CONTAMINATION OF PLANTS, SOIL, AND BUILDING STONES AT A ROMAN HERITAGE ARCHAEOLOGICAL SITE IN AN URBAN AREA

Abeer Al Bawab[1,2,*], Afnan Al-Hunaiti[1,3], Saida Abu Mallouh[2], Ayat Bozeya[2],
Rund Abu-Zurayk[2], Tareq Hussein[4,5]

[1]Department of Chemistry, The University of Jordan, Amman, Jordan
[2]Hamdi Mango Center for Scientific Research, The University of Jordan, Amman, Jordan
[3]Department of Chemistry, University of Petra, Amman, Jordan
[4]Department of Physics, The University of Jordan, Amman, Jordan
[5]Institute for Atmospheric and Earth System Research, University of Helsinki, Helsinki, Finland

ABSTRACT

Some cultural heritage sites in Jordan are in urban areas being exposed to anthropogenic pollution. Therefore, it is important to evaluate the contamination at these sites to protect them. Here, we considered a Roman archeological site (Nymphaeum) situated in Amman. The contamination in soil, plants, and building stones did not show spatial distribution within the site. The contamination was the highest in soil (heavy metals 10^4–10^7 ppb and sulfur ~3.5×10^6 ppb) whereas in plants was the least for Cr (~400 ppb) and in building stones it was the least for Cu (~860 ppb). The highest contamination in plants and building stones was found for Al (~5×10^4 and ~6.2×10^5 ppb respectively). The sulfur content in plants (~7.6×10^5 ppb) was higher than that in the building stones (~2.3×10^5 ppb). The heavy metals and sulfur contamination in the building stones were lower than what was reported elsewhere outside Jordan.

KEYWORDS:
Nymphaeum, Heavy Metals, Sulphur, Stone Degradation, Stone Restoration.

INTRODUCTION

Anthropogenic activities produce a vast range of pollutants that end up and accumulate in the environment in the form of gas, solid and liquid state [1]. Even at low concentrations, pollutants might alter both the physical and chemical properties of environmental systems. For example, sulfuric and nitric acids, carbon monoxides, volatile organic compounds emitted into the atmosphere during fuel combustion processes can be transported for long distances causing severe impacts on both the environment and the human health. Many harmful effects have been linked to acid rain including damage to water resources, buildings, agricultural crops, etc.

In general, Vanadium (V) and Nickel (Ni) are contaminants produced during energy production processes. Usually, atmospheric C, Br, and Pb are tracers for automobile emissions whereas Cr, Mn, Fe, Cu, Zn, As, Se, and Pb are tracers for industrial activities and smelters [2-5]. Marine aerosols have high contents of Na and Cl as well as mineral dust, which is characterized by Al, Si, K, Ca, Ti, Mn, Fe, and Sr. Eventually, air pollution settles down on environmental surfaces, which mainly include plants, surface water, soil, and buildings [1,6]. As a matter of fact, plants and soil as well as mosses can be considered as good indicators for certain air pollutants during a certain period prior of assessment time [7-11].

Plants absorb and accumulate pollutants from the soil, water, and the atmosphere. Some plants are known to be susceptible to very low concentrations of air pollution and exhibit a characteristic foliar injury following the exposure period. Therefore, most plants are considered as receptors of pollutants and toxicants with variations in their response with respect to the chemical and physical characteristics of the surrounding environment [11]. During the past few decades there has been an increase in the use of plant leaves as bio-monitors of heavy metal pollution in the terrestrial environments. Though the heavy metals like, Cd, Pb and Ni are not essential for plants growth, but they are taken up and accumulate in plants in many toxic forms. Because plants (especially perennial grasses) have a high storage capacity of such metals in their shoots, they can be used to determine the presence of air pollution in a given area [12]. For instance, plants that grow spontaneously and naturally in our surrounding environment can be used for long-term environmental pollution assessments [13]. The most common used bio-indicators in air quality biomonitoring studies are leaves of higher plants, pine (*Pinus eldarica Medw*) bark, sunflower plants, vegetables and fruits, roadside plants, herbs and medicinal plants, and Bryophytes [14-31].

Another concern is the deposition (dry and wet) and accumulation of air pollutants on buildings causing the deuteriation and weathering of the outer shell of the buildings [32-39]. This becomes very important when the concern is about cultural heritage buildings [40-43]. Therefore, surface treatments with a protective layer coating (e.g. made of polymer, nano particles, nano-composite, superhydrophobic material, etc.) has been a common practice to preserve and protect heritage building from deterioration [44-46]. Some coatings also provide self-cleaning and de-polluting mechanism to reduce the impacts of pollutants accumulation on the building stones [47-48].

In Jordan, environmental studies about plants and soil with heavy metals and sulphur are very rare. This brings up a serious issue about the difficulty in understanding the dynamics and pathways of pollution in the Jordanian ecosystem. In addition, the accumulated amounts of heavy metals and sulphur in heritage building stones has never been reported nor assessed in Jordan. Jordan is known to have many cultural heritage sites, some of them are dated several thousand years old. Therefore, in this study, we aimed at quantifying heavy metals and sulfur contamination in plant, soil, and building stones samples collected at a Roman archeological site (Nymphaeum) situated in the downtown of Amman, Jordan. The selected location is unique in many ways: it is central, intact, and exposed to common types of urban contamination processes in Jordan. Therefore, it can be considered as a representative for a large area of the city, especially the downtown area. Jordan is also known of its historical buildings that were built and developed during the era one–two thousand years and passing through several historical eras. This study at the Nymphaeum site will give us a clear understanding about the pollution level at this site specifically but the results are to be interpreted to understand the damage found in archeological buildings in Jordan and possibly elsewhere.

