Effect of urbanization on the city pollution based on soil and tree leaves in Valencia, Spain

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Abstract

The accumulation of the toxic metals can result in the degradation of neighboring ecosystems and reducing their value to humans in terms of aesthetic properties and utility. Therefore, the aim of our research was to investigate the effect of urbanization on level of metals in *Citrus sp*. tree leaves and soil samples along an urbanization (rural, periurban and urban) in Valencia, in Spain. There were significant differences for the content of clay, pH, electrical conductivity (EC), soil organic matter (SOM), concentration of Ca and exchangeable sodium percentage (ESP). A significant difference was not found in the case of elemental concentration of soil. There were significant differences for the concentration of Cu on Citrus sp. leaves, only. Based on our findings Valencia did not exhibit a mathematical relationship between the element concentrations and the urban gradient except for the case of copper in the leaf samples. The difference in observation could indicate the homogenous nature of the Valencia soil due to the agriculture focused use of the soil within the city.

Keywords: Citrus sp., metals, bioindicators, pollution level

Introduction

The urbanization is defined as the transition from an economy centered around agriculture products into a service economy with the use of technology and facilities to reduce the cost of production (Liang & Yang, 2019). Through the viewpoint of demography, urbanization is the aggregation of the population from rural communities into highly dense cities (Uttara et al.

2012, Kuddus et al. 2020). In the case of environmental science, the study of urbanization follows the impact of urban expansion and the urban city itself in regards to the changes that it incurs to the surrounding environment.

The main type of pollutant was classified as atmospheric pollutants which were sourced from vehicles and factory emissions in the context of an urban environment. For pollutant measurement in soil and air pollution was through the using of bioaccumulator or bioindicators which can absorb or collect pollutants into their systems (Brookes et al. 1995). Bioindicators are organisms which are capable of exhibiting a form of chemical or physical transformation in response to environmental change and can be used to study the effects of local pollutants (LaGreca & Stutzman 2006).

The aim of our study was to investigate element concentration in soil and *Citrus* sp. plant leaves along an urbanization gradient in Valencia, Spain. Our hypotheses are as follows: (i) there are significant differences in pollutant levels among the stages of urbanization along the urbanization gradient (urban, periurban and rural area). (ii) The highest metal concentration in soil and leaves are in the urban, while the lowest concentration is in the rural area.

Material and methods

Study area

Valencia is the third most populated city in Spain with a population of approximately 788,000 as of 2021 (https://www.citypopulation.de). The area of the city is 139 km^2 resulting in a population density of 5,662/km^2 (https://www.citypopulation.de). Valencia is considered as a port city with 3 distinct ports alongside 3 international airports used for touristic and economic purposes (https://www.valenciaport.com). In terms of energy generation, Valencia has a multitude of energy suppliers, thus understanding sources of energy for Spain as a whole is able to summarize the energy production for Valencia. As of 2021, Spain has multiple sources for energy production with the 3 largest contributors being wind, nuclear and natural gas, the latter being the largest producing 71,000 GWh out of the total 250,000 GWh that Spain produces during 2021 (https://www.iea.org). This concludes the characterization of the cities and potentially highlights sources of pollution that will be discussed later on in the research.

In the case of *Citrus sp*. in Valencia, approximately over 15,000 individual *Citrus* trees were reported by farmers in 2019 and Valencia is renowned for being the 2nd largest orange

exporter for the European Union (Torregrosa et al. 2019, Nyambura & Bonorchis 2022). The choosen *Citrus sp.* trees were healthy, and neither pests nor symptoms of disease were found by visual examination. The sampling areas were located in an urban area (a busy park in the city center), a periurban area, and a natural, rural area. We randomly chose 5 tree specimens at each sampling area, and we collected 30 leaves from each tree specimen. Samples were stored in paper bags and placed in the refrigerator at -21 °C. At each sampling area, five soil samples were collected from five places. All samples were taken from a depth of 0–20 cm with a small hand spade. Samples were placed into poly bags and kept at −21 °C in the refrigerator.

Sample preparation

Sample processing started with a surface wash for the leaves samples to remove any surface debris. It is important that the washing is done while using tap water and not deionized water as it may alter the elemental composition of the leaf specimens. After washing, the leaf samples were put to dry in an oven set at 70° C for 1-1.5 hours Following this step, the leaf samples were homogenized using a scientific blender (Retsch GM 200) at 6000 rpm for 10 seconds. Directly after the homogenization step, 0.1000g of the leaf samples measured on an analytical balance into 100 mL beakers with known mass. The beaker containing the leaf samples would then be placed in an oven at 105° C overnight to completely evaporate the water content. Following the drying process, the mass of the leaf sample was remeasured using an analytical balance to determine the exact mass of the sample. After this step, the leaf sample was ready for the digestion process.

In the case of the soil sample, 0.1000g of the soil was directly measured into a 100 mL beaker of known mass directly after the collection step. The beakers were then similarly placed into an oven at 105° C overnight and on the following day, the mass of the soil samples were measured on an analytical balance.

