One of the primary causes of environmental degradation is attributable to rapid global population growth. Population growth threatens the environment, due to the expansion and intensification of industry and agriculture, uncontrolled urbanization, and over-exploitation of natural resources. This leads to envi-

Distribution of chromium, nickel, copper and zinc in the Al Zintan area, northwestern Libya

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Abstract. Global population is growing rapidly. As a result, increasingly large areas are being settled and farmed. This devastates soils and causes pollution by heavy metals and other components. Heavy metals in the environment originate from both natural and anthropogenic sources. Natural sources generally include rock weathering and the propagation of heavy metals, such as Cr and Ni, from ultrabasic rocks. These are natural processes that generally do not threat human health. Anthropogenic sources include industry and inappropriate disposal of waste in the environment. In such cases concentrations of heavy metals can be harmful to people and other living beings. Al Zintan is a city located in northwestern Libya, on a plateau mainly built up of Cretaceous sediments. Since the 1980’s, nomadic population has rapidly been settling this area. As a result, a former part of the desert was transformed and is used for farming. Soil sampling at Al Zintan was conducted in 2017, across a 2×2 km grid. A total of 143 samples were collected from depths of about 30 cm. The samples weighed 2 to 2.5 kg and generally comprised sand with a clay component. A Niton Xl3t goldd+ instrument was used for chemical analyses, based on which GIS heavy-metal distribution maps were generated. The distribution of Cr, Ni, Cu and Zn is discussed on the paper.

Key words: heavy metals, distribution, sampling, Al Zintan, Libya.

Апстракт. У свету је присутан рапидан раст људске популације. Са тим у вези све више површине се користи за изградњу насеља и као пољопривредно земљиште. Као последица поменутог долази до процеса девастације земљишта и загађења тешким металима и другим компонентама. Тешки метали присутни су у животном окружењу као резултат природних и антропогених фактора. Природни фактори су углавном распадање стена и дистрибуција тешких метала, нар. хром и никал из ултрабазичних стена, али и низ других метала. Антропогени фактори су углавном промена средине као резултат деловања антропогена на животну средину. У овом случају могу бити опасне по људско здравље и друга жива бића. Ал Зинтан је град који се налази на низу срединама на северозападу Либије. Од 80-тих година долази до наглог насељавања номадског становништва у ово подручје. Са тим у вези, раније пустинске површине се трансформису и користе за пољопривреду. Током 2017. године извршено је узорковање тела Ал Зинтана по мрежи од 2×2 km. Укупно је узето 143 узорка са дубине од око 30 cm. Узорци су били тешки од 2 до 2,5 kg, углавном изграђени од песка са глинитовим компонентом. Уређајем Niton Xl3t goldd+ урађене су хемијске анализе, а на основу њих су генерисане карте дистрибуције тешких метала у ГИС-у. У овом раду је дат приказ дистрибуције хрома, никла, бакра и зинка.

Кључне речи: тешки метали, дистрибуција, узорковање, Ал Зинтан, Либија.
ronmental pollution and degradation (RAY S. & RAY I.A., 2011). Such trends are noted in nearly all countries of the world, especially big and rapidly growing cities. Al Zintan in Libya is an example. It is one of the biggest cities in northwestern Libya, situated roughly 130 kilometers southwest of Tripoli, in the Nafusa Mountains area. The city and its surrounding areas have a population of approximately 50,000 (UNICEF, 2016). The population and the city grew rapidly in the latter half of the 20th century and at the beginning of the 21st. Demographic and industrial expansion has led to many issues, such as increasing land prices, random construction, greater demand for goods and services, and the generation of various types of waste. The primary consequence is environmental pollution in all parts of the city, both urban and rural, as well as in the surrounding desert. A lack of building land has also resulted in the city encroaching on farmland, which intensified soil pollution and degradation. Soil contamination is brought about by many different anthropogenic sources of heavy metals, along with other pollutants that affect both agricultural and urban land (ALLOWAY, 2012).

