46]; see also [45].

The operational principle is shown in Figure 1. The radiation source (a mercury lamp) is placed in a permanent magnetic field H. The mercury resonance line $6s^2\,{}^3P_1$-$6s6p\,{}^1S_0$ at $\lambda = 254$ nm is then split into three polarized Zeeman components (π, σ^+ and σ^-, respectively). When radiation propagates along the direction of the magnetic field, only the radiation of the σ-components is present (see, e.g., Ref. [45], Figure 4.9). The lamp contains a separated Hg isotope, the radiation of which is considerably spectrally displaced with regard to the pressure-broadened envelope of the natural mercury isotope distribution [53]. Then, only one of the magnetically displaced σ-components from the lamp can be absorbed by ambient mercury. When mercury atoms appear in the light path, the difference between the intensities of the σ-components increases as the mercury vapor concentration grows.

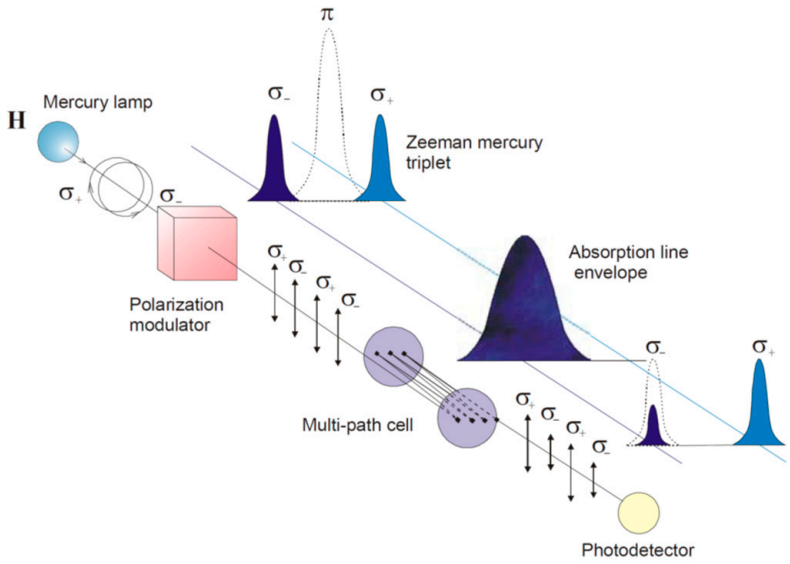

Figure 1. Lay-out of the Zeeman modulation correlation spectrometer (Lumex RA-915M; Courtesy: OhioLumex Corp., Cleveland, OH, USA).

The two σ-components (with opposite circular polarization) are separated by a polarization modulator. Since the modulation is specific to mercury, other potentially interfering gases do not affect analyzer readings, which are obtained as the output of a lock-in amplifier, operating at the modulation frequency (Ref. [45], Figure 6.72). A multi-path cell with an effective length of about 10 m is used to enhance the sensitivity of the analysis. The instrument was operated from a car in city traverses and was hand carried in all further measurements.

2.2. Measurements of Atmospheric Atomic Mercury

As mentioned, our measurements refer to Guangzhou City, Guangdong Province, China. The Lumex optical mercury analyzer was calibrated before the measurements, and intermittently during the cause of the recordings. An internal, highly temperature-stabilized mercury vapor calibration cell was used for the calibration. Initially, the instrument was allowed to stabilize for 20–30 min. After the baseline was stable, the ambient air was introduced through a PVC pipe to the gas inlet of the analyzer. In our study, we collected mercury concentration data every 10 s during the measurement period. Data are available in real time in this fast and direct analytical method.

Measurements were performed on roads with large traffic flow, with maps shown in Figure 2. Figure 2a shows the road from the Guangzhou University City to the Baiyun area (36 km), and monitoring was pursued in both directions and on two different occasions. Figure 2b shows a series of highways, crossing the central part of the city from West to East and with a length of 10 km, and measurements were taken on one occasion. When measuring, the instrument is operated from the back seat of a car, with the extraction tube extending out from the car window.