For the first step of the digestion process, both the soil and leaf samples were pre-treated with 5mL of 65% HNO_3 overnight. On the following day, the samples were placed onto a hot plate to completely evaporate the HNO_3 solution. This was an important step as the digestion process requires the use of concentrated hydrogen peroxide (H_2O_2) which is able to react with the 65% HNO_3 to form gaseous NO_X alongside an exothermic reaction releasing high amounts of heat. To decrease the likelihood of this incident, after evaporating the HNO_3, 2 mL of deionised water was added into the beaker with the samples and allowed to evaporate completely on the hot plate. After this step, 200 µL of 30% (m/m) H_2O_2 was added into the beaker and once again placed onto the hot plate until complete evaporation. The last step for

the digestion process was the addition of 10 mL of 1% HNO_3 into the beakers and following this, the samples were ready for analysis using ICP-OES. Peach leaves (1547) CRM were used, and the recoveries were within 10% of the certified values for the elements (Simon et al. 2013, 2014, 2016, 2021).

Statistical Analyses

Statistical analyses were conducted with SPSS Statistics 20 (IBM) statistical software .The normality of the distribution was tested using the Shapiro–Wilk test. The homogeneity of variances was tested with Levene's test. The differences among samples were tested using analysis of variance (ANOVA) for each variable. Tukey's test was used for pairwise comparison between the groups. Canonical discriminant analysis (CDA) was used to reduce dimensions and to identify those variables that most efficiently discriminated the study area as the dependent variable (De Sá, 2007).

Results

Based on main physical and chemical parameters of soil, canonical discriminant analysis (CDA) showed total separation among the studied areas (Fig. 1). The first discriminant functions (CDF1) contributed to 79.7% of the total variance, while the second one (CDF2) contributed 20.3% of the total variance. The canonical correlation was 0.963 for CDF1 and 0.873 for CDF2. Statistical differences were not found based on the CDF1 and CDF 2 ($p = 0.057$ and $p = 0.260$). Similar separation was found in the case of elemental concentration of soil (Fig. 2). The first discriminant functions (CDF1) contributed to 94.1% of the total variance, while the second one (CDF2) there was 5.9% of the total variance. The canonical correlation was 0.978 for CDF1 and 0.763 for CDF2. Statistical differences were also not found based on the CDF1 and CDF 2 ($p = 0.162$ and $p = 0.773$).

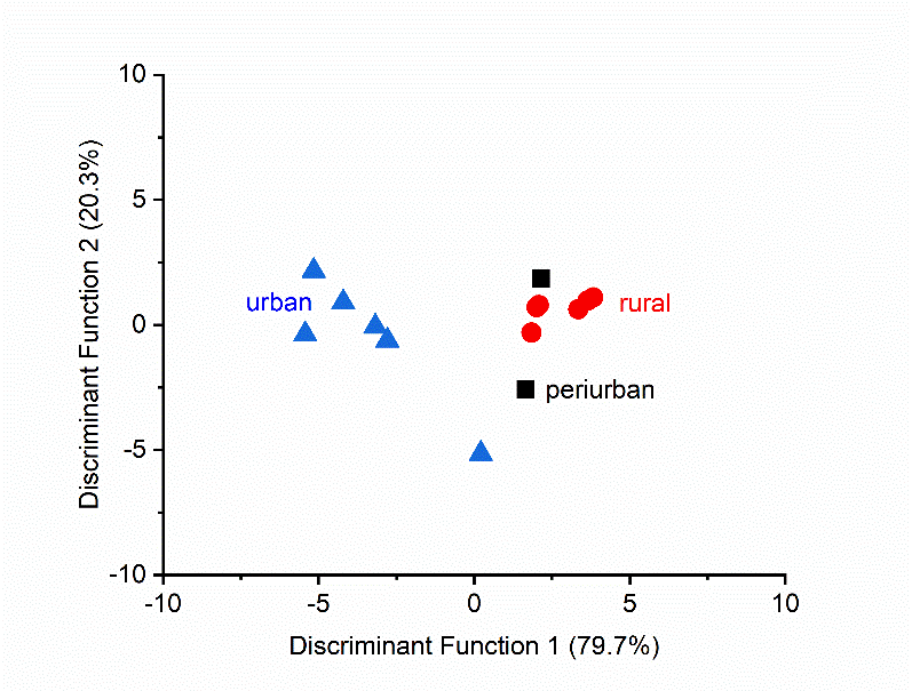

Figure 1. Scatter plot of canonical discriminant analysis based on the main physical and chemical parameters of soil among the studied areas

Table 1 Summary statistics of main physical and chemical parameters of soil (mean ± SE). Notations: EC = electrical conductivity; SOM = soil organic matter; CEC = cationic exchangeable capacity; ESP = exchangeable sodium.

