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Original Scientific Article

Availability of Selected (Pollutant) Elements and their Influence on Soil Composition in Urban Area

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Abstract. Interest in growing fruits and vegetables in private gardens is rising due to nowadays ecological awareness. Avoiding artificial fertilizers and plant protection products does not guarantee the absence of toxic substances, especially heavy metals in the soil and thus in the fruits harvested. Due to either geological bedrock weathering or environmental pollution, garden soils may be rich in certain potentially toxic elements. In the present study ten garden soils from central Croatia have been analysed by the BCR method for the contents and bioavailability of aluminium, cadmium, chromium, cobalt, copper, lead, manganese, nickel and zinc.

The total amounts of the elements are in the concentration range as reported for agricultural soils in different geographical regions. Only two soils of the capital Zagreb have higher concentrations of pollutant metals, such as chromium, cobalt, copper, lead, manganese and zinc. Regarding nutrients, all soils have met the needs of common garden plants.

Keywords: BCR; ICP-AES; heavy metals; plant nutrients; garden soils; pollutants

INTRODUCTION

The importance of home gardening is rising in the last years due to the elevated ecological awareness. Fertilizers and plant protection products are considered to lower food quality by their specific toxic properties. Organic farming represents growing plants without synthetic fertilizers and pesticides or genetically modified organisms; however, the inorganic composition of the soils is not regulated.[1] Only general limits of levels in soils used for agricultural purposes are given by different jurisdictions.[2,3] In general, plants are useful indicators of environmental heavy metal contamination and can be used to monitor pollution across both spatial and temporal scales.[4] Fruits produced by organic agriculture in private gardens may also contain toxic elements, such as cadmium, lead, and arsenic due to contamination via air or by uptake from polluted soils.

The favorite products of home gardening are vegetables, like tomatoes and lettuce, and fruits, especially many types of berries, *e.g.* strawberries, blackberries, raspberries and currants.

Each of these plants has special requirements regarding micro-nutrients and trace elements, *i.e.* vitamins or minerals needed in small amounts for normal function of the organism. That a micro-nutrient is essential is indicated by its presence in healthy tissue and that its uptake and distribution are homeostatic control. Only small amounts of such nutrients are needed and any deficiency can cause diseases or ill-health, retarded growth and poor harvest. Plants require the following elements: nitrogen (N), phosphorus (P), calcium (Ca), magnesium (Mg), manganese (Mn), iron (Fe), boron (B), copper (Cu), zinc (Zn), and aluminium (Al).[5]

Plants tend to selectively uptake and accumulate certain metals as ions; the level of essential elements depends where the plant is grown, *i.e.* it is affected by the geochemical characteristics of a soil. The resulting elemental pattern is thus determined by the bioavailability of the elements present in soil and the selectivity of their accumulation. In plants, the major uptake occurs