MATERIALS AND METHODS

Measurement site: "Nymphaeum" archeological site. Amman, the capital of Jordan, has a long-time history that goes beyond the Ammonites, which occupied the northern Central Trans-Jordanian Plateau during the latter part of the 2nd millennium BC to the middle of the 1st millennium BC. Therefore, Amman, especially its city center, includes many archeological old sites. For example, the earliest settlement in the area was a Neolithic site. Its successor was known as "Rabbath Ammon", which was the capital of the Ammonites. Later on, it was renamed as "Philadelphia", which belonged to the Decapolis during the Roman time in the Levant region.

Nymphaeum site is one of the historical sites found in Amman (Figure 1). It was built in the 2nd century CE, during the same period as the nearby Theatre and Odeon during the Roman era. It was one of the Roman public fountain sites, which were very common in Roman cities at that time. This Nymphaeum is believed to have contained a 600 square meters pool which was three meters deep and was continuously refilled with water.

Nowadays, the Nymphaeum is a partially preserved archeological site. During October 2014 – December 2017, The University of Jordan (UJ), University of Petra, the Hashemite University, Ministry of Tourism and Antiquities (Department of Antiquities; DoA), Greater Amman Municipality as well as professional technicians performed a restoration for the site under a project funded by the U.S embassy in Amman, which was called as US Ambassador Fund for Culture Preservation (AFCP). The restoration process included cleaning the structure stone by stone as well as replacing portions of the stone lost due to erosion, cracking and flaking.

As a central location in the city center, the site is surrounded by many anthropogenic pollution sources; mainly tailpipe and non-tailpipe traffic emissions. These atmospheric emissions are deposited on the environmental surfaces at this site including building stones, soil, and plants. Besides that, the site suffered several floods after heavy rain. Since this site is one of the lowest points in the city, the floods bought a wide range of pollutants (e.g. including heavy metals) that settled in the soil and the nearby area. Such pollutants might have a severe effect and increase the degradation of the structure of the archeological site.

Samples collection. Samples were collected from plants, soil, and building stones at the Nymphaeum site in May 2016 (Figures 2–3). The samples included 43 plant samples, 10 soil samples, and 15 building stone samples. Soil samples were taken from the ground surface. Plant samples were taken from the upper parts (without roots). Building stones samples were taken from the internal and outside building façade by scrapping the outer surface of some stones picked up randomly at different locations and heights. All samples were packed in separate polyethylene bags.

Chemical analysis. Sample preparation and acid digestion. Plant samples were dried in a well-ventilated and shady place at room temperature for few weeks and grinded into powder before taken to the chemical analysis. Then, they were digested according to Jones (1984) [49]. The plant sample (about 0.5g) was heated with a $HNO_3/HClO_4$ mixture (5ml:1.5ml of 70%:60% concentration) until the brown fumes disappeared. The solution was cooled down and 1:1 diluted with 5ml HCl. The diluted solution was then filtered and diluted with distilled water up to 25ml.

The soil and building stones samples were digested according to Momani et al. (2009) [50], using conventional Aqua Regia digestion. About 5g from each sample was digested in 75ml of Aqua Regia (19ml HNO_3+ 56ml HCl) and heated in 95℃ for two hours and then for 30 min at 80℃. Finally, the samples were diluted with distilled water to 100ml.

Elemental analysis. Heavy metals and sulfur. Determination of heavy metals (Ni, Cd, Cr, Pb, Cu, Zn, Fe, Al) and sulfur were analyzed in triplicates by Inductively Coupled Plasma–Optical Emission Spectrometry (ICP-OES) equipped with 40.68 MHz operating frequency generator, 1,800 L/mm t67holographic grating that allows for a wide range analysis from 160–800 nm and up to 6 pm resolution. This method meets the EN655011, IEC801-2, IEC801-3 and IEC801-4 EMC standards. The ICP-OES parameters used are available in the supplementary material.