	Urbanization gradient		
Parameters	rural	periurban	urban
content of sand. %	30 ± 4	35 ± 2	42 ± 2
content of silt. %	37 ± 4	34 ± 5	35 ± 1
content of clay. %	33 ± 2	30 ± 6	23 ± 2
pH	8.3 ± 0.1	8.3 ± 0.1	7.6 ± 0.1
EC. dS m^{-1}	0.2 ± 0.1	0.1 ± 0.1	0.3 ± 0.1
SOM. %	2.4 ± 0.2	2.5 ± 0.3	4.3 ± 0.6
CaCO3. %	25 ± 4	22 ± 9	34 ± 2
CEC. %	19 ± 1	18 ± 1	22 ± 1
CaCO3. %	12 ± 1	12 ± 2	17 ± 1
ESP. %	1.6 ± 0.3	3.1 ± 1.4	3.3 ± 0.3

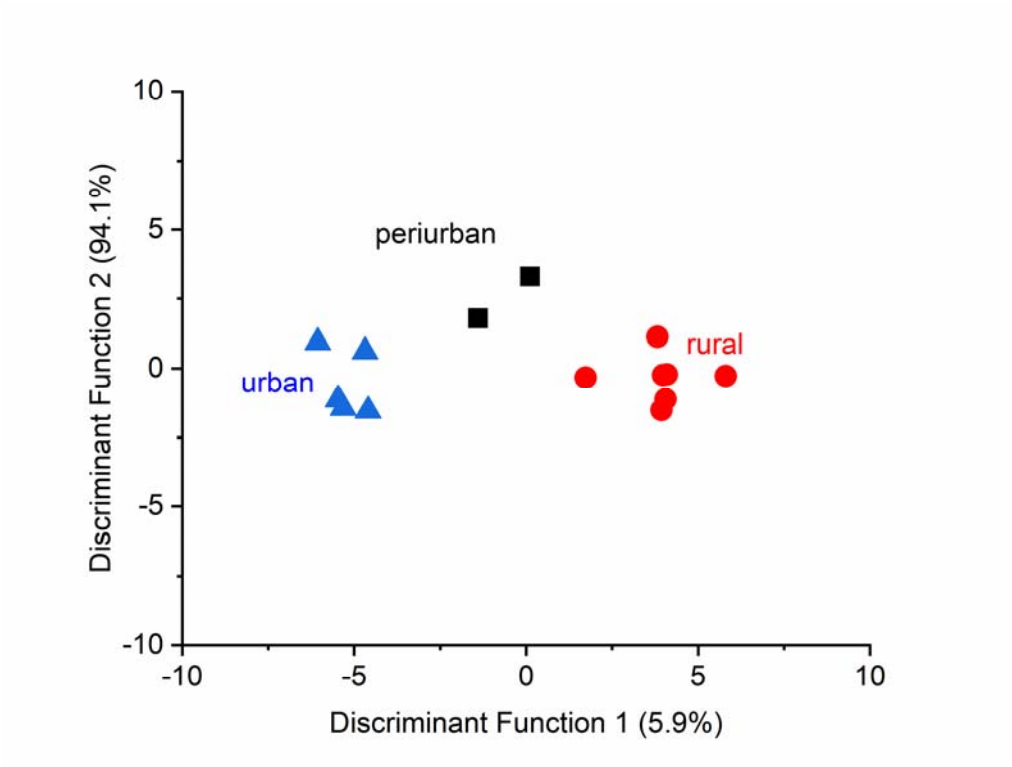

Figure 2. Scatter plot of canonical discriminant analysis based on the elemental concentration of soil among the studied areas

Table 2 Summary statistics of elemental concentration of soil (mg kg^{-1}, mean ± SE).

	Urbanization gradient		
Parameters	rural	periurban	urban
Al	10331 ± 1227	6837 ± 88	8855 ± 1868
B	15 ± 1	11 ± 1	15 ± 1
Ba	71 ± 4	72 ± 7	103 ± 17
Bi	30 ± 3	22 ± 1	28 ± 4
Ca	112117 ± 14156	139178 ± 19176	114214 ± 24389
Cd	5.9 ± 0.2	5.5 ± 0.2	5.8 ± 0.3
Co	4.9 ± 0.4	3.7 ± 0.1	4.5 ± 0.6
Cr	19 ± 1	25 ± 15	28 ± 4
Cu	24 ± 4	23 ± 8	56 ± 21
Mg	7094 ± 886	10155 ± 5476	9478 ± 2550
Ni	16 ± 2	18 ± 3	15 ± 2
P	1250 ± 219	1613 ± 585	1226 ± 182
Pb	53 ± 9	58 ± 35	88 ± 25
S	539 ± 79	511 ± 1	672 ± 115
Sr	172 ± 18	208 ± 41	213 ± 36
Zn	79 ± 1	79 ± 7	150 ± 94

There were significant differences for the content of clay, pH, electrical conductivity (EC), soil organic matter (SOM), concentration of Ca and exchangeable sodium percentage (ESP) (Table 1) ($p < 0.05$). Significantly lower results were found in the urban area for the content of clay and pH. While the highest results were also found in the urban area for electrical conductivity (EC), soil organic matter (SOM), concentration of Ca and exchangeable sodium percentage (ESP). A significant difference was not found in the case of elemental concentration of soil (Table 2).