Heavy metals are found in the environment as a result of natural and anthropogenic factors. In nature, excessive levels of trace metals may be caused by geographical phenomena like volcanic eruptions, weathering of rocks, and leaching into rivers, lakes and oceans due to the action of water. Their natural abundance and distribution in soils are controlled by many factors, e.g. the parent rocks, maturity of the sediments, stability of minerals etc. (EL-SAYED et al., 2017). Industrial activity, generation of various types of energy, wastewater discharges, disposal of harmful solid waste, mining operations, exhaust gas emissions, and the like, constitute the emissions, exhaust gas emissions, and the like, constitute the charges, disposal of harmful solid waste, mining operations of various types of energy, wastewater discharge, etc. (GRACE et al., 2016; MILADINOVIĆ et al., 2012). Heavy metals that are the most frequently encountered environmental pollutants, and which need to be removed or immobilized as far as possible, are copper, cobalt, chromium, cadmium, nickel, lead, mercury, manganese, zinc, iron, etc. (WU et al., 2010).

Living beings depend on heavy metals, or their ions, in many different ways. In low concentrations, some of these metals are essential for biological processes. However, in high concentrations they tend to be extremely toxic. In such cases they represent very harmful pollutants, given that their ions are not biodegradable like most organic substances (NIEL & SILVER, 2007).

From a biological perspective, heavy metals can be divided into two groups. The first group includes micro elements in low concentrations, which have a physiological function in living beings (NIEL & SILVER, 2007). Metals like cobalt (Co), copper (Cu), chromium (Cr), iron (Fe), magnesium (Mg), manganese (Mn), molybdenum (Mo), nickel (Ni) and zinc (Zn) are essential nutrients, needed for a number of biochemical and physiological processes (WORLD HEALTH ORGANIZATION, 1996). Various illnesses or deficiency syndromes of living beings are caused by an inadequate supply of these micro nutrients (WORLD HEALTH ORGANIZATION, 1996). Heavy metals are also considered to be trace elements because of generally low concentrations in nature (less than 10 ppm), in various environmental matrices (KABATA-PENDIA & PENDIA, 2001). Their bioavailability is influenced by factors such as temperature, phase association, adsorption, and sequestration, but also chemical factors (HAMELINK et al., 1994). Biological factors like the characteristics of the species, trophic interactions and biochemical/physiological adaptation, also play an important role (VERKLEJ, 1993). The second group includes macro elements, or toxic heavy metals harmful to human health and the environment (e.g. emissions of cadmium and mercury vapors and precipitation of lead, manganese, cobalt and nickel). At the cellular level, these metals cause various physiological irregularities (NIEL & SILVER, 2007; BANFALI, 2011). The toxicity of heavy metals depends on their concentration, degree of contamination, chemical form, penetration method, solubility in bodily fluids, and biochemical reactions through which they take part in metabolic processes (SAWICKA-KAPUSTA et al., 2010).

The concentrations of heavy metals in the fourth period on the periodic table (chromium, nickel, copper and zinc), which are found in the mainly sandy soils in and around Al Zintan, and their distribution within the city and in the extended area, are presented in the paper.

Materials and methods

Sampling

The samples were collected on pre-determined locations, in an area that was 19.5 km × 22 km in size, with an average spacing between the samples of 2 km and depths of about 30 cm. The sampling locations were selected keeping in mind: that the distribution of the samples is regular in general and that they cover densely populated areas, sparsely populated areas and farmland. Another consideration pertained to information obtained from Al Zintan Municipality, whether the settlements were old or recent. The sampling points were predefined in ellipsoid WGS 84, UTM zone 33. The weight of the samples was from 2 to 2.5 kg. According to the geological map of Mizdah, scale 1:250,000, the city of Al Zintan and surrounding areas are largely situated on Cretaceous sediments, overlain by sand.

Chemical analyses

Chemical analyses were performed by X-ray fluorescence (XRF). The elemental analysis of powder was conducted on an XRF Niton X13t Goldd+ analyz-
er at the University of Belgrade, Faculty of Civil Engineering. Each sample was tested twice, for about 180 to 240 seconds in the Soil mode, and checked by TestAll geo. The samples were ground to 70 µm. The following elements were measured: Cr, Ni, Cu and Zn. All the measured concentrations were expressed in ppm (mg/kg) units and the distribution of mentioned elements in the Al Zintan area was shown.

Fig. 1. Basis for displaying the distribution of measured elements.
Distribution of the tested elements in the study area

The concentrations of the tested heavy metals and their distribution and environmental impact were determined by remote detection using the Geographic Information System (GIS). As raster basis for the maps shown in this paper was used application SAS.Planet 160707.9476, Landscape w/o names (Google).