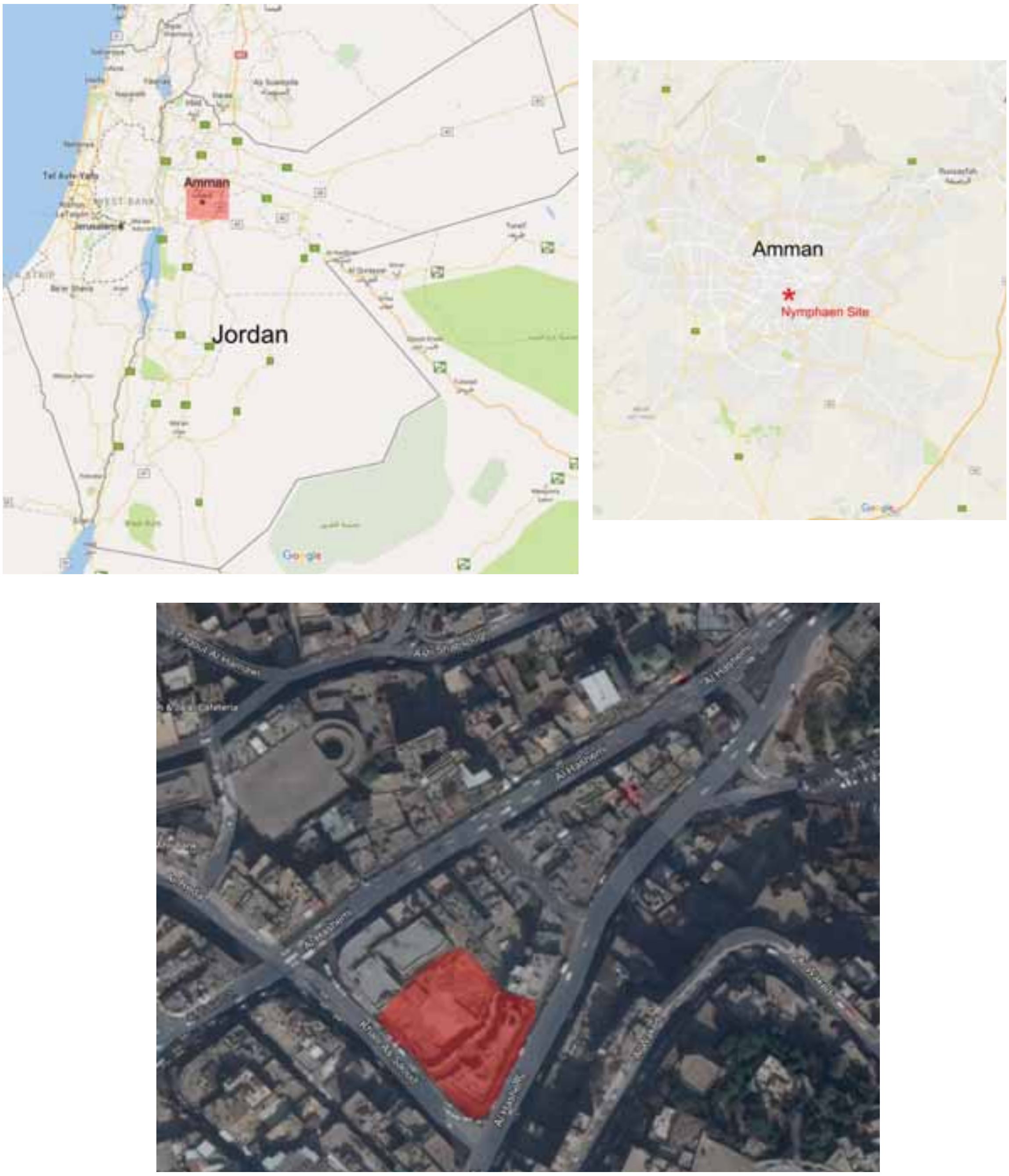

FIGURE 1
(a) Jordan map, (b) Greater Amman district, and (c) the Nymphaeum archeological site with the sample collection locations highlighted

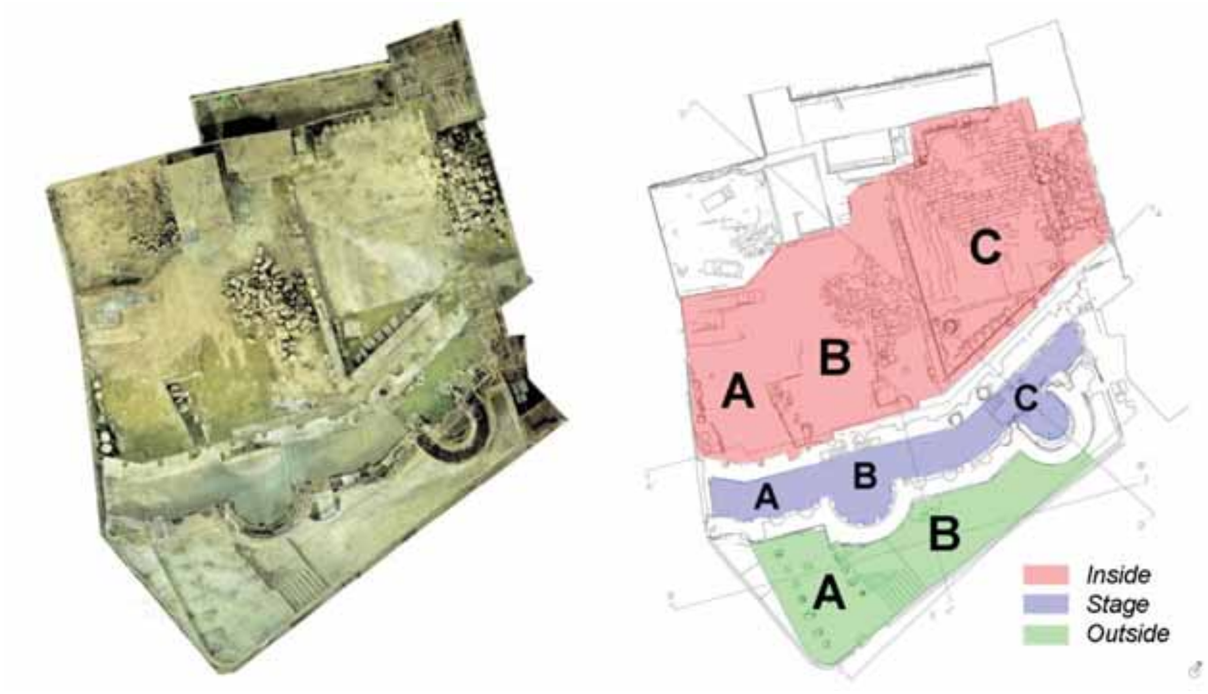

FIGURE 2
A sky view photo and a sketch showing the Nymphaeum archeological site with indications of the soil and plants sample collection areas: inside, outside, and stage. [51]