Based on elemental concentration of *Citrus sp.*, significant differences were not found among urban, suburban, and rural areas using canonical discriminant analysis (CDA), although total separation was found (Fig.3). The first discriminant functions (CDF1) contributed to 88.6% of the total variance, while the second one (CDF2) contributed 11.4% of the total variance. The canonical correlation was 0.980 for CDF1 and 0.868 for CDF2. Statistical differences were not found based on the CDF1 and CDF 2 ($p = 0.188$ and $p = 0.590$). There were significant differences for the concentration of Cu ($F = 5.397$, $p = 0.023$) (Fig. 4, Table 3).

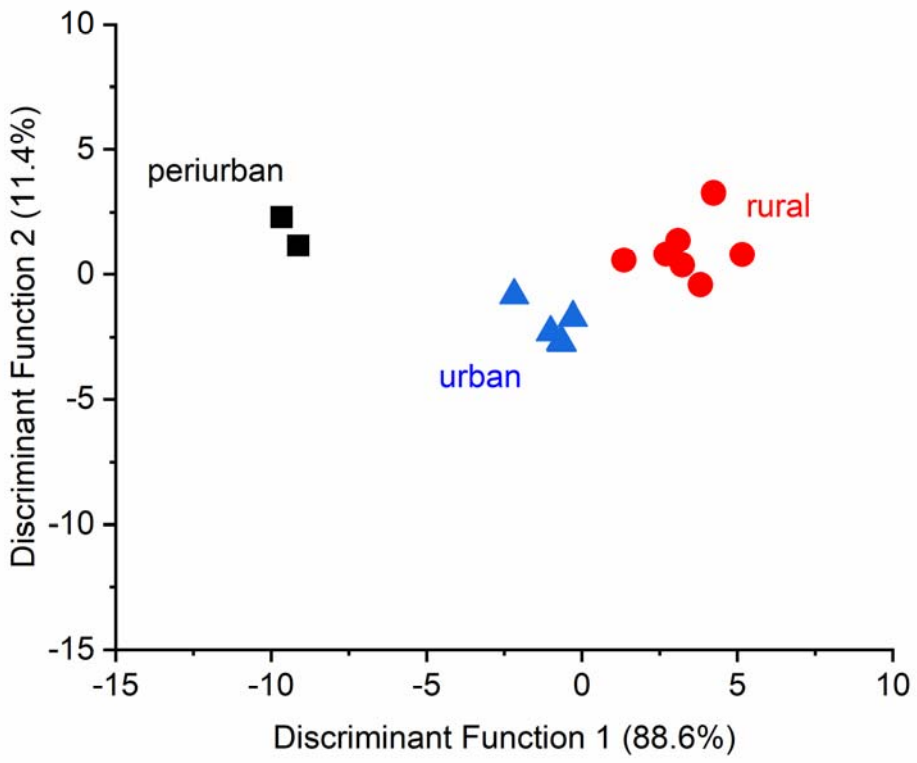

Figure 3. Scatter plot of canonical discriminant analysis based on the elemental concentration of *Citrus sp*. leaves among the studied areas

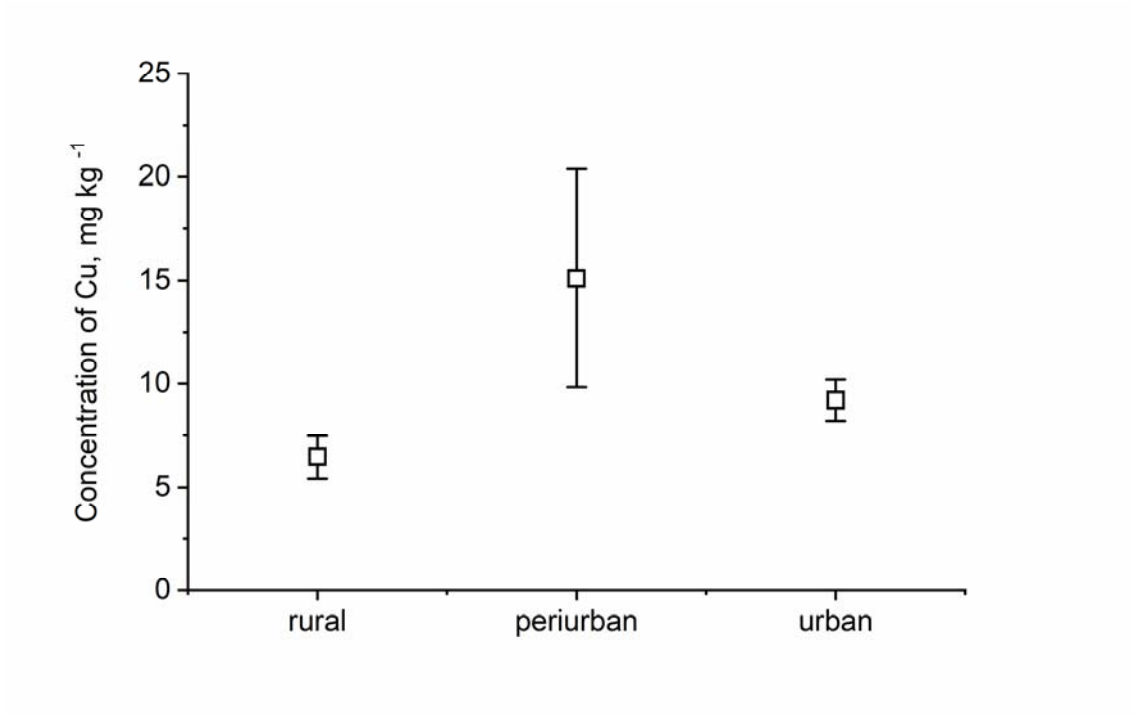

Figure 4. Elemental concentration of Cu (mean ± SE) among the studied areas

Table 3 Summary statistics of elemental concentration of *Citrus sp.* leaves (mg kg^{-1}, mean ± SE).

