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Spatial and Temporal Variability of Road-Deposited Sediment (RDS) Within the Greater Manchester Urban Conurbation, UK

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Abstract

Road-deposited sediment (RDS) has become an increasingly important medium for analysing anthropogenic urban metal accumulation. This study aims to understand the environmental risk of RDS, through its spatial and temporal variability, across the Manchester urban conurbation. Using an acid digest and spectrometry, the concentrations of iron (Fe), copper (Cu), manganese (Mn), zinc (Zn) and lead (Pb) in the RDS were determined. The geochemical maps presented show a high degree of spatial variability; however, all five metals display high concentrations within Manchester City centre and low concentrations in Salford Quays. A comparison with historical data finds that potentially toxic element (PTE) concentrations have predominantly increased over time. Pb was the only PTE with a lower average concentration since a 2006 study, albeit still high due to its persistent nature.

1. Introduction

1.1. Urban pollution

Environmental pollution concerns are growing in parallel with the growth of the human population. The world's population is over three times larger than in the mid-twentieth century and is expected to rise to over 10 billion by 2059 (United Nations, 2022). One major environmental issue is a large population situated in a dense geographical area, aggravating pollution and congestion (Mitra, 1984). In 2018, 23% of the world's population lived in a city with at least 1 million inhabitants and this figure is expected to rise to 28% by 2030 (Government Office for Science, 2021). The digital age is creating a new epoch of environmental concerns, alongside increasing urbanisation. Therefore, understanding the processes affecting urban systems is a significant global concern.

The term "urban sediment" has been defined as the accumulated sediment found on street surfaces (Taylor, 2007). Taylor (2007) describes the highly dynamic urban sediment system from the sources, transport mechanisms, and deposition into the urban environment. For example, the sediments deposited and stored on street surfaces can be classified as temporary storage elements (Taylor and Owens, 2009). Wind can locally redistribute finer sediment onto road surfaces, substantially influencing air quality and human health due to airborne particulate matter. Waterbodies also serve as receptors, urban runoff conveys pollutants into receiving canals, rivers, or docks through the movement of

water on impermeable surfaces. This makes it challenging to analyse the spatial distribution of the sediment due to its dynamic and interactive nature. A review by Dietrich *et al.* (2022) notes additional outputs to those described by Taylor (2007), including street sweepings. Metals are known to be bound to these sediments, meaning that the urban sediment cascade provides an avenue for researching and mitigating trace metal concentrations in the urban environment.

1.2. Heavy metal pollution

Metallic elements with a relatively high density compared to water have been referred to as heavy metals in the past (Fergusson, 1990). The term "heavy metals" has been replaced with "Potentially Toxic Elements" (PTEs) which, for the purpose of this study, is a more relevant term (Pourret and Hursthouse, 2019). PTEs can be naturally exposed to humans and ecosystems from plant macronutrients or natural phenomena (such as weathering) sourced from the earth's crust (He *et al.*, 2005). However, research has shown that exposure to PTEs through anthropogenic pathways significantly impacts people and the environment (Vareda *et al.*, 2019). Among numerous other environmental pollutants, PTEs occur within urban conurbations around the globe because of concentrated industrial and traffic-related sources (Nachana'a and Ezekiel, 2019). PTEs are known to be potentially toxic and non-degradable, yet are prone to accumulate environmentally and biologically (Chen *et al.*, 2016). Over time, bioaccumulation of certain PTEs,

such as Pb and Mn, will increase respiratory illnesses and carcinogenicity in humans through inhalation or ingestion from contaminated vegetation and livestock, inhalation, and adsorption (Yousaf *et al.*, 2016; Sodhi *et al.*, 2022). According to a study by Rai *et al.* (1981), a heavy metal's toxicity can be affected by the presence of other metals through synergistic or antagonistic interactions. Manchester is widely known to be the first industrial city in the UK, predominantly from its cotton industry which used coal-powered steam engines. Many types of PTEs are associated with the burning of coal, including lead (Pb), mercury (Hg), and arsenic (As) (Li *et al.*, 2018). Post-industrial revolution, the environmental legacies from coal smoke and other anthropogenic sources of pollution have been a significant issue for Manchester's modern development.

1.3. Road-deposited sediment

The term 'road-deposited sediment' (RDS) has begun replacing the older term 'road dust', as it implies that the sediment is only composed of fine-grained material

(Robertson and Taylor, 2007). RDS is a compound made from assorted grain sizes of organic and inorganic material abundantly found in urban environments (Taylor and Owens, 2009). It is often found to contain natural and anthropogenic sediments, where several sources, including combustion products and deterioration of vehicles, can be liable (Beckwith *et al.*, 1986). This study will focus on the inorganic metal compounds; however, it is important to recognise that organic contaminants can also be found in RDS, including polycyclic hydrocarbons (PAHs) (Dietrich *et al.*, 2022). It can contain accumulated elements, including PTEs, as a medium for physical, chemical, and biological transport pathways. A study by Eriksson *et al.*, (2007) found that 30 metals and trace inorganic compounds may be contained in stormwater runoff which has come into contact with impermeable surfaces like roads and roofs. RDS has become an increasingly important environmental sampling approach for analysing anthropogenic metal accumulation (Stone and Marsalek, 1996).