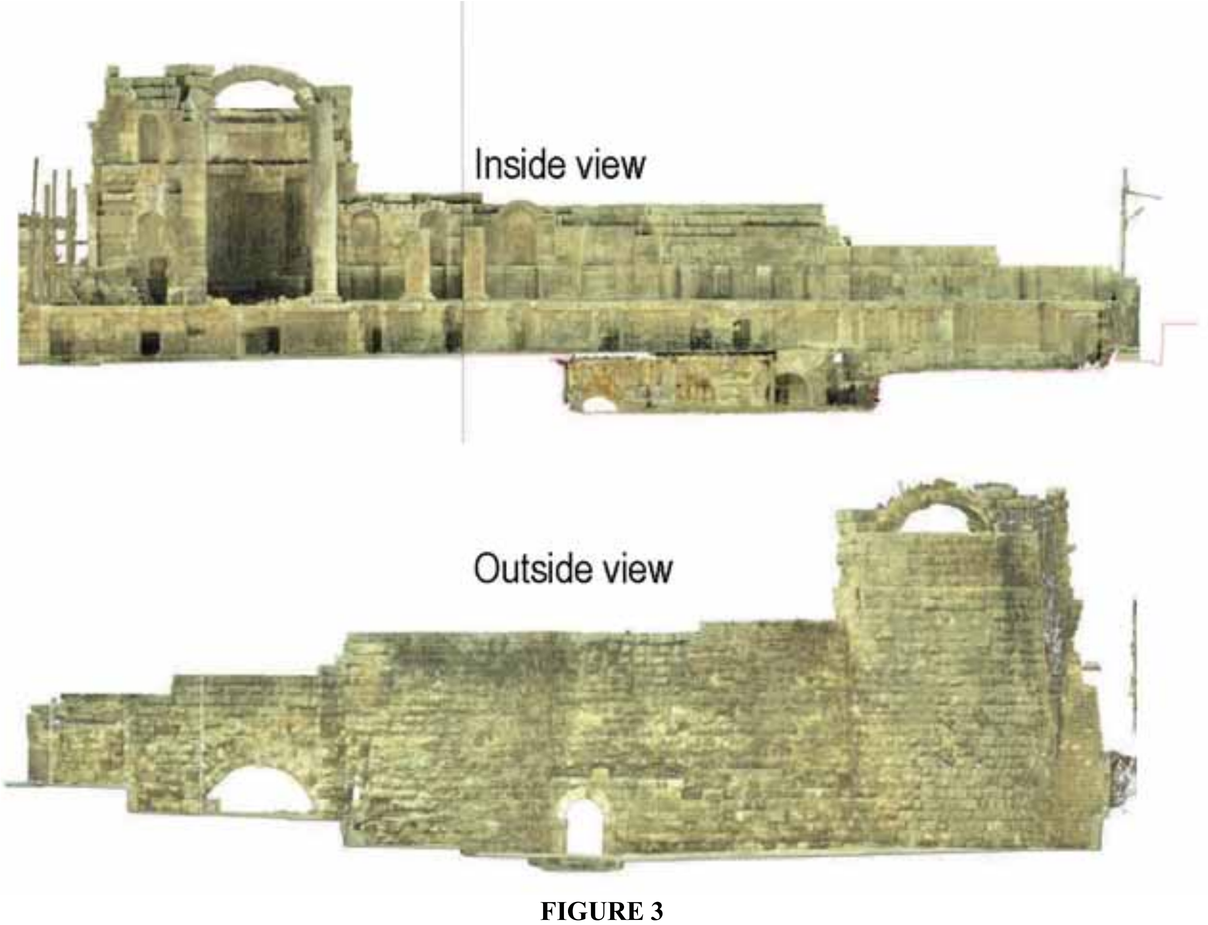

FIGURE 3
Side views of the Nymphaeum archeological building. [51]

To calculate limit of detection (LOD), a calibration curve was constructed using five points, 0 ppm, 0.01 ppm, 0.1 ppm, 0.5 ppm, 1 ppm and 2 ppm. After ensuring the linearity of the calibration curve; calibration blanks were analyzed 10 times for all elements. Limits of detection were equal to three times the standard deviation of the ten blank measurement results. Table 1 lists the LOD for each element.

TABLE 1
Limit of detection (LOD).

Element	Detection limit (ppb)
Pb	113.046
Ni	19.148
Cd	2.670
Co	5.943
Cu	29.272
Zn	5.562
Cr	80.963
Fe	2.777
Al	239.328
S	355.670

RESULTS AND DISCUSSION

As a general observation in this study, the heavy metals concentrations in soil samples were the highest whereas in the plants samples they were the lowest (Figure 4). This can be attributed to the fact that heavy metals are naturally present in soil, and certain activities may further increase their concentration in soil. They exist as separate entities or in combination with soil components such as silica and plants may not uptake heavy metals with large amounts from soil. Sulfur concentration was also the highest in soil samples but the lowest in building stones samples. The sulfur source in the soil is mainly atmospheric contamination from burning oil and gas; such contamination is washed out by wet deposition and accumulated in the soil.