	Urbanization gradient		
Parameters	rural	periurban	urban
Al	62 ± 12	118 ± 79	97 ± 12
B	108 ± 26	65 ± 1	88 ± 26
Ba	18 ± 1	22 ± 6	22 ± 2
Ca	28477 ± 1436	27852 ± 2370	30569 ± 2047
Cd	2.7 ± 0.3	3.4± 0.1	3.7 ± 0.3
Cr	0.3 ± 0.1	1.6 ± 1.5	0.5 ± 0.1
Cu	6 ± 1	15 ± 5	9. ± 1
Mg	3085 ± 292	3967 ± 714	2983 ± 111
Ni	5.3 ± 0.9	6.8 ± 0.6	4.9 ± 0.9
P	1268 ± 51	1193 ± 181	1179 ± 123
Pb	3.8± 0.5	4.8 ± 0 .1	4.6 ± 0.7
S	2637 ± 127	2986 ± 40	3833 ± 540
Sr	406 ± 35	504 ± 37	501 ± 58
Zn	34 ± 1	39 ± 10	38 ± 3

Discussion

Contrary to our hypothes the main chemical and physical parameters and elemental concetration for the soil did not differ significantly in Valencia, Spain among the different areas along the urbanization gradient. Also, as hypothesized, we found differences among areas based ont he Cu concentration of Citrus sp. leaves, which a is a typically anthoropgenic element.

Similar to our findings, Francos et al. (2016) also measured the surface soil properties before and after rainfall and wildfire events in Valencia. Within the comparison the data for the rural measurements was used as the majority of the data collected by Francos et al. (2016) were originating from areas susceptible towards wild fire such as forests. In terms of the major elements as calcium, potassium and phosphorus were measured by Francos et al. (2016) with the values of 30230 mg/kg for calcium, 338 mg/kg for potassium and 43.5 mg/kg for phosphorus. The percent difference between the measured calcium, potassium and phosphorus concentration were ±115%. ±165% and ±187% respectively. In terms of the minor non-toxic element. they measured a concentration of 401 mg/kg for sodium which was a percent difference of -20% with the measured sodium concentration.

In the case of Valencia leaf samples the major elements were Ca as the most abundant followed by K, S and Mg. The explanation for the presence of S in the Valencia leaf sample was similarly attributed as the calcium found in the Valencia soil sample as the elements are added from the use of fertilizers. The use of S in citrus production increases the yield of the citrus tree by 23-57% (https://www.yara.us/crop-nutrition/citrus/). Additionally. the immense magnitude difference between the most abundant element and the following element can still be observed in the leaf samples of Valencia as the proportion between the concentration is approximately 3.88x between calcium and potassium. Observed pattern for copper concentration is highest in peri-urban sites followed by urban and rural sites in the Valencia leaf sample.

Marin et al. (2018) reported a decreasing tendency with the assessment of metal levels in foodstuffs in Valencia. While, Martin et al. (2013) demonstrated the anthropic effect on the soil based on the Cd, Pb and Zn concentration in Spain. They found spatial patterns with significant differences in territorial localisation. Ramos-Miras et al. (2020) found moderate ecological risk with the study of mercury and chromium in greenhouse soils in Valencia.

Conclusion

Based on our findings Valencia did not exhibit a mathematical relationship between the element concentrations and the urban gradient except for the case of copper in the leaf samples. The difference in observation could indicate the homogenous nature of the Valencia soil due to the agriculture focused use of the soil within the city. This perhaps could indicate a stronger regulation of soil quality within the city to meet the necessary standards for commercializing their citrus crop.

Conclusively. this study assessed a range of elements from soil and leaves samples the pollution levels within an urban gradient using analytical methods and technologies. However, this research can be expanded on further by studying different urban cities to determine a larger or more concise pattern between element concentration and urban interactions in the context of pollution.