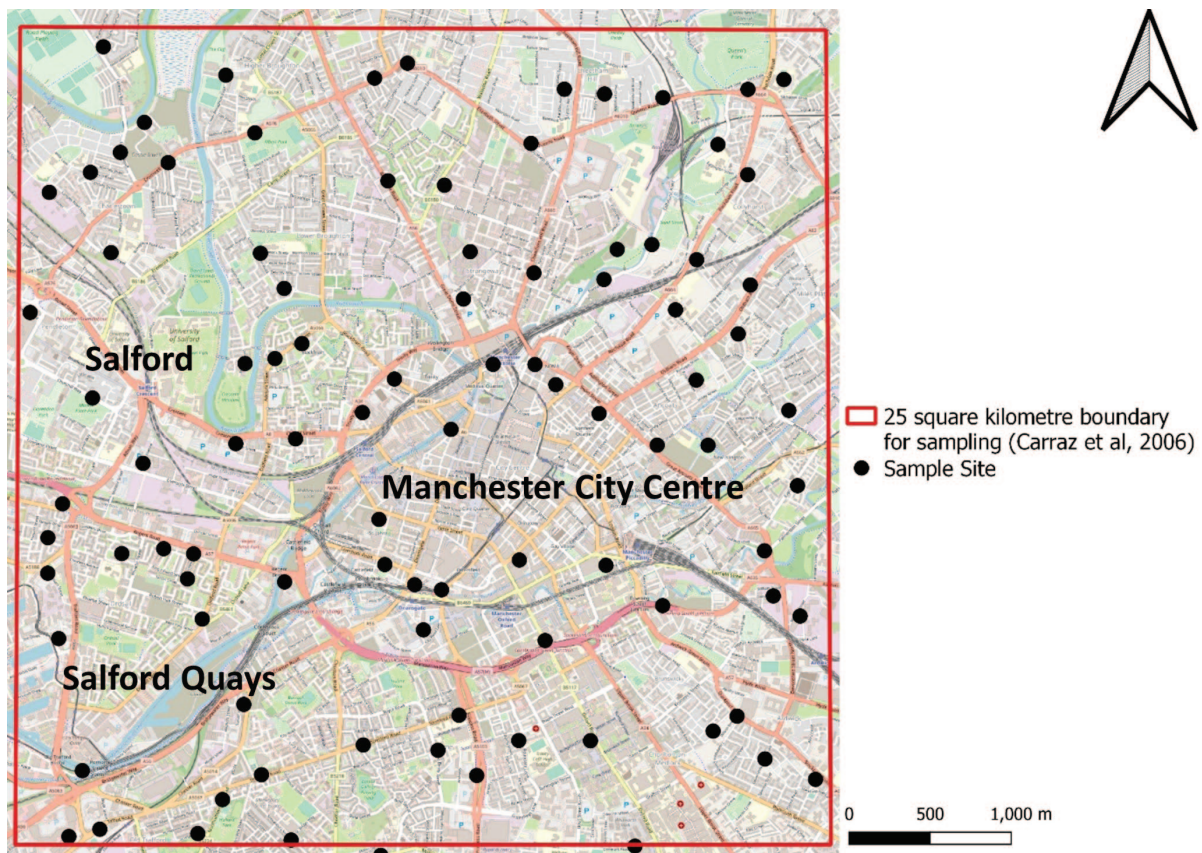


Figure 1: Map made on QGIS showing the 95 sample sites where the road-deposited sediment was collected, within the 25 km² sampling boundary as described in Carraz *et al.* (2006).

1.4. Knowledge gap

Urban pollution, particularly particulate air pollution, has been widely reported on by academics (Beckett *et al.*, 1998; Liang *et al.*, 2020; Sicard *et al.*, 2023) alongside journalists and authorities with policies put in place to reduce its impacts. It also highlights the necessity for improved monitoring and sampling of urban sediment. Numerous studies (Zhao *et al.*, 2013; He *et al.*, 2015; Suvarapu and Baek, 2017; Crispo *et al.*, 2021; Gao *et al.*, 2022) have discussed anthropogenic pollution in soils, rivers, and the atmosphere. The monitoring and analysis of RDS have been carried out since the 1970s; for example, a study by Laxen and Harrison (1977) discussed Pb in RDS from the use of leaded fuel. In recent years, more research in fine-grained RDS has been studied internationally, with an emphasis on grain size and spatial distribution (Zhao *et al.*, 2010; Owens *et al.*, 2011; Sutherland *et al.*, 2012; Herath *et al.*, 2013). The results, which analysed PTE concentrations found in RDS, followed a similar trend. For example, the Sutherland *et al.* (2012) study in Oahu, Hawaii, found that sediment with a grain size of <63 had the highest loading of all the metals examined. Zhao *et al.* (2010) in Beijing, China, found that the smallest-grained-sized particles (<44) contained the highest metal concentrations. There are notably fewer studies on the temporal changes of RDS (Vermette *et al.*, 1991; Robertson and Taylor, 2007). The Robertson and Taylor (2007) study was in Manchester City Centre. However, it only looked at the monthly variability in metal concentrations. There is a lack of research on the temporal change of RDS contaminants across a longer time frame.

1.5. Aims and objectives

The overall aim of this study is to supply new data on the state of RDS and the associated metal particulates in the Greater Manchester urban conurbation, UK. This new data will be compared to those published by Carraz *et al.* (2006) in North West Geography, which presented data on the spatial variability in road-deposited sediment composition. This will be achieved by meeting the following objectives: To understand the environmental risk of RDS and its spatial variability and to investigate the temporal changes of metals in RDS within a major urban conurbation.

2. Methodology

2.1. Sampling strategy

Sampling sites were selected to overlap with the historical data presented in Carraz *et al.* (2006). Figure 1 below presents the 95 sample site locations collected within the 25 km² sampling boundary. Sampling took place over 7 days in

August 2022 when the climate was more likely to be dry. Ninety-five RDS samples were collected from the curb side across Manchester City centre using a polyethylene dustpan and brush, with the site coordinates recorded; a similar method was undertaken by previous studies (Davies and Watt, 1987; Orgunsoola *et al.*, 1994; Xie *et al.*, 1999).