Within plants samples, the highest concentration was found for iron (Fe: median 9.9×10^4 ppb, mean 1.1×10^5 ppb) and the lowest concentration was found for chromium (Cr: median 4.1×10^2 ppb, mean 5.2×10^2 ppb). On the other hand, aluminum concentration was found the highest in soil (Al: median 1.9×10^7 ppb, mean 2.1×10^7 ppb) and building stones (Al: median 6.2×10^5 ppb, mean 1.8×10^6 ppb). Cadmium concentration was the lowest in soil (Cd: median 1.2×10^4 ppb, mean 1.3×10^4 ppb) and building stones (Cd: median 6.5×10^3 ppb, mean 7.2×10^3 ppb).

Plants contamination. In more details, the lowest concentrations in the plants were found for Cd followed by Ni, Cr, and Cu (median value ranging from about 410 ppb to about 2370 ppb) whereas the highest were found in S (~10^6 ppb) followed by Fe (~10^5 ppm). Specifically, the pattern of heavy metals and sulfur concentrations in the plant samples was S> Fe> Al> Zn> Pb> Cu> Cd> Ni> Cr (Figure 4–5). According to the World Health Organization (WHO) guidelines, the heavy metals concentrations observed in our samples were higher than the permitted standards [52].

In general, there were slight differences in the concentrations of the same element observed in different plants collected from different areas within the site. The differences could be due to the plants age, type, and location. It was emphasized that heavy metals toxicity is species specific [53] and affected by soil acidity, fertility and on the presence of other toxic substances [54]. Plants have the capacity to bioaccumulate heavy metals when they are grown on polluted soil [55-57]. For example, the uptake of Fe and Al by some plants could increase its concentration to more than 10^5 ppb [30].

Heavy metals contamination in plants might affect their growth and photosynthesis activity [58]. Bearing in mind not exceed harmful levels, Al has an important role in enzymes activation and in physical properties controlling for plants and Fe plays a major role in energy transformation in plant cells.

Plants usually absorb sulfur from the soil in the form of sulfate ions. Sulfur can also be absorbed through leaves in the form of sulfur dioxide or sulfur trioxide from the atmosphere. Regarding sulfur concentration in plants in this study, there is no sulfur contamination as for healthy leaves sulfur content ranges from 5×10^5 to 14×10^6 ppb [59].

Soil contamination. With a closer look at heavy metals concentrations in soil samples they had a different trend than that found in plants samples (Figures 4 and 6). The lowest concentrations were found for Cd (median value 11780 ppb) and then followed by Ni, Cr, Cu, and Pb (median value ranging from 39300 ppb to 1.2×10^5 ppb). The highest heavy metals concentrations were found for Al (1.9×10^7 ppb) followed by Zn (median value 6.9×10^5) and Fe (median 4.2×10^5). In general, Al contamination in the soil was about 380 times higher than that in the plants whereas that for Cr was about 280 times higher in soil than in plants. As for Ni, it was about 116 times higher in soil than in plants. The Fe, Cd, Cu, and Zn contaminations in the soil were about 4, 6, 37, and 30 times higher in soil than in plants; respectively.

Interestingly, sulfur contamination in soil samples collected from area C was even higher than that found in plants samples. For instance, sulfur median concentrations in area C soil exceeded 4.2×10^6 ppb and compared to sulfur median concentrations did not exceed 1.2×10^5 ppb in all plants samples collected from all areas. Area C was for some time in the past a storage for some heavy machinery and parts operated with diesel fuel, which is rich in sulfur in Jordan. It is expected that the toxicity of heavy metals in plants would increase due to soil acidification caused by sulfur deposition [60]. Thus, a high mobility rate of trace metals in soil contaminated by sulfur must be considered as a significant factor in the disturbance of natural metal cycles [61].