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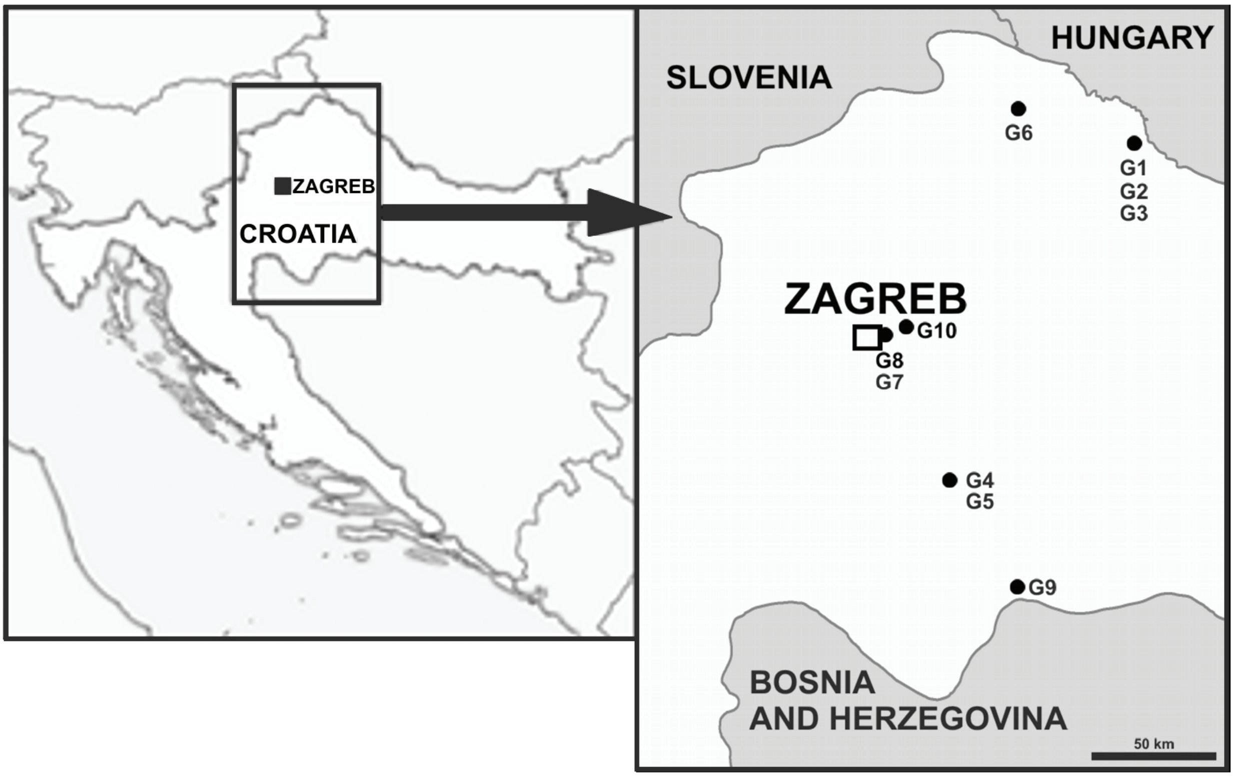

Figure 1. Soil sampling localities.

via their roots. Additional sources of these elements are environmental parameters, such as rainfall, atmospheric dusts (dry deposition), plant protection agents and fertilizers that can be absorbed through their leaves.[6] Soil analysis is important since the chemical composition of soil reflects both the soil bedrock and the anthropogenic inputs such as pollutants from industrial processes. Information on the mobility or bioavailability of metals however is scant, and special extractions steps are needed to determine the bioavailability of the elements in the plant.[7] The most frequently applied method is recommended by the European Commission, Community Bureau of Reference (BCR) for sediments and soils, due to its simplicity.[8]

The aim of the present study was the quantitative determination of the elemental content of ten private garden soils from central Croatia. Toxic as well as essential elements were selected, namely Al, Cd, Co, Cr, Cu, Fe, K, Mg, Mn, Ni, Pb, and Zn. Their availability was studied by the BCR method.

MATERIALS AND METHODS

Soil Samples

The garden soil samples from the A-horizon were collected in September 2009 at ten sampling sites in Zagreb and its surroundings (see Figure 1). The bedrock geology of the sampling sites is shown in Table 1. After collection the soil samples were dried for 24 hours at 105 °C, ground with a metal-free device and stored at a cool place.

Chemicals and Glassware

Nitric acid (HNO_3; 65 % *w*/*w* p.a.) and the ICP Multielement Standard IV, both from Merck (Darmstadt, Germany), were used to prepare the standard calibration solutions as well as for the digestion step. The reagents for the extraction steps, *i.e.* acetic acid (CH_3COOH), hydroxylamine hydrochloride ($NH_2OH \times HCl$), hydrogen peroxide (H_2O_2), ammonium acetate ($NH_4C_2H_3O_2$) and hydrochloric acid (HCl) were analytical grade and purchased from Kemika (Zagreb, Croatia). Before use all glassware was soaked in 7 mol/L nitric acid for 24 hours, and then rinsed with supra-pure water.

Extraction Procedure

Sequential extraction was based on a modified BCR protocol.[9] The acid-soluble and exchangeable fraction in step 1 was prepared by adding 40 mL of acetic acid (0.11 mol/L) per approx. 1 g of dry soil sample and shaking for 16 hours at room temperature by an orbital shaker at 250 rpm. The residue was treated with 40 mL of 0.5 mol/L hydroxylamine HCl (pH = 2) to obtain the reducible fraction (step 2). The extraction condi-