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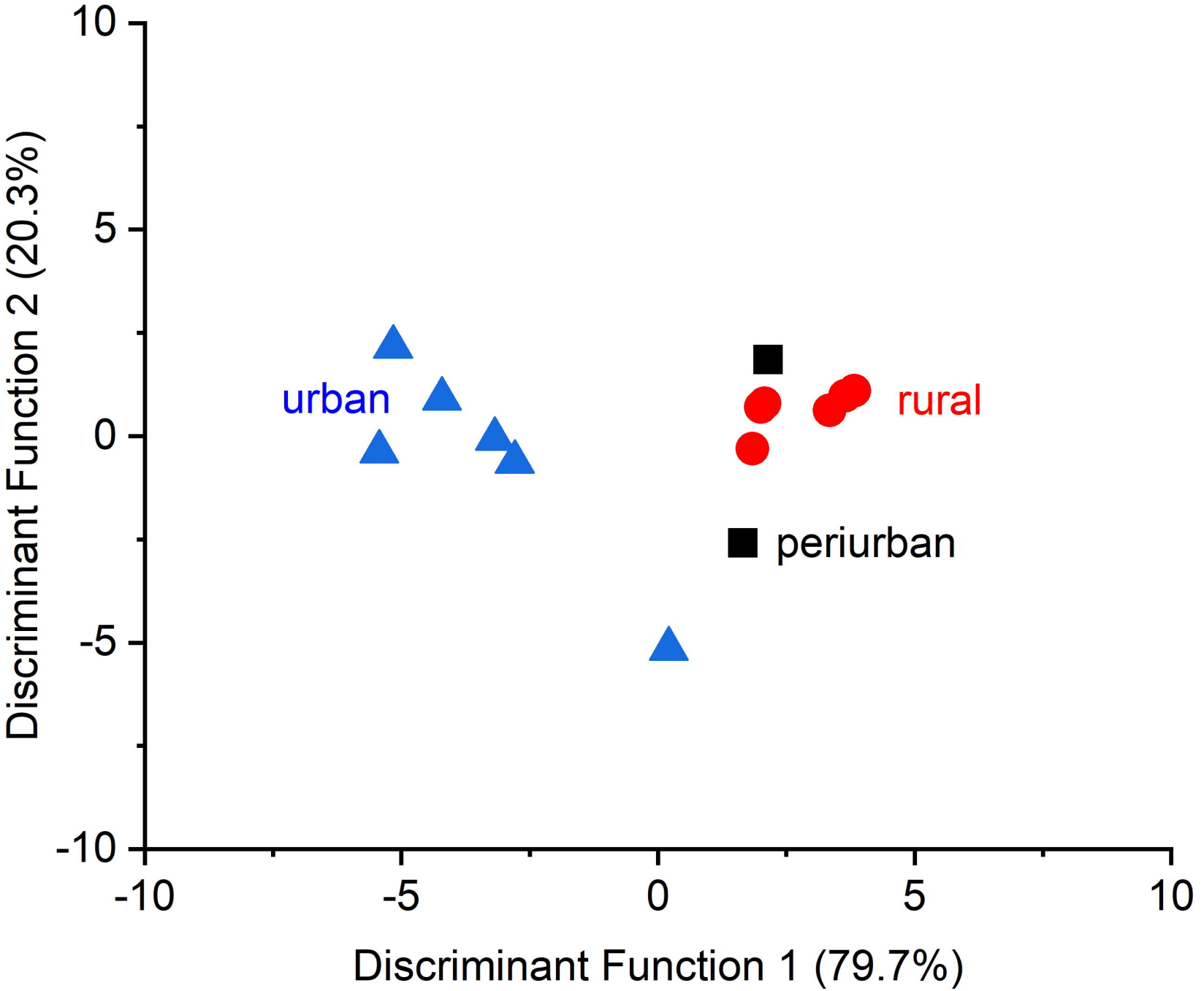
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Discriminant Function 2 (20.3%)
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