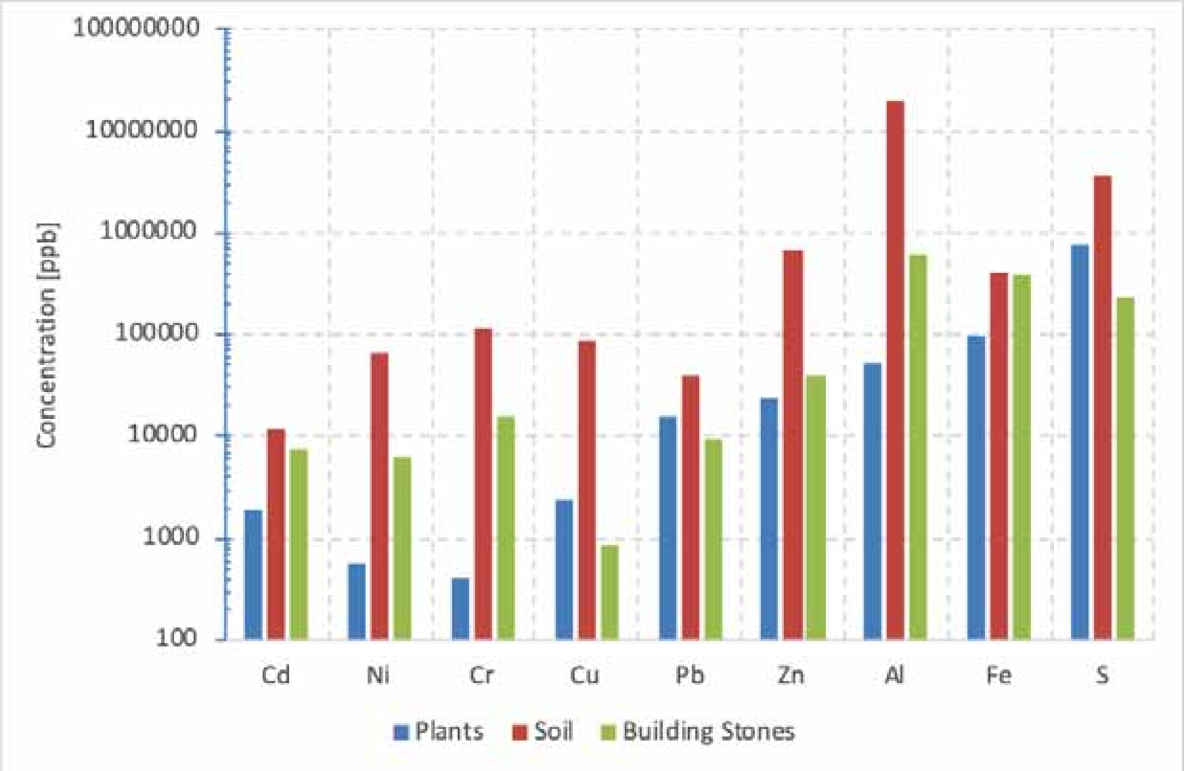

FIGURE 4
Heavy metals and sulfur overall median concentrations.

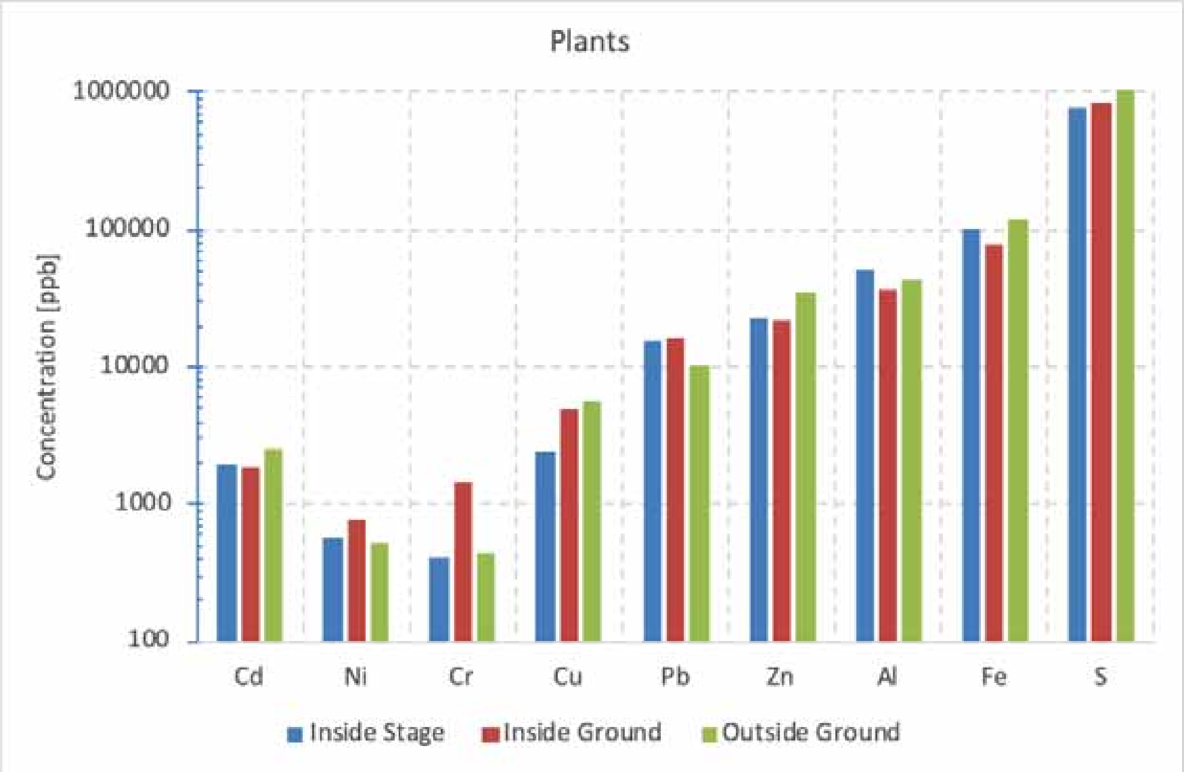

FIGURE 5
Heavy metals and sulfur overall median concentrations in plants samples.