2.2. Acid digestion and metal analysis

The 95 samples were dried in a 40°C oven for over 48 hours to prepare for metal analysis. Each dried sample was then sieved to <2 mm to separate any large debris from the targeted fine dust particles. To ensure an accurate comparison with the historical data, the Carraz *et al.* (2006) methodology was used during the acid digestion and subsequent metal analysis. 0.5 M of HCl(aq) is the required concentration to determine the bioavailable metals in the samples following Sutherland *et al.* (2004) This was used by Carraz *et al.* (2006) where 0.5 g of sediment was added to 10 ml of 0.5 M HCl(aq). To begin the metal analysis, using a pipette, 10ml of the prepared 0.5 M HCl(aq) was added and placed into an Erlinmeyer flask containing 0.5g of the sediment sample. Each flask was covered with parafilm and shaken on the orbital shaker for 1 hour (Sutherland *et al.*, 2004). Once shaken, each sample was filtered into 25 ml volumetrics, then into universals for spectroscopy. No.1 filter paper was used, made of cellulose, with an aperture size of 11 µm. Following Carraz *et al.* (2006), the metal concentrations were determined using ICP-OES spectroscopy, where all five elements (Cu, Fe, Mn, Zn, Pb) are analysed simultaneously. Six calibration standards were made up to 0 ppm (blank standard), one ppm, two ppm, three ppm, four ppm and five ppm of each element. See Appendix A for the Cu standard calibration curve as an example.

2.3. Spatial and temporal analysis through geochemical maps

To conduct a qualitative comparison with Carraz *et al.* (2006), geochemical maps were created using IDW interpolation on the concentrations through QGIS. This was done due to the large sampling area and to better visualise the spatial variation. Since the concentrations have an extensive range, the concentrations were presented using the quantile method to improve the spatial variation in the geochemical maps and for a better temporal comparison with the historical maps (Carraz *et al.*, 2006).

3. Results & discussion

3.1. Spatial variability of trace metals in RDS

The spatial variability of the PTE concentrations (mg kg⁻¹)

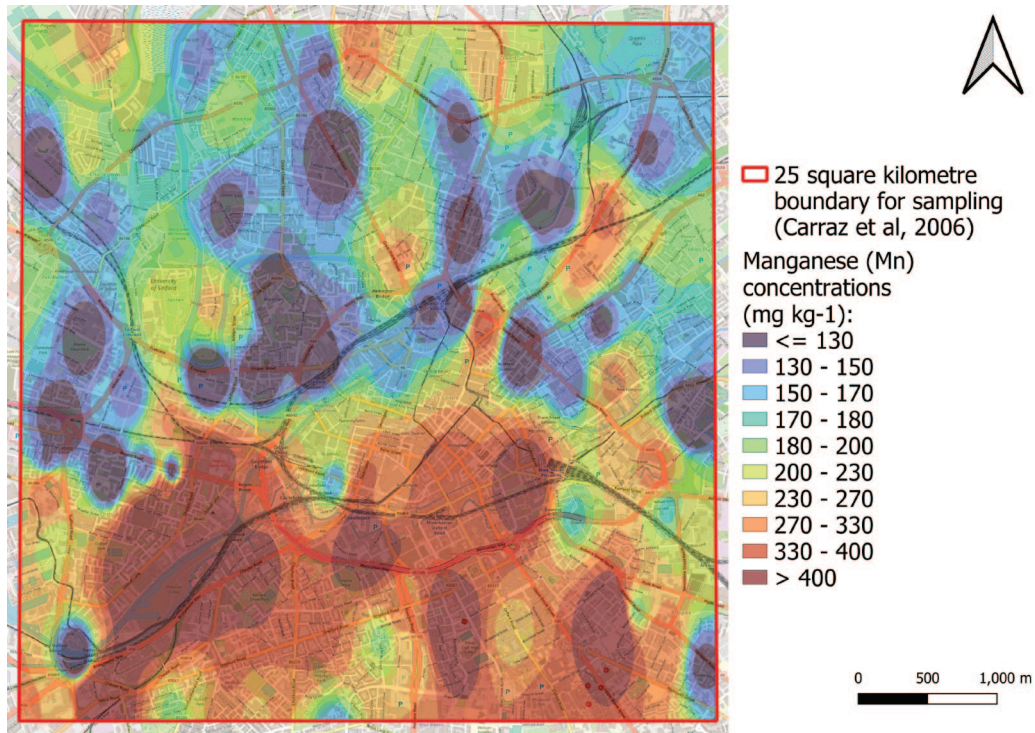


Figure 2: Geochemical map presenting the Mn concentrations found in the RDS samples over the 25 km² sampling area, made using QGIS.

in the RDS is shown in the geochemical maps in figures 2–7 below. There is a high degree of spatial variability, however, the majority of the metals display high concentrations within Manchester City centre and low concentrations in Salford Quays.

Mn has the highest concentrations focused mainly on the south area of the map, with the highest levels (>400 mg kg⁻¹) found towards Salford Quays and Old Trafford (figure 2). This also runs over the River Irwell and Manchester Ship Canal, which are connected upstream to the river Mersey.