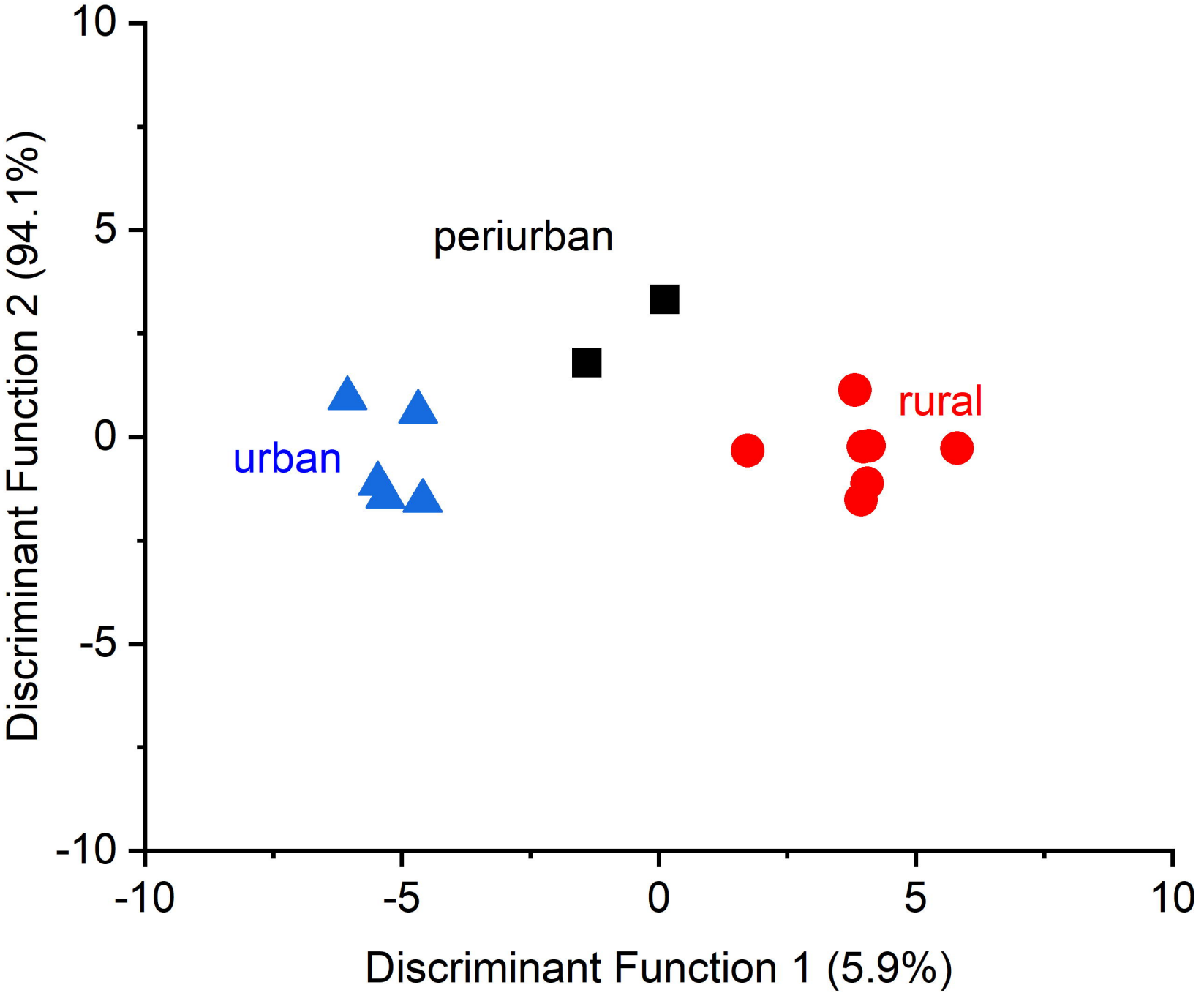
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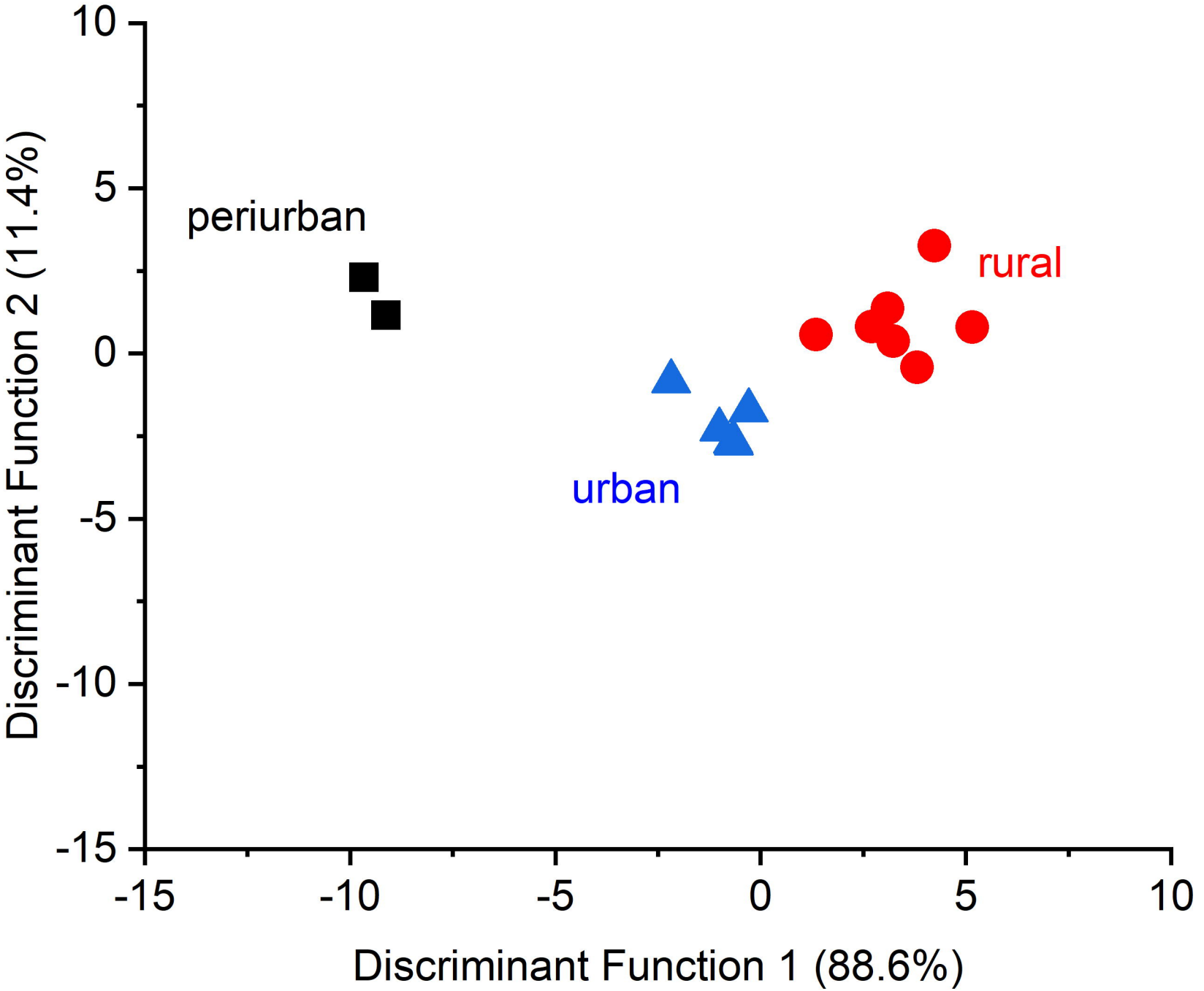
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Discriminant Function 2 (11.4%)