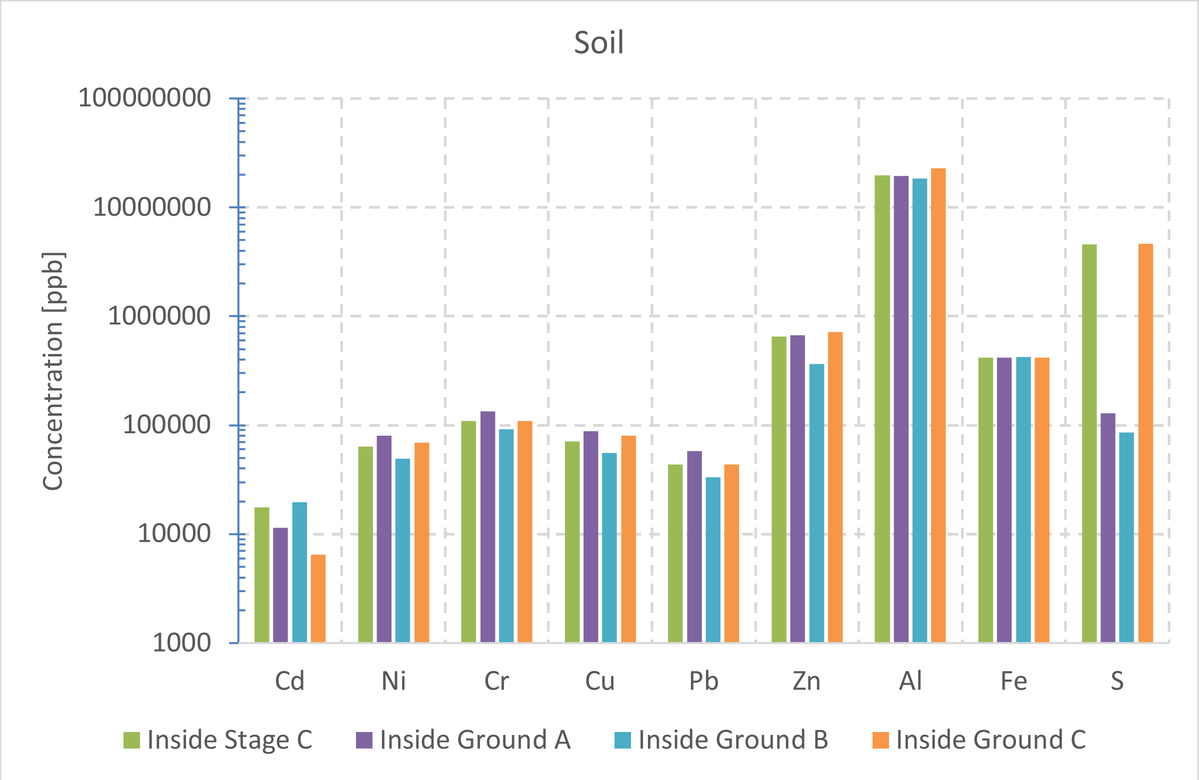

FIGURE 6
Heavy metals and sulfur overall median concentrations in soil samples.

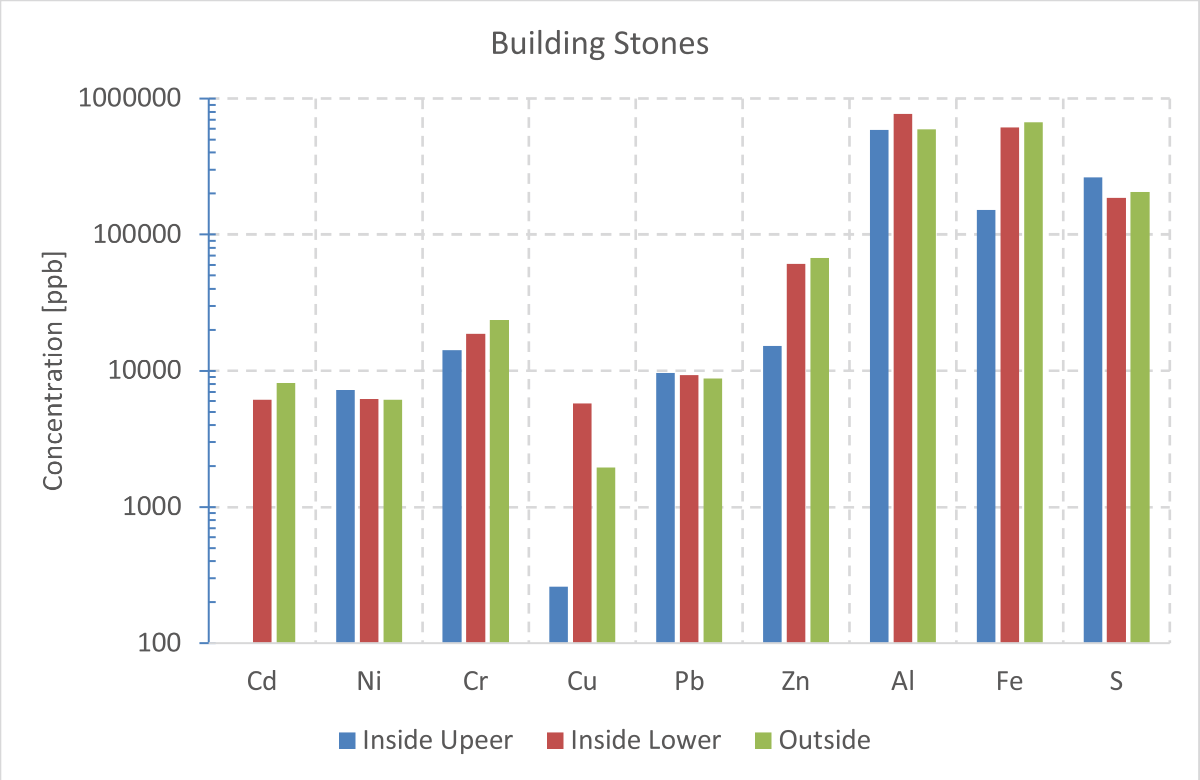

FIGURE 7
Heavy metals and sulfur overall median concentrations in building stones samples.