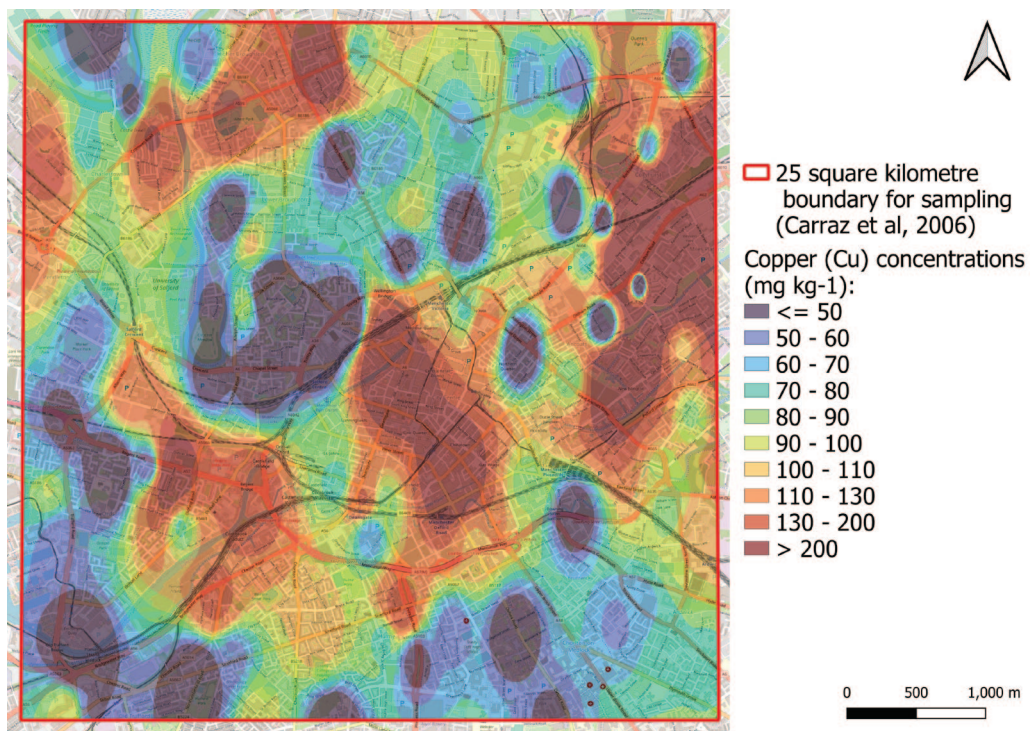


Figure 3: Geochemical map presenting the Cu concentrations found in the RDS samples over the 25 km² sampling area, made using QGIS.

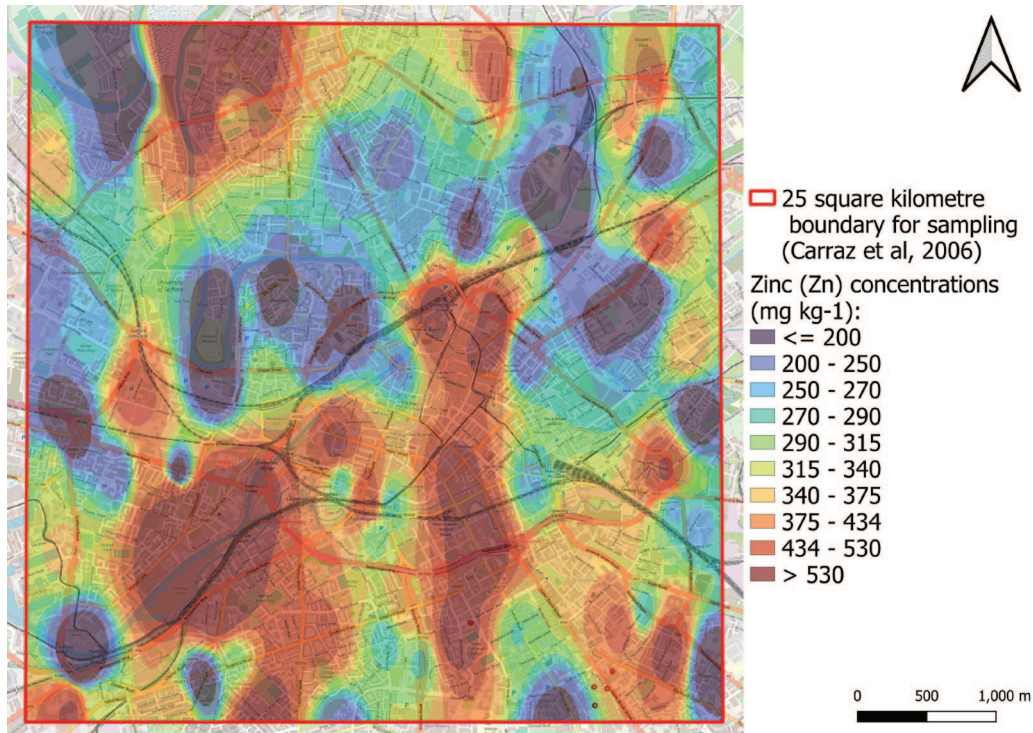


Figure 4: Geochemical map presenting the Zn concentrations found in the RDS samples over the 25 km² sampling area, made using QGIS.

A study by Joselow *et al.* (1978) found that organic Mn compounds were being substituted for Pb in fuel since it was banned in the US. These organic Mn compounds, known as methylcyclopentadienyl manganese tricarbonyl (MMT), are also used in fuel used in the UK, providing a potential

explanation for the increase in Mn since 2006 (European Parliament, Council of the European Union, 2009). Like the release of Pb during fuel combustion, Mn can accumulate particularly in urban environments through variables such as traffic density (Loranger *et al.*, 1994).

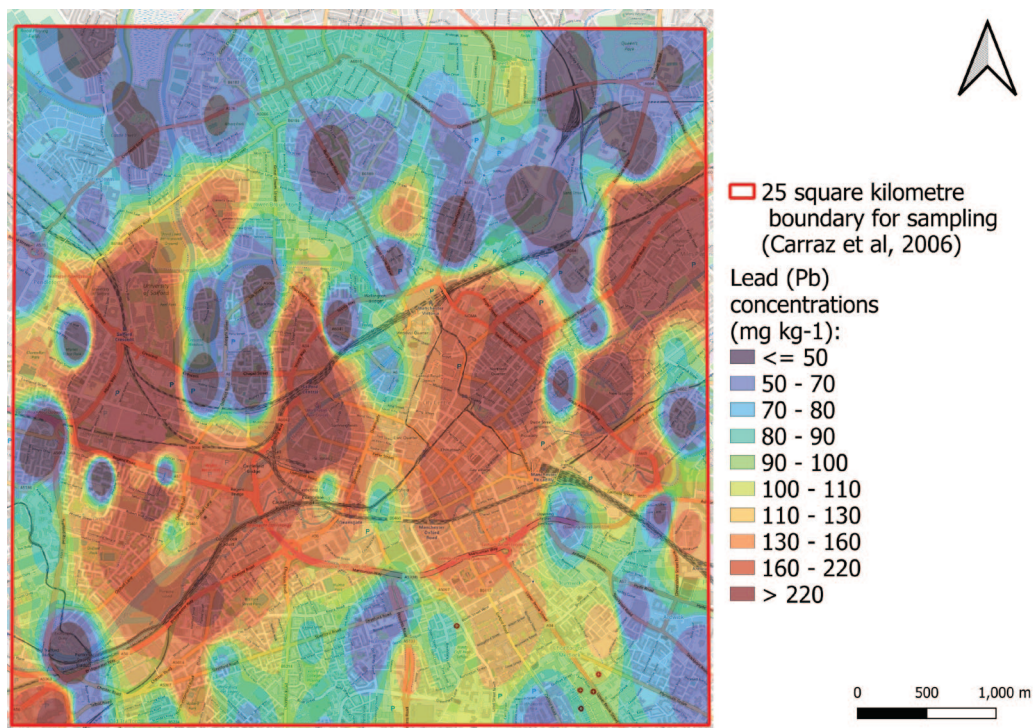


Figure 5: Geochemical map presenting the Pb concentrations found in the RDS samples over the 25 km² sampling area, made using QGIS.