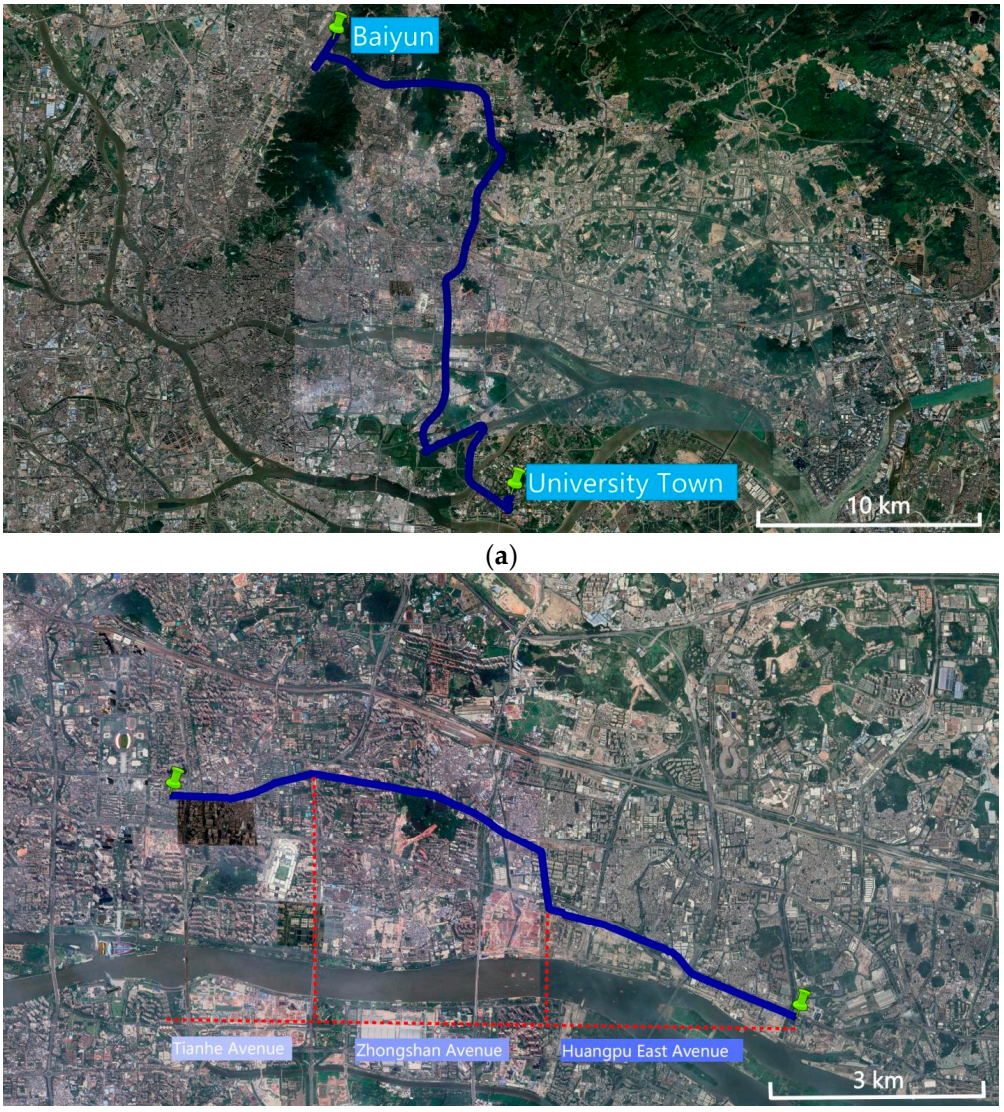

Figure 2. Maps of traverses covered across the city of Guangzhou. (**a**) University Town—Baiyun, (**b**) Central Guangzhou, West → East.

We also studied university campus locations with different laboratory buildings. Further, we conducted extensive spot-monitoring at multiple locations in a major hospital, as well as in a small hospital. The instrument was hand-carried while continuously recording in these applications.