Each heavy metal contamination is linked to and traced to certain anthropogenic activities [16, 58, 62-64]. For example, industrial activities produce huge amounts of heavy metals (e.g. Zn, Cu) that can be accumulated in soil either nearby the facilities themselves or be transported in underground and surface water. Fe and Al are major constituents of lithosphere, in addition to the abundance of Al in clay minerals. They have several applications in industry such as construction, transportation, electrical and chemical productions, paper manufacturing, leather tanning and others [58]. Interestingly, the presence of some heavy metals may affect the fate of others in the soil and plant [64]. Heavy metals contamination in soil may have different effects. One effect is on microbial activity which is inhibited significantly in the heavy metal contaminated soil, so they severely inhibit the biodegradation of organic contaminants. Another one is the effect on plants which can be poisoned, and it even leads to death of the plant at high concentrations of heavy metals. In addition, heavy metals in urban soil may enter into the human body through inhalation and skin absorption of dust and thus cause a damage to human's health especially for children [66-67].

Lead is mainly found as water-insoluble chemical forms in the soil, thus it is usually not available to plants [68]. Furthermore, up to 90% of lead absorbed by plants remains in the roots and very limited percentage transported to the shoots [69-71] that probably explains the accumulation of lead under the permitted limits.

Building stones. Similar to soil contamination, heavy metals concentrations in building stones showed a similar trend as that observed for soil samples (Figures 4 and 7). The lowest heavy metals concentrations was observed for Cu (median value 850 ppb) followed by Ni, Cd, and Pb (median value ranging from 6450 ppb to 16050 ppb) whereas the highest were found for Al (median 6.2×10^6 ppb) and Fe (3.9×10^6 ppb). Median concentrations for sulfur exceeded 10^5 ppb in samples collected from different points on the façades. In general, the contamination levels were rather similar in the building stones samples collected from both the inside and outside façades.

High concentrations of sulfur and heavy metals in building stones can be attributed to mobile sources of emissions, especially the high vehicular traffic in this area. The deposition of particles rich in heavy metals can accelerate the oxidation rate of SO_2 deposited on stone surfaces and consequently contribute to accelerate stone decay [35]. The stones are typically blackened, and this can be due to the accumulation of atmospheric pollutants on their surfaces. In addition, the formation of black crusts on building stones might be due to the growth of gypsum, sheltered from water and attacked by an SO_2 polluted atmosphere, which was confirmed by many studies that showed close correlation between environmental pollution levels and development of black crusts [32].

Gypsum or limestones are affected by atmospheric pollution in several ways. First, they might be damaged and cracked because of water droplets accumulation which freezes and expanded during winter. Second, the highly corrosive effect of acidic rain due to sulfur dioxide, sulfur trioxide and nitrogen oxides [72-73]. The effect of acidic rain known to be increased in the presence of heavy metals (especially Fe) and carbonaceous particles which act as catalysts for sulfation process [74]. For example, Zappia, Sabbioni, and Gobbi (1998) [75] reported that as Fe concentrations on stones surface increase from 5114–19850 ppm the sulfate formation increased from 62–854 ppm.

It is, therefore, necessary to conduct stone restoration for archeological buildings. For the studied sight, we recommend a technique by using urethane restoration [76]. Another recommended technique is by using synthetic polymers to improve both the mechanical properties of the stones and the wall appearance [77] .

CONCLUSIONS

Jordan has many cultural heritage sites, some of them are dated several thousand years old. It is therefore important to quantify and understand the state of heavy metals contamination in the building structure of heritage buildings in Jordan. This will help us to put clear strategic plans to restore and protect these buildings from deterioration, especially those located in the urban areas as the center of pollution in soil, plants, and air. According to our knowledge, such studies have never been reported before; and therefore, in this study, we quantified heavy metals and sulfur contamination in plants, soil, and building stones samples collected at a Roman archeological site (Nymphaeum) situated in the downtown area in Amman, Jordan. This site is in a central location, intact, and exposed to common types of urban contamination.

In this study we had 43 plant samples, 10 soil samples, and 15 building stone samples taken from different location within the Nymphaeum site. These samples were analyzed (Inductively Coupled Plasma–Optical Emission Spectrometry, ICP-OES) looking for contamination of heavy metals and sulfur.

The soil samples contained the highest concentrations of heavy metals (ranging from $\sim10^4$ ppb for Cd to $\sim10^7$ ppb for Al) and sulfur ($\sim3.5\times10^6$ ppb). The heavy metals concentration in plants was the least for Cr (~400 ppb) whereas in building stones it was the least for Cu (~860 ppb). The highest heavy metals concentration in plants and building stones was found for Al ($\sim 5\times10^{4}$ ppb and $\sim 6.2\times10^{-5}$ ppb respectively). The sulfur content in plants sample was higher than that in the building stones; $\sim 7.6\times10^{-5}$ ppb and $\sim 2.3\times10^{-5}$ ppb respectively. The heavy metals and sulfur contamination in soil, plants, and building stones samples did not show a clear spatial distribution within the archeological site.

Since Jordan has many cultural heritage sites located in urban areas, this study can be considered as a good representative for other sites all over the country.

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CORRESPONDING AUTHOR

Abeer Al Bawab
Department of Chemistry,
The University of Jordan,
Amman – Jordan

e-mail: drabeer@ju.edu.jo