Figure 1 shows the geographic position of the study area, based on which the measured elements were displayed.

Results and Discussion

A total of 143 soil samples were collected in the study area, from a depth of about 30 cm. Assaying covered 33 elements (Mo, Zr, Sr, U, Rb, Th, Pb, Au, Se, As, Hg, Zn, W, Cz, Ni, Co, Fe, Mn, Cr, V, Ti, Se, Cu, K, S, Ba, Cs, Te, Sb, Sn, Cd, Ag and Pd). The following elements were below the detection limit in 90% of the samples: Mo, U, Th, Au, Se, As, Hg, W, Cu, Co, Sc, S, Cs, Te, Sb, Sn, Cd, Ag and Pd. Of the remaining 14 elements, eight (Zr, Sr, Rb, Zn, Fe, Ti, Ca and K) were detected in all the samples and six (Pb, Ni, Mn, Cr, V and Ba) in more than 50% of the samples.

The paper presents the results for Zn, Cu, Ni and Cr. Table 1 shows the statistical data.

The layouts below show the measured concentrations of the four tested heavy metals in soil samples.

Literature sources that contain background levels of the tested heavy metals in similar soils, as well as threshold values and maximum recommended concentrations of the metals in soil, were used to assess potential soil contamination in Al Zintan.

Given that there is virtually no topsoil, the land in Libya is generally covered by sand, clay, gravel, rock outcrops, and remnants of saltwater lakes (GECONT, 2018). Table 2 shows average background levels in similar uncontaminated soils from literature sources.

Table 2. Arithmetic (A) and geometric (G) mean concentrations of some trace metals (mg/kg) in soils from various textural groups (KABATA-PENDIAS & PENDIAS, 1999).

<table>
<thead>
<tr>
<th>Metal</th>
<th>Light sandy</th>
<th>Medium loamy</th>
<th>Heavy loamy</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cr</td>
<td>8.0</td>
<td>7.0</td>
<td>15.3</td>
</tr>
<tr>
<td></td>
<td>14.6</td>
<td>25.6</td>
<td>24.3</td>
</tr>
<tr>
<td>Ni</td>
<td>5.5</td>
<td>4.8</td>
<td>11.8</td>
</tr>
<tr>
<td></td>
<td>10.9</td>
<td>23.4</td>
<td>21.5</td>
</tr>
<tr>
<td>Cu</td>
<td>10.4</td>
<td>7.2</td>
<td>3.2</td>
</tr>
<tr>
<td></td>
<td>11.8</td>
<td>20.3</td>
<td>18.5</td>
</tr>
<tr>
<td>Zn</td>
<td>41.7</td>
<td>32.5</td>
<td>59.7</td>
</tr>
<tr>
<td></td>
<td>51.5</td>
<td>91.0</td>
<td>79.5</td>
</tr>
</tbody>
</table>

Table 2 shows threshold and guideline values of the given metals in soil.

The standards established by Finnish legislation for contaminated soils (MINISTRY OF THE ENVIRONMENT - MEF, FINLAND, 2007) were used in the present study following a review of various approaches and thresholds values for heavy metals in soils (TOTH et al., 2016). These standard values represent a very good mean-value approximation of different national systems in Europe and India, and they have been applied in the international context for agricultural soils as well (UNITED NATIONS ENVIRONMENT PROGRAMME, UNEP, 2013). The legislation sets forth concentration levels for each hazardous element, to identify soil contamination and remediation requirements. It establishes low and high concentration levels, which indicate the need for action if exceeded. The so-called “threshold value” (limit) is equally applicable to all sites and points to the need for further assessment of the area. “Guideline values” (recommended values) are values that should not be exceeded. If that happens, the observed area has a contamination level that poses either an ecological or health risk. Higher concentrations are determined by

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<table>
<thead>
<tr>
<th>Heavy metal</th>
<th>Threshold value (ppm)</th>
<th>Low guideline value (ppm)</th>
<th>High guideline value (ppm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Chromium (Cr)</td>
<td>100</td>
<td>200</td>
<td>300</td>
</tr>
<tr>
<td>Nickel (Ni)</td>
<td>50</td>
<td>100</td>
<td>150</td>
</tr>
<tr>
<td>Copper (Cu)</td>
<td>100</td>
<td>150</td>
<td>200</td>
</tr>
<tr>
<td>Zinc (Zn)</td>
<td>200</td>
<td>250</td>
<td>400</td>
</tr>
</tbody>
</table>

Table 3. Threshold and guideline values for metals in soils (defined on the basis of ecological risks) (TOTH et al., 2016).
prevailing land uses (i.e. industrial areas or transport sites), whereas lower guideline values are applicable to all other land uses (Toti et al., 2016).