3. Measurements and Results

3.1. Air Concentrations Retrieved from City Traverses

Measurements along the road from the University City to Baiyun and back were conducted on an Autumn and a Spring occasion. Data from the city traverses on 23 September 2019 and 31 March 2020 are shown in Figure 3. From the graphs, we can see that the mercury concentration monitored on the three traverses shown in panels (a–c) is relatively low, with values varying in the range of 2–5 ng/m^3. The mercury concentration in the (d) chart is higher, and varies in the range of 3–25 ng/m^3. The concentration of mercury on the highway is clearly related to the volume of traffic. Rush hour conditions in China occur from 4:30 pm to 6:00 pm with large traffic volume on the highways, and the vehicles are often in a state of stagnation. Therefore, the exhaust emissions of automobiles are relatively concentrated and the diffusion is frequently slow, which results in high and varying mercury concentrations [11–13].

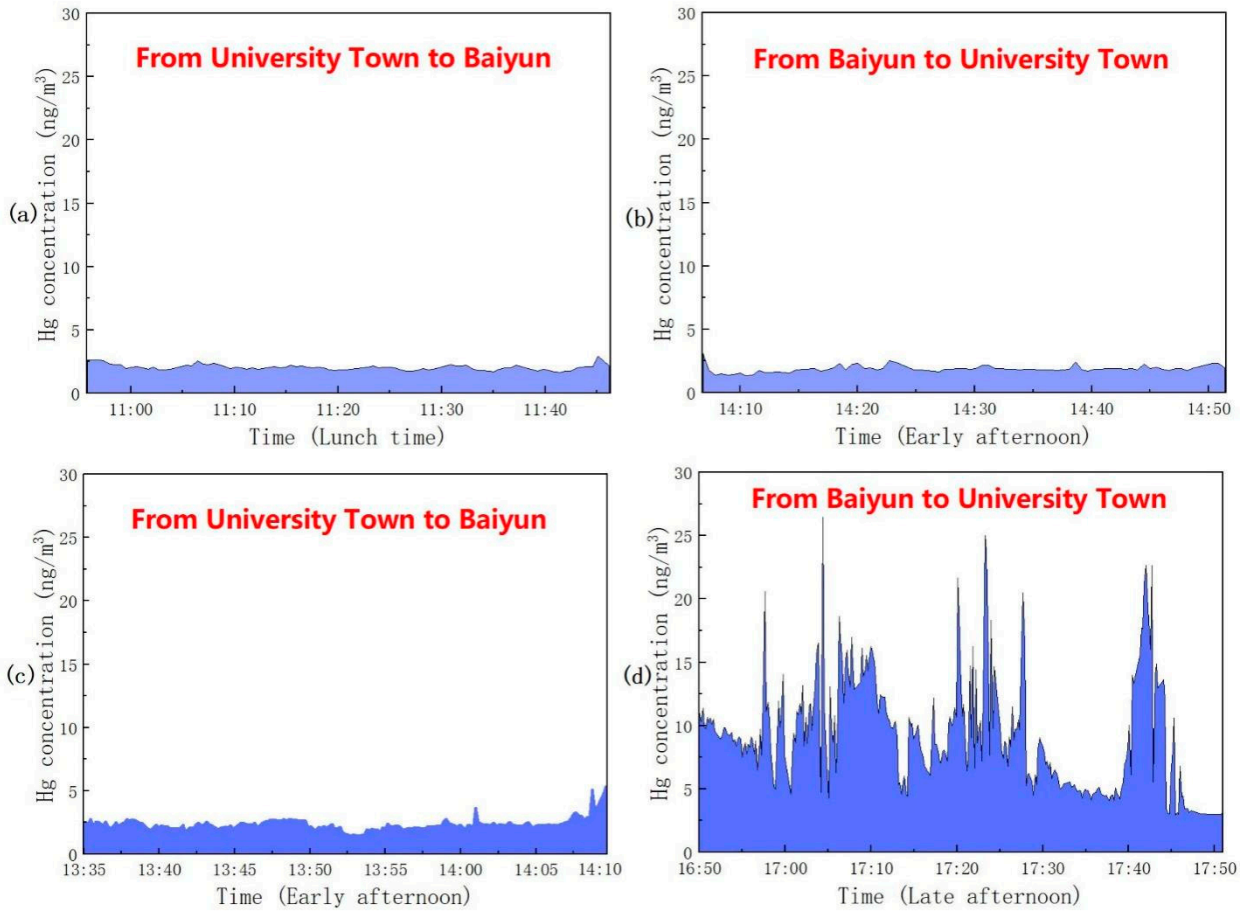

Figure 3. (**a**,**b**) Measurements from University Town to Baiyun and back to University Town on 23 September 2019; (**c**,**d**) corresponding data for 31 March 2020.