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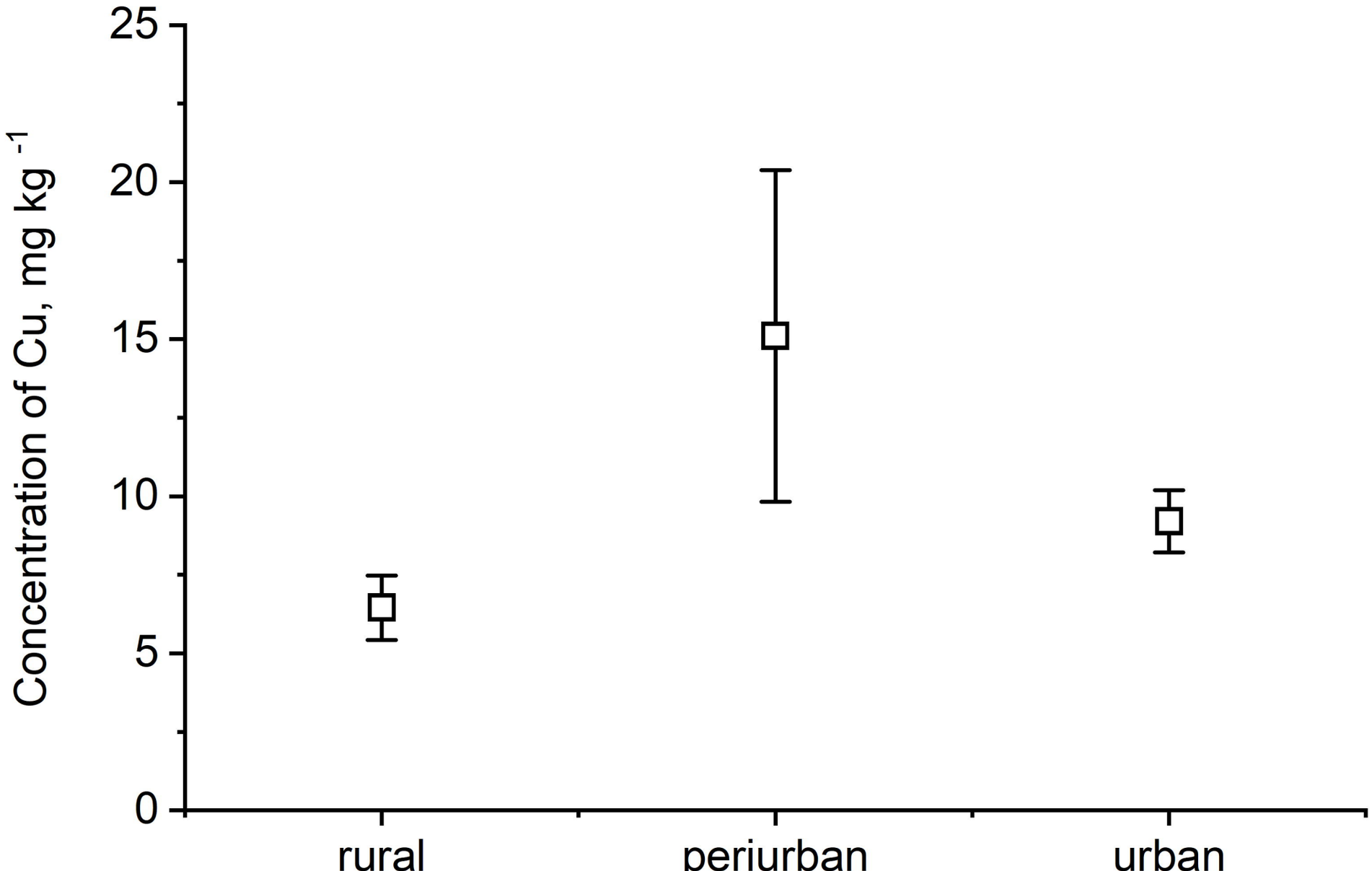
Concentration of Cu, mg kg -1
25
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