As shown in Figs. 2 through 5, the measured chromium concentrations in soil range from 11.53 to 51.23 ppm, of nickel from 32.77 to 74.55 ppm, of copper from 21.97 to 28.42 ppm, and of zinc from 12.36 to 35.19 ppm.

Compared to the values in Table 2, the conclusion is that the tested soil contains elevated concentrations of chromium, nickel and copper, compared to their potential background levels. The situation is somewhat different in

![Legend](image).
the case of zinc, given the measured concentrations. Namely, they are lower than the expected background levels.

Table 3 leads to the conclusion that the measured concentrations of all the tested heavy metals are lower than recommended, except in some parts of the city where nickel concentrations slightly exceed threshold values but are still in the guideline range.

Keeping in mind that elevated concentrations of the studied metals are the most harmful to agricultural soils because crops are able to absorb soluble com-

Fig. 3. Measured concentrations of total nickel (ppm).
pounds of heavy metals via their roots and thus introduce them into the food chain (CROMMENTUIN et al., 1997; LIU et al., 2013; KELLEPERTZIS, 2014; WU et al., 2015), the conclusion is that the situation at the time of the study was not alarming from a human health perspective, with a possible exception of nickel. On the other hand, apart from ingestion, soil particles that contain these trace elements can be inhaled (WU et al., 2015), so further investigations would be needed to assess the composition of air in the study area.

Fig. 4. Measured concentrations of total copper (ppm).
The distribution of the heavy metals in the studied parts of the city is very important because of the potential toxic effect. The layouts show the distribution of the heavy metals and the distribution of pollution in the urban part of Al Zintan and surrounding rural and desert areas.

Based on the pollutant distribution, it is not possible to conclude whether the highest concentrations of the studied heavy metals are found in the rural/desert or urban areas. The above figures show different spatial distributions of the four metals within the city and indicate that there are no correlations among them.

Fig. 5. Total concentrations of total zinc (ppm).
The possible reasons for this are: the natural distribution of the metals in the Earth’s crust, the types and locations of industrial facilities and thermal plants in parts of the city, and the diffusion of soluble compounds of these pollutants through leaching and municipal wastewater.

An observation of particular interest is that the city of Al Zintan is situated on a plateau, at an elevation of approx. 670–710 m, but increased concentrations of Ni, Cr, Zn and rarely detected Cu were found in samples collected about 6 km north–northeast, at elevations of about 300 m, in zones of pronounced drainage systems. These occurrences have a similar distribution pattern to that in the populated areas, such that the concentrations represent recent pollution because there are no settlements, farmland or geologic units at the lower elevations (N–NW of the central parts of Al Zintan) which would carry elevated concentrations of Ni, Cr, Cu and Zn (Figs. 2–5).

Conclusions

The current situation is not alarming, as corroborated by a comparison of analyzed concentrations of toxic elements Ni, Cr, Cu and Zn with background levels in similar soils (Table 2) from literature sources, as well as threshold values and guidance levels in soils (Table 3).

The presence of chromium and nickel in basaltic rocks has been noted worldwide. While the Cr ore mineral, chromite, is generally found in ultramafic rocks, it is also known that Cr is present in basaltic magmas, with magnetite and ilmenite which contain Cr (TUREKIAN, 1963).

Nickel is usually in association with rock-formative magnesium – iron silicates. Due to weathering processes, nickel can migrate over large distances, along with its solutions. Also, it is combined with Fe and Mn hydroxides (BARALKIEWICZ & SIEPAK, 1999).

There are outcrops of Quaternary outflows of basalt lava (olivine metabasalt, ANTONOVIĆ, 1977) east of Al Zintan, at a distance of about 40 km, altitude 730 m, heading east-southeast to about 60 km. As Al Zintan is at altitudes of 680 to 720 m, it is possible that Cr and Ni were brought from these locations, as products of weathering – dust and sand carried by winds.