In order to complement the above observations, we conducted further mercury concentration monitoring on a road with a large traffic volume crossing Guangzhou from West to East: Tianhe Avenue continuing into Zhongshan Avenue, and further on to Huangpu East Avenue, in total 10 km. The mercury concentrations along these roads are shown in Figure 4, during the rush hours of 30 March 2021.

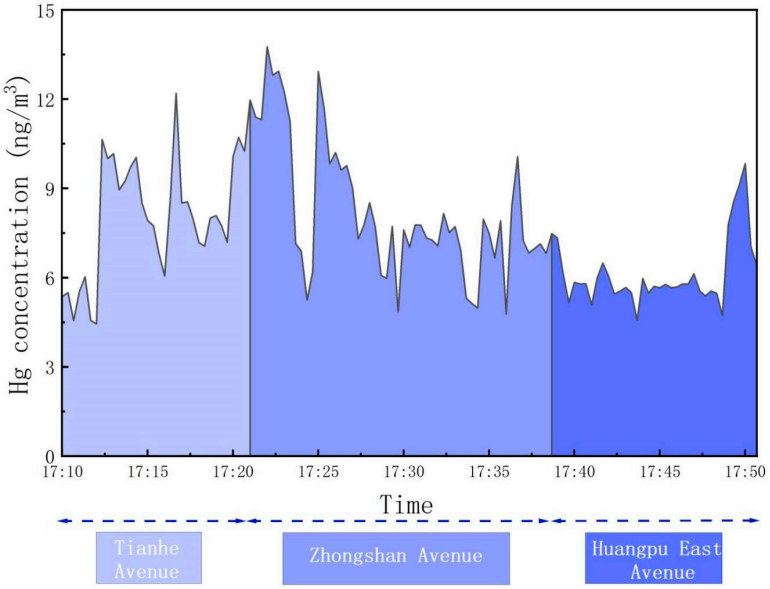

Figure 4. Measurements on 30 March 2021 from West to East across the city of Guangzhou along the Tianhe Avenue, the Zhongshan Avenue, and the Huangpu East Avenue.

As shown in the figure, the mercury concentrations on these three roads are higher than those shown in Figure 3a–c, and the values for Zhongshan Avenue and Tianhe Avenue are slightly higher than those of Huangpu East Avenue. This confirms an observation that the mercury concentration on highways is related to the traffic density. The mercury pollution of automobile exhaust seems to be a main source of atmospheric mercury pollution, with correlation to the volume of traffic.

3.2. Concentration Data at Selected Locations of a University Campus

Mercury concentration measurements were performed at several locations in the Guangzhou University City (see lower part of Figure 2a) and the results are shown in Figure 5. The concentration of mercury atoms at Laboratory 1 (related to chemistry) is higher than at Laboratory 2 and Laboratory 3 (related to physics/optics). Concentrations are low at a lake and at a grove location.