Table 1. Bedrock geology of the sampling area for the investigated soil samples

Sample	Locality	Bedrock geology
G1	Legrad	Alluvial sediments (gravels, sands and silts) (Holocene)
G2	Legrad	Alluvial sediments (gravels, sands and silts) (Holocene)
G3	Legrad	Alluvial sediments (gravels, sands and silts) (Holocene)
G4	Sisak	Alluvial sediments (pebbles, sands and silts) (Holocene)
G5	Sisak	Alluvial sediments (gravels, sands and silts) (Holocene)
G6	Čakovec	Gravels and sands (Holocene)
G7	Zagreb	Clastitic sediments (Pliocene-Quaternary)
G8	Zagreb	Clastitic sediments (Pliocene-Quaternary)
G9	Kostajnica	Carbonate and clastic sediments (Lower Sarmatian/Panonian)
G10	Zagreb	Carbonate and clastic sediments (Lower Tortonian)

tions were as in step 1. Step 3 (the oxidisable fraction) was prepared by adding of 10 mL of 8.8 mol/L hydrogen peroxide and 50 mL of 1.0 mol/L ammonium acetate (pH = 2) to the residue from step 2 and by using again the same extraction conditions as above. Finally, the residue from step 3 was leached with aqua regia. The extracts from each step were separated from the solid by centrifugation (3000 rpm for 20 min), decanted into polyethylene bottles and stored at 4°C until analysed.

ICP-AES Measurements

The instrument used was a Prodigy High Dispersive ICP spectrometer operating in simultaneous mode; at settings listed in Table 2. All measurements were carried out in triplicate at the emission lines shown in Table 3.

The calibration standard solutions at concentrations of 0.05, 0.10, 0.20, 0.50, 1.0, 2.0, and 5.0 mg/L were prepared in 2 % *w*/*w* HNO_3 from a multi-element standard stock solution (1000 mg/L).

Table 2. ICP-AES operating conditions

Instrument	Prodigy High Dispersive ICP
Spectrometer	High resolution echelle polychromator Large format programmable array detector (L-PAD)
RF-Generator	40 MHz “free-running”
Output power	1.1 kW
Argon flow	Coolant:18 L/min Auxiliary: 0.8 L/min Nebulizer: 1 L/min
Peristaltic pump	1.0 mL/min
Nebulizer	Pneumatic (glass concentric)
Spray chamber	Glass cyclonic
Plasma viewing	Axial
Replicates for each analysis run	3
Sample uptake delay	30 s

For all analytes and all types of samples the repeatability and precision of the method were determined. The sensitivity of the method was estimated from the slope of the calibration curve. The accuracy was estimated from the recovery of the analytes from the extraction solutions spiked at 0.5 and 2 mg/L. Standard reference materials supplied by the International Atomic Energy Agency (Vienna, Austria) were treated and measured like the samples: IAEA-SL1 (lake sediment), IAEA-Soil 7, IAEA 405 (stream sediments) and IAEA SL 3 (lake sediment).

RESULTS AND DISCUSSION

ICP-AES Validation

The accuracy of the method was evaluated by determining the recoveries by the analysis of CRMs and by spiking experiments of all analytes in the extracts of all four extraction steps. The mean recoveries of both concentrations range from 90–112 % and are listed in Table 3 along with their limit of detection (LOD). Regarding the tested CRMs the recoveries ranged from 87 to 110 % for the certified elements. Except for a few elements in single steps all LODs are < 3 μg/L. The precision for all elements ranged from 0.5 to 2.4 % in the four extraction steps. The repeatability was < 1.3 %, the intermediate precision < 5.7 %, the day-to-day reproducibility < 6.8 % and the overall uncertainty of measurement was estimated to be 4–8.5 % for all elements analysed.[10] The validation of analytical procedure optimized was found to be acceptable for environmental analyses.[11]

Metal Content and Extractability

The results (expressed in μg/g soil) for each extraction step together with the percentage extracted per step are

Table 3. Recoveries and limits of detection for the elements in the extract solution of all four sequential extraction steps

	step 1 (CH_3COOH)		step 2 ($NH_2OH\times HCl$)		step 3 ($H_2O_2 + CH_3COONH_4$)		step 4 (aqua regia)	
Element and wavelength / nm	Recovery %	LOD μg L^{-1}	Recovery %	LOD μg L^{-1}	Recovery %	LOD μg L^{-1}	Recovery %	LOD μg L^{-1}
Al 308.215	101	2.79	97	2.26	106	2.20	98	2.00
Cd 214.441	111	0.02	103	0.15	103	0.21	103	0.58
Co 228.615	103	0.95	98	2.60	100	0.76	93	1.62
Cr 206.149	101	1.99	98	1.71	111	1.68	101	2.01
Cu 224.700	97	4.74	102	0.64	100	1.97	96	1.62
Mn 257.610	101	0.83	97	5.97	97	1.71	99	0.12
Ni 231.604	110	6.23	98	0.13	112	0.97	99	1.57
Pb 220.353	105	2.41	110	1.50	105	3.17	102	4.85
Zn 213.856	92	5.28	100	3.84	99	0.18	95	0.37