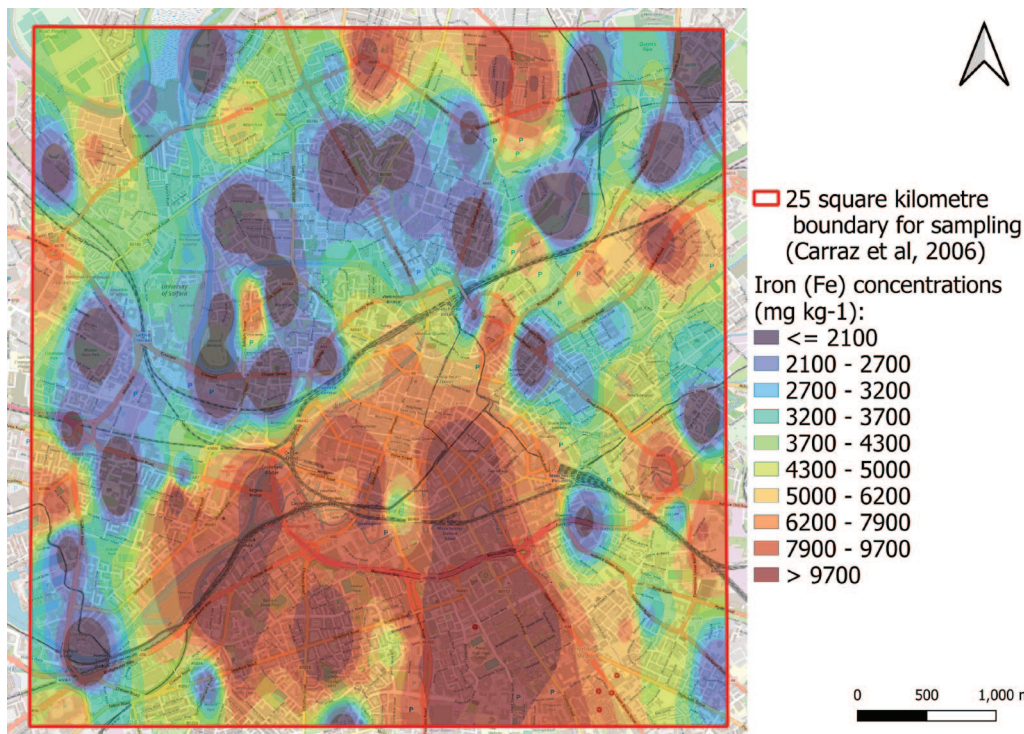


Figure 6: Geochemical map presenting the Fe concentrations found in the RDS samples over the 25 km² sampling area, made using QGIS.

There is high spatial variability in Cu concentrations (figure 3); however, there are two prominent areas (>200 mg kg⁻¹) in Manchester City centre and northeast of the map towards Miles Platting. The findings for Cu in the Carraz *et al.* (2006) study present high concentrations in the south of Manchester City centre, which differs from the spatial distribution found in the 2022 study. The 2006 paper concluded that additional, unidentified sources were a reason for the observed spatial distribution. The present-day Cu concentrations were also higher on average than the 2006 data. This change in spatial distribution and increase in concentration could be due to a rise in vehicular traffic since 2006. A study by Bookter (2017) found that the primary sources of Cu in an urban area were vehicle brake wear, roofing materials, car parks, and vehicle exhausts.

The spatial distribution of Zn is varied (figure 4). The areas containing the highest concentrations (>530 mg kg⁻¹) include the southern side of Manchester city centre, southwest of the city centre towards Salford Quays and Old Trafford. These findings follow a similar distribution pattern to the Zn geochemical map in Carraz *et al.* (2006), with high concentrations in Manchester City centre and Salford. The 2006 study suggested that increased traffic density could be a reason for the higher concentrations. Several studies have found that tire-tread materials contain Zn, and when the tread is lost on road surfaces due to abrasion, Zn is released (Councill *et al.*, 2004; Baensch-Baltruschat *et al.*, 2020).

The distribution of high Pb concentrations (>220 mg kg⁻¹) is primarily spread east to west across the map, including in Manchester City centre (figure 5). Most low Pb concentrations (<=50 mg kg⁻¹) are north of the map, particularly around Harpurhey. These findings are comparable to the geochemical maps made by Carraz *et al.* (2006), where the highest Pb concentrations were located in the Manchester City centre. The reasoning for this was due to increased traffic density, where vehicular pollution was a source of Pb. However, this suggestion has been discounted for the 2022 data since no correlation was found between any of the metal concentrations and traffic flow data. Yellow road paints have been discovered to contain high levels of lead throughout Europe, with amounts between 100 and 1000 mg kg⁻¹ reported in 148 out of 236 paints sampled (Turner *et al.*, 2023). Urban areas are likely to have a increased need for road paints due to the higher density of road surfaces providing a potential explanation for the higher concentrations of Pb in the city centre.