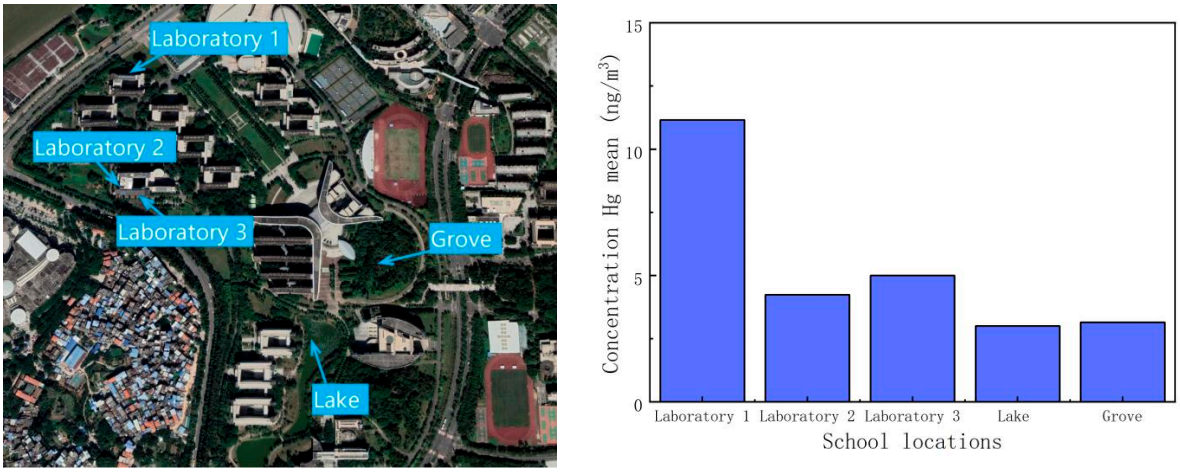

Figure 5. Measurements at different locations on the Guangzhou University City campus.

3.3. Indoor Concentrations Data at Selected Locations in Two Hospitals

In order to further illuminate potential mercury pollution exposure, we conducted fixed-point surveys at several departments of a major hospital on two occasions, separated by 18 months, and performed measurements on one occasion at a much smaller university clinic. The mercury concentrations at the different locations of the major hospital are shown in Figure 6. Figure 6a,b is the mercury concentration monitored on 23 September 2019. Figure 6c,d is the corresponding data for 31 March 2021. On both occasions, the peak concentrations were found in the emergency clinic, especially near the door of an operating room. Due to the unique physical characteristics with a very high vapor pressure of mercury at room temperature, the accidental breakage of, e.g., clinical glass thermometers or sphygmomanometer containing mercury may explain the high mercury vapor concentration in such emergency clinics. Additionally, the concentration of mercury at the dentistry department is relatively high, and is related to mercury-containing amalgams (about 50% is mercury).