listed for all elements investigated in Table 4 a–l. Each element is discussed separately. The elemental soil composition (Figure 2) shows the median total amounts of the metals analysed. The extraction behavior of all elements is compared by cluster analysis (Figure 3). Aluminium and chromium (three valent ions) are grouped together in all steps except in step 3. Each extraction step showed a different pattern.

Aluminium

Aluminium, one of the most important non-essential elements in soils, can affect the development of plant roots and reduce the plant's growth rate.[12] The total amounts of aluminium ranged from 6.5 to 10.7 mg/g dry soil, while 73–89 % were not extracted. This can be attributed to the high binding affinity of Al to humic substances.[12] Only less than 1 % was leached by acetic acid. In step 2, 7–11 % were extracted except from soils G7 and G8 with 14 % and 19 %, respectively. In the oxidisable fraction 2.7 up to 12 % were extracted, with a median of 4.7 %. Similar extraction behaviour was also described by Li *et al.*,[13] who analysed soils in mining and smelting areas in England. There the total Al amounts in soil were mainly higher, approx. 20 g/kg (range: 7.6–35.4 mg/g). No limit concentrations were found for Al in agricultural soils.[14]

Cadmium

Cd in soil occurs either naturally or is derived from human activities.[15] In the analysed soils cadmium levels

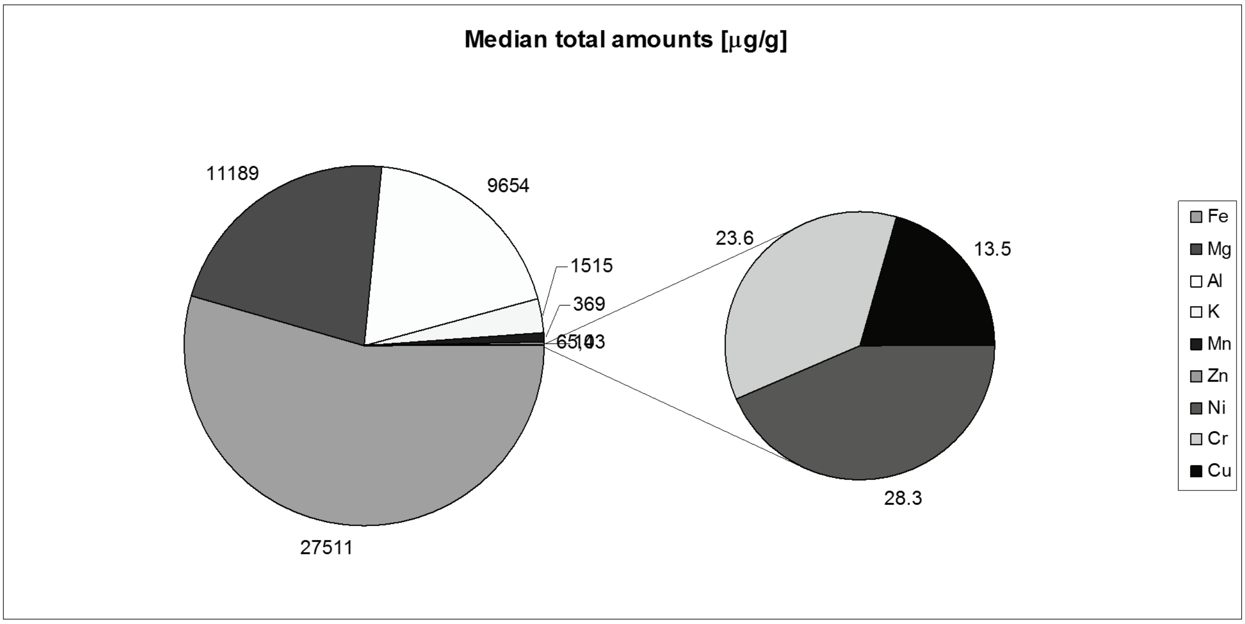

Figure 2. Median total soil concentrations of elements analysed (soil treated with aqua regia).