There is a clear area of high Fe concentrations south of Manchester City centre and towards Hulme and Greenheys (see figure 6 above). These findings differ from the conclusions in the Carraz *et al.* (2006) study, where the highest Fe concentrations were located outside of Manchester City centre. The suggestion for this was Fe being sourced from soils or a source that is rare in city centres. However, as the 2022 data presents high levels within the

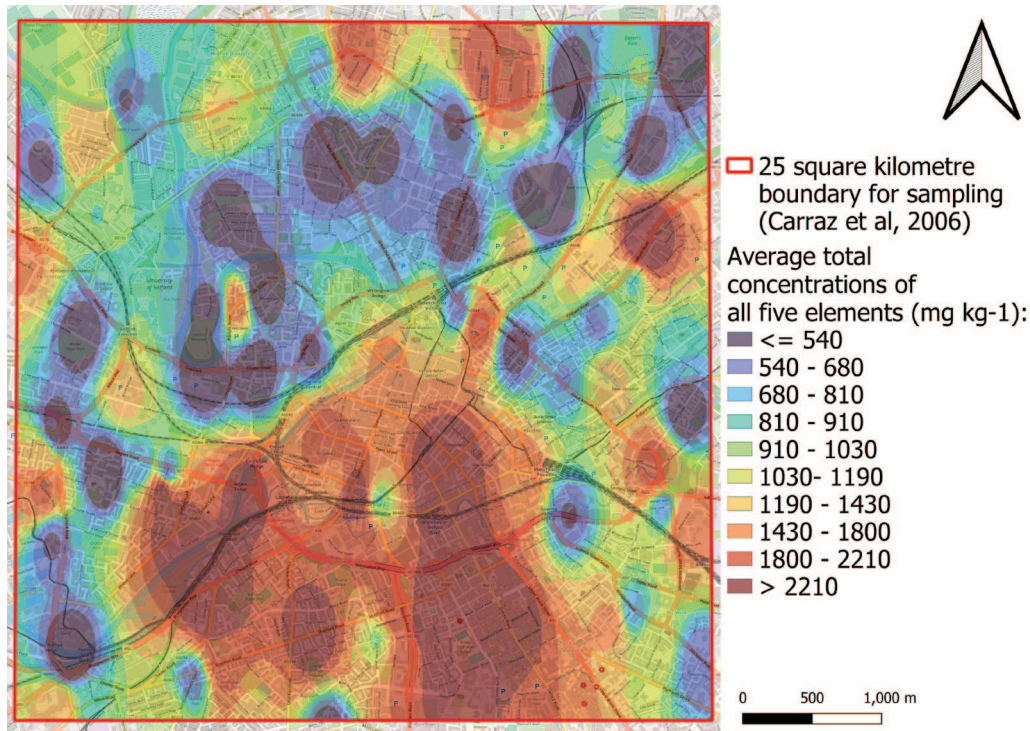


Figure 7: Geochemical map presenting the average total concentrations of all five elements found in the RDS samples over the 25 km² sampling area, made using QGIS.

city centre, there is a possibility that different sources are the reason. The other possibility is that new transport pathways for Fe have been created since 2006, changing the spatial distribution. Studies such as Hopke *et al.* (1980) explain how Fe can come from many sources, such as geogenic background sources. Another study by Pattammattel *et al.* (2021) found that the majority of Fe found in the urban environment was suggested to come from anthropogenic activities, including abrasion from vehicle braking systems and engine combustion wear. It is worth noting that there are fewer studies on the environmental and health impacts of Fe accumulation compared to the other four elements in this paper; it also is not included in environmental quality standards (discussed in section 3.2). However, for easier comparison of the Carraz *et al.* (2006) data and considering that other studies have found Fe to be associated with vehicular wear and tear, it has still been included in this study.

The average total concentrations (figure 7) indicate that the highest concentrations of metals were found within the south area of the map in both Manchester City centre and its perimeter. Salford City Centre and Salford Quays had lower average concentrations of ≤ 540 mg kg⁻¹. The areas containing the lowest concentrations were also found away from the city centre. The spatial distribution in the geochemical maps created by Carraz *et al.*, (2006) found that most of the low concentrations were located in the

Manchester City centre and higher concentrations were found away from it. This was suggested to be from increased road sweepers within the city centre. Opposite findings are shown in the 2022 data; if street sweepers were reducing metal concentrations in the city centre by reducing RDS, new plans could have changed the frequency of street sweepers in the city centre, affecting the level of RDS.

Manganese and Zinc had the most significant positive correlation ($r=0.532$ $p<0.001$ $R^2=0.283$), displaying the most homogeneous distribution patterns. Figures 2 and 4 show Mn and Zn have high concentrations southwest of the city centre towards Salford Quays and Old Trafford. There are no studies that discuss Mn and Zn interactions in RDS. Therefore, this correlation could be due to Mn and Zn having similar sources or transport pathways. Without further study and evidence, however, this is only a presumption. Weaker yet still significant correlations were observed between Fe and Zn ($r=0.299$ $p<0.01$ $R^2=0.090$) and Fe and Mn ($r=0.287$ $p<0.01$ $R^2=0.082$). Fe and Cu ($r=0.198$ $p<0.05$ $R^2=0.039$) and Pb and Cu ($r=0.240$ $p<0.05$ $R^2=0.058$) had weaker correlations but were still statistically significant with a P-value of less than 0.05. No correlation or significance was observed between Cu and Mn, Fe and Pb, Mn and Pb, Cu and Zn, and Pb and Zn. This differs from the study by Carraz *et al.* (2006) where the most significant correlation was between Zn and Pb ($r=0.454$, $P<0.001$ $R^2=0.009$). They also found a significant relationship between Cu