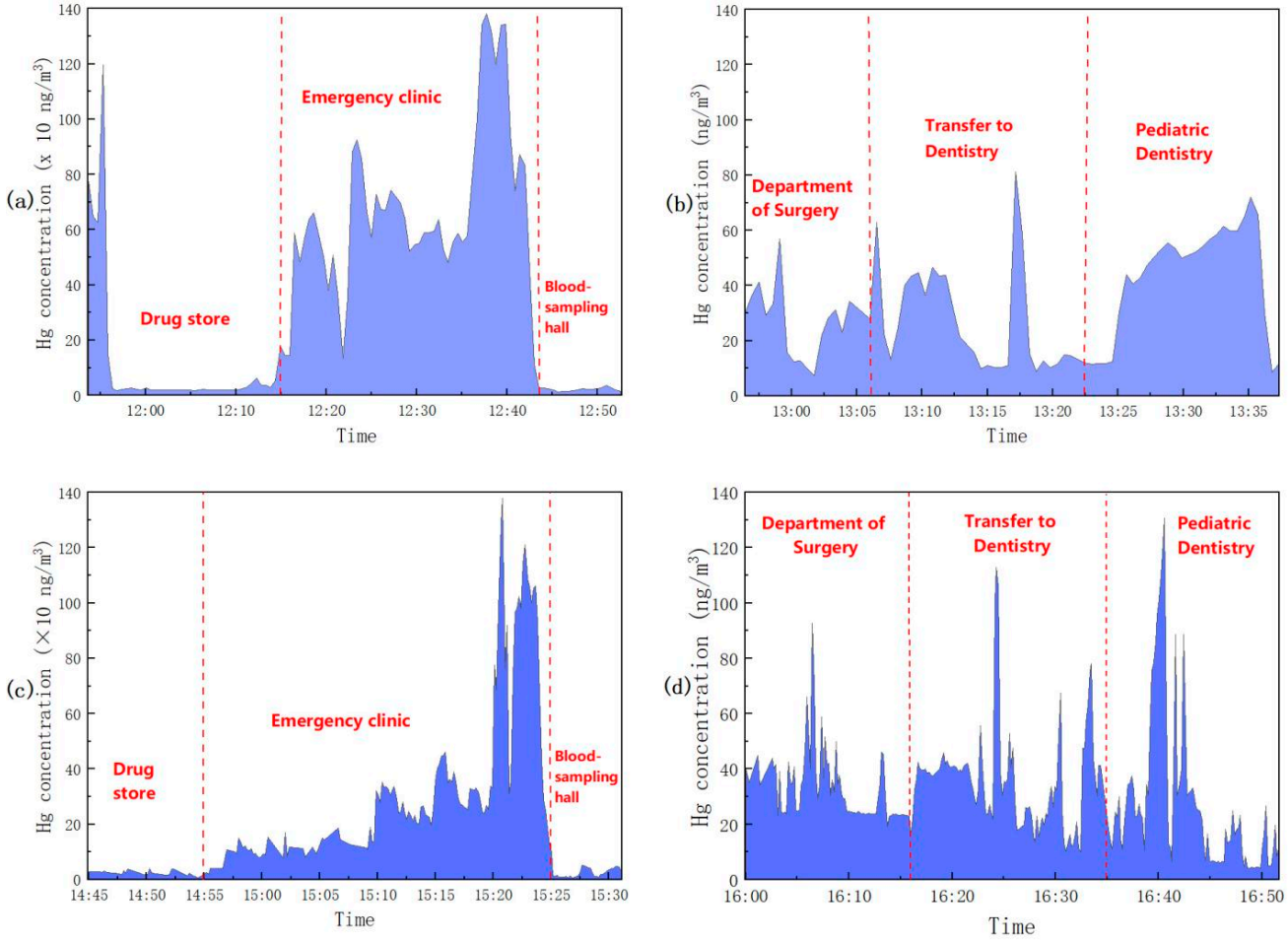

Figure 6. Measurements at different sections of a major Chinese hospital on 23 September 2019 (**a**,**b**), and at corresponding sites on 31 March 2021 (**c**,**d**). Note the multiplicative factor of ×10 in diagrams (**a**,**c**).

For comparison, we also conducted a study of departments of a much smaller hospital, serving a university community. It can be seen from Figure 7 that mercury concentrations vary in the range of 20~35 ng/m^3, which is significantly lower than the values observed in the emergency clinic of the major hospital, as shown in Figure 6.

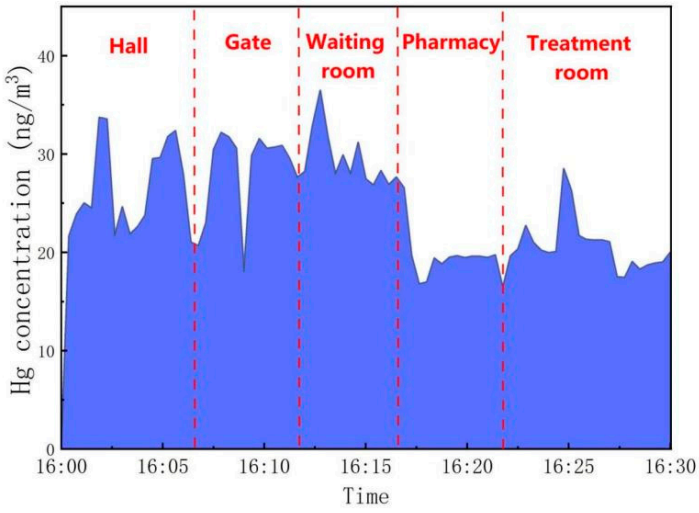

Figure 7. Measurements at different sections of a small Chinese hospital, on 21 September 2020.