Zn and Cu are typical chalcophilic elements. According to BARNES (2016), Zn could be described as slightly chalcophilic and Cu as highly chalcophilic. Specific geological sources of Zn and Cu cannot be found on the geological map of Libya, 1:250 000, sheet Mizdah. The distribution of these elements also shows that they are not specifically associated with urban zones, farmland or areas devoid of anthropogenic impact.

As the city of Al Zintan continues to grow, the recommendation is to take the 2017 status as a reference point, given that soil analyses of this type had not previously been undertaken on any scale. Since the city is expanding in an uncontrolled manner, sampling should be undertaken at the same points, or even using a higher-density grid (especially in places where the concentrations of the studied metals were found to be elevated), at equal time intervals (e.g. every two to five years). Awareness raising among farmers, pollution control, and the construction of a regional landfill could certainly maintain or even improve the present status. Monitoring would especially be needed to track developments 6 to 10 km N–NW of the center of Al Zintan, because it is very likely that pollutants from the contaminated areas are reaching the previously unpolluted drainage systems.

References


Резиме
Дистрибуција хрома, никла, бакра и цинка у подручју Ал Зинтан, северозападна Либија

У свету је присуtan рапидан раст људске популације. Са тим у вези све више површине се користи у урбано и пољопривредне сврхе. Као последица долази до процеса девастације земљишта и загађења тешким металима и другим комплекснама. Тешки метали присутни су у животном окружењу као резултат природних и антропогених фактора. Природни фактори су углавном радио стена и дистрибуција тешких метала, нпр. хром и никл из ултрабазичних стена, ониме је природан процес и не доводи до угрожавања здравља људи. Антропогени фактори су углавном индустрија и неадекватно одлагање отпада у животну средину. Концентрација тешких метала у том случају могу бити опасне по људско здравље и друга животиња.
вреду. Током 2017. године извршено је узорковање тла по мрежи од 2×2 km на овом простору са 143 узорка узетих на дубини од око 30 cm. Узорци су били тески од 2 до 2,5 kg, углавном изграђени од песка са глиновитом компонентом. Уређајем Niton XL3t goldd + урађене су хемијске анализе, а на основу њих су генерисане карте дистрибуције тешких метала у ГИС-у. Олеатама су приказане дистрибуције испитиваних тешких метала, као и дистрибуција загађења у односу на урбане део града Зинтана, окончно пољопривредно земљиште и пустињски предео. У овом раду је дат приказ дистрибуције хрома, никла, бакра и цинка.

За даљу анализу потенцијалне контаминације земљишта у граду Ал Зинтану коришћене су литературне вредности природне заступљености испитиваних тешких метала у земљишту сличном оном на подручју овог града, као и граничне и препоручене максималне концентрације датих метала у земљишту. Имајући у виду да су повећане концентрације испитиваних тешких метала најопасније на подручју пољопривредног земљишта услед способности агрономских култура да преко коренова система апсорбују растворљива јединења наведених тешких метала и на тај начин их унесу у ланац исхране, може да се закључи да за течено стање није алермантно с аспекта очувања здравља људи.

На основу дистрибуције загађења испитиваним тешким металима не може да се закључи да ли се највеће концентрације испитиваних тешких метала налазе у пољопривредно - пустињском или урбаном подручју. На горе наведеним олеатама запажа се да је просторна дистрибуција сва четири метала у земљишту града Зинтана различита, те да нема међусобне корелације између концентрација испитиваних тешких метала. Разлог може да буде природни фактор распрострањености датих метала у Земљиној кори, врста и позиција индустријских и термоенергетских постројења у одређеним областима града, као и дифузија растворљивих јединења ових полутаната оцедним и комуналним водама.

Посебно занимљива опсервација је да је град Ал Зинтан на висоравни на надморској висини од приближно 670 до 710 m, али да су повећане концентрације Ni, Cr, Zn и ретко констатованог Cu такође уочене у узорцима узетим на око 6 km у правцу север–северозапад, на надморским висинама од око 300 m, у зони изражених дренажних система, и прате патерн дистрибуције поменутих загађивача у насељеним срединама, тако да су те концентрације у ствари новонастало загађење, јер у подручјима, на нижим надморским висинама на поменутом север–северозапад правцу од централних делова Ал Зинатана нема ни насеља ни пољопривреде, а ни геолошких јединица које би носиле повишене концентрације Ni, Cr, Cu и Zn (Слике 2, 3, 4 и 5).

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