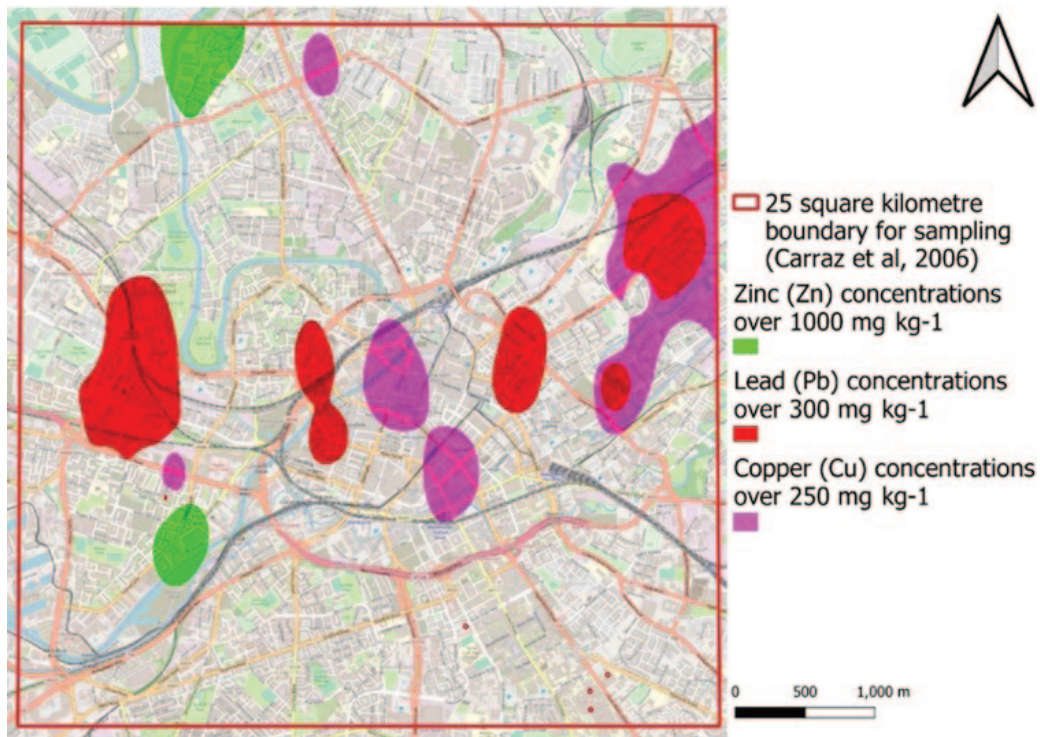


Figure 8: Geochemical map presenting the PTE concentrations over the threshold trigger concentration over the 25 km² sampling area, where phytotoxic and zootoxic effects are expected (ICRCL, 1990).

and Zn ($r=0.329$, $P<0.01$ $R^2=0.005$) which contradicts the 2022 data where no correlation or significance was found. Spearman's rank correlation can be valuable for finding relationships in continuous data. However, it is difficult to infer whether the data accurately represents the spatial distribution considering urban sediment dynamics and the mobility of RDS.

3.2. Environmental risk of trace metals in RDS

The threshold trigger concentrations (TTC), established by the ICRCL (1990), present environmental standards for PTE concentrations, where phytotoxic and zootoxic effects are expected. A TTC value was only available for Pb, Zn and Cu (figure 8). This is most likely due to numerous studies considering these metals as toxic to ecosystems and humans (Lambert *et al.*, 2000; Tchounwou *et al.*, 2014). However, a study by Mosby *et al.* (1996) concluded that 35 metals, including Fe, Mn, Cu, Pb and Zn, were relevant due to residential and occupational exposure. This suggests that TTC values need to be established for Fe and Mn, creating an environmental standard that improves the environmental management of these metals. The majority of the concentrations are separate with little overlap, apart from on the east side of the map where unsafe levels of Cu and Pb are found together. A large proportion of the RDS over a metal TTC is situated within the middle and centre of the map, east and west of the city centre. Cu and Pb had the

most significant areas over the TTC, with Manchester City centre containing metal concentrations higher than both metals' TTC, indicating the need for mitigation strategies in these areas. The highest concentration measured for Cu was 4897 mg kg⁻¹, which is significantly higher (a 1858.8% increase) than its TTC of 250 mg kg⁻¹. This is like Pb, where the highest concentration was 3184 mg kg⁻¹, 961.3% higher than its TTC of 300 mg kg⁻¹. Considering leaded fuel has been banned since 1999, the Pb has accumulated over time from legacy sources or a new point source of pollution. Zn's highest concentration was also significantly higher than its TTC, at 140.1% above TTC.

The TTC, published by the ICRCL, is guidance for metal concentrations in soils, not RDS. There are several guidelines and standards for soils or channel sediments (such as CLEA, 2009), but there is a lack of environmental standards for RDS. Considering this, publishing a new set of guidelines specifically for RDS would benefit future research and increase understanding of urban sediments. However, one key issue with RDS is its mobility, which means the distribution could vary over time due to scenarios like flushing events. It is also known that geochemical data tends to follow a skewed frequency distribution due to the various sources and processes mixing (Zhao *et al.*, 2018). This should be considered when implementing future monitoring programmes.

Several studies have highlighted the relationship between vehicular traffic and PTE concentrations in RDS (Zhang *et al.*, 2012; Wang *et al.*, 2016; Ferreira *et al.*, 2016). It is also widely known that more vehicles will increase the number of PTEs released during abrasion and engine combustion in urban environments (Kheir *et al.*, 2014; Peng *et al.*, 2017). Callender and Rice (2000) saw a correlation between population and traffic density which is also strongly related to Pb and Zn concentrations. Although this study does not show a strong correlation between traffic flow and the concentrations, the variability in RDS and its transportation could provide a different result if samples were collected again.