4. Discussion

We have performed exploratory measurements of atomic mercury concentrations at various locations in the Chinese city of Guangzhou. Our measurements show that the mercury concentrations correlate with the traffic flow on given roads. The monitored mercury concentrations were low when the traffic volume was low on the road connecting the University City to Baiyun, varying in the range of 2–5 ng/m^3. In contrast, from 4 to 6 o'clock during the rush hour, the traffic flow was large, and the mercury concentration could reach up to 30 ng/m^3. Clearly, the mercury pollution due to car exhausts is substantial. Such emissions not only cause atmospheric mercury pollution, but also affect the soil and vegetation close to the road. Green areas with lower traffic showed values of about 3 ng/m^3.

The outdoor atmosphere mercury concentrations observed close to the ground in the present study can be compared with data for the University City of Guangzhou, measured by differential atmospheric lidar by our group. At altitudes of the order of 100 m, values of 4–7, 10–13, and 5–7 ng/m^3 were recorded on different occasions [54–56]. Lidar measurements in the Xi'an area gave mercury concentration data in the 2–13 ng/m^3 interval [57].

The indoor atmospheric mercury content varies a lot in relation to different types of activities. Physics and chemistry laboratories could be expended to have elevated concentrations, but in our study (Figure 5) they were found to be moderate. Hospitals are known to have much higher concentrations than other places. As mentioned, this is because many types of medical equipment in hospitals contain mercury. Improper operation of medical equipment may cause leakage of mercury, causing hazards. In large hospitals, mercury-containing medical equipment and medical materials are used relatively frequently in emergency rooms and dentistry, and mercury content can be expected to be much higher than in other departments. This is confirmed in our studies (Figure 6), where concentrations as high as 1300 ng/m^3 were recorded. Dependent on the hospital size, and related to the number of beds, in- and out-patient volume, etc., the amount of mercury loss can vary greatly [28]. Since the number of hospital visits and the number of inpatients at a small hospital is relatively small compared with numbers pertaining to the large hospital discussed earlier, lower values, 20 to 35 ng/m^3 (Figure 7), were observed in a reference unit, serving a university community.

In summary, our measurements on few selected occasions in the major Chinese city of Guangzhou revealed atmospheric mercury levels in the outdoor environment along roads reaching 10 ng/m^3 and sometimes even higher. These levels are in conformity with more systematic studies; see [31], where the Guangzhou levels were found to be higher than those

of, e.g., Beijing. A Chinese review study [29] states that the gaseous mercury concentrations in urban areas of China are often 1.5–5-fold higher compared to the corresponding settings in North America and Europe. Recent examples of such studies are from Boston/US [58], Toronto/Canada [59] and Basel/Switzerland [60]. As a reference, the global, clean air background level is 1.3–1.7 ng/m^3 [6,52,61], and clearly it is difficult to approach such values in a major city environment.

Certain indoor environments, in particular in hospitals and dentistry clinics, can reach extremely high levels; in our study, they reached up to 1300 ng/m^3. Problems of this kind are well known from many previous studies [32–42]. Because of the confinement, indoor air, even in households, easily can have a higher mercury pollution level than the outdoor air [60].

Our study in no way intends to be comprehensive, and is clearly not indicative of the averaged, time-integrated pollution levels. However, we believe that in a pedagogical way, through comprehensible diagrams, it illustrates what atmospheric mercury levels citizens in major cities may be exposed to.

Clearly, a study of the kind presented here can be extended to give a fully comprehensive view of the mercury pollution situations in out- and indoor environments. An instrument of the kind used in our study is easily moved between different locations. It provides real-time information, including readily detection of hotspots. These can be due to accidental minor spills, e.g., in a hospital environment, or due to prior industrial activities, in both cases allowing clean-up activities requiring limited efforts once the situational conditions are revealed by measurements.

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Conflicts of Interest: The authors declare no conflict of interest related to this paper.

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