3.3. Temporal changes in RDS trace metal concentrations

As discussed in section 3.1., there is a high degree of spatial variability in the Carraz *et al.* (2006) and 2022 geochemical maps. Table 1 below summarises the PTE concentrations (mg kg⁻¹) in the RDS. Fe has the highest average concentration of 5168 mg kg⁻¹, with Cu having the lowest average concentration of 2.17 mg kg⁻¹. All five elements display an extensive range; the highest concentrations are at least three times higher than the average concentration for each element. A large range of metal concentrations is expected in RDS due to its complex dynamics in an urban system (Taylor, 2007). Cu, Fe, Mn, and Zn have a higher average concentration in the 2022 samples, with a larger range of concentrations than the 2006 sample data. Fe's highest concentration, for example, is over three times higher in the

2022 data compared to 2006. The study by Robertson and Taylor (2007) determined the monthly temporal changes in RDS in Manchester City centre, concluding that there was significant temporal variability in metal concentrations. Considering this study is comparing data over a much longer period, it is appropriate to infer that the 2022 data has highly significant temporal variability in comparison to the 2006 data. In addition, the monthly variability in the RDS metal concentrations indicates that concentrations reflect seasonal changes and other short term variables. The variability in metal concentrations over a 16 year period can outline the effects of long-term changes, including legislative changes, societal changes and technological advancements, adding a new outlook and layer of data to this field of study. Pb is the only element with a higher average concentration in 2006 compared to 2022, although the values of other elements are still high and the reduction in concentration is only slight. Previous studies have indicated that fuel additives are the most essential sources of human-induced Pb in road dust (De Miguel *et al.*, 1997; Sezgin *et al.*, 2003). Although leaded fuel has been banned in the UK since 1999, Pb is a persistent element that can accumulate in soils and the food chain for prolonged periods. A study by Resongles *et al.* (2021) explains that the remobilisation of historical Pb is a suggested source for its long-term persistence. The study site, based in London, found evidence that Pb deposited by fuel combustion still contributes to the city's pollutants as it is deposited into soils and road dust due to being an airborne particulate.

Table 1: Summary data for RDS PTE concentrations from the 2022 and 2006 samples (Carraz *et al.*, 2006).

	Cu (mg/kg ⁻¹)		Fe (mg/kg ⁻¹)		Mn (mg/kg ⁻¹)		Pb (mg/kg ⁻¹)		Zn (mg/kg ⁻¹)	
	Carraz <i>et al.</i> (2006)	2022	Carraz <i>et al.</i> (2006)	2022	Carraz <i>et al.</i> (2006)	2022	Carraz <i>et al.</i> (2006)	2022	Carraz <i>et al.</i> (2006)	2022
Mean	88	141	2005	5169	170	266	164	140	268	353
Range	14-342	2-4897	438-5251	49-19087	63-856	49-4238	45-1461	3-3184	65-990	37-2401
Interquartile range		61		5937		154		78		197
Median		75		3975		190		74		285

4. Further research opportunities

Recent studies have concluded that these five PTEs are still a significant issue for the urban environment. However, more research into other elements present in the RDS is necessary to keep up with new pollutant sources and technological developments. Electric vehicles, for example, have significantly increased in popularity; in 2016, 2 million electric cars were on the road globally, which increased to over 16 million in 2021 (IEA, 2022). Some studies, such as Liu *et al.* (2022) and Boretti (2019), explain that the nature of electric vehicles, which are heavier and possess a faster acceleration than conventional vehicles, means that they produce more particulate matter from tyre and brake wear. It would be interesting to investigate if any of these elements are present in the RDS and the potential environmental impacts they could be causing now and in the future.

5. Conclusions

We are now an urban species with increasingly complex environmental issues. Understanding urban sediment dynamics and trace metals in RDS is a significant problem which needs addressing. This study aimed to supply new data on the state of RDS and the associated metal particulates in the Greater Manchester urban conurbation, UK. Comparing the spatial variability of the historical and 2022 maps, Pb and Zn had the most similar spatial pattern since high concentrations were found within Manchester City centre and Salford. The Fe, Mn and Cu concentrations had the least similarities with the historical data, with high concentrations, also found within the city centre. Conclusions on the environmental risk include

the concentrations of Pb, Zn and Cu which were high in multiple areas across the sample site, with concentrations above the threshold trigger concentration (TTC), suggesting intervention and remediation strategies are needed. New environmental standards designed for metal concentrations in RDS are a suggestion to help improve and manage PTEs in urban environments. Creating standards for Fe and Mn is also advised, as studies have found these elements are relevant to metal pollution and exposure. Although previous studies have found a relationship between vehicular traffic and metal pollution, this study found no correlation between metals and traffic flow at the study site. Therefore, it is important to conclude that RDS is highly mobile and is within the dynamic urban sediment system, so its distribution is constant. Although no correlation was found in the traffic data from these samples, future sampling could find differing results. This is also an important point to consider when implementing future monitoring programmes. The comparison of the historical and 2022 data found that the PTEs concentrations have primarily increased over time. Pb was the only PTE with a lower average concentration since the previous paper, albeit still high due to its persistent nature. It suggests that banning leaded fuel has positively affected Pb concentrations over time.

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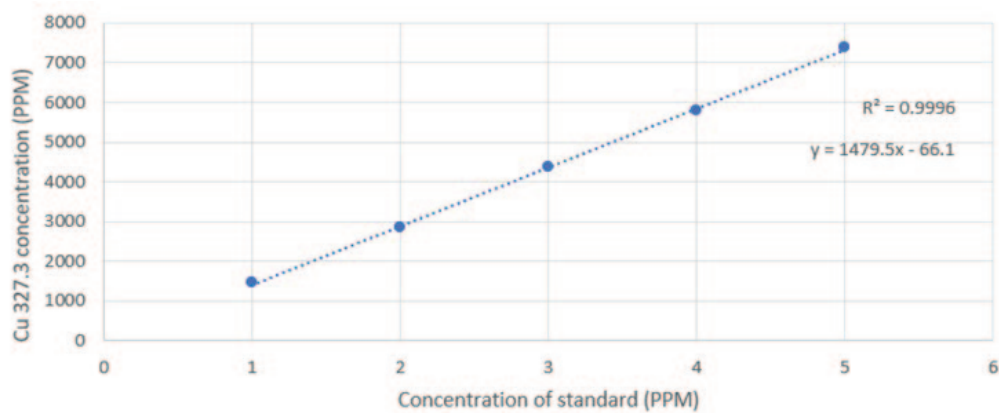
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Appendix



Appendix A: Graph presenting the Cu 327.3 concentration standards from the OES-spectrometer, showing the calibration curve with an accuracy of >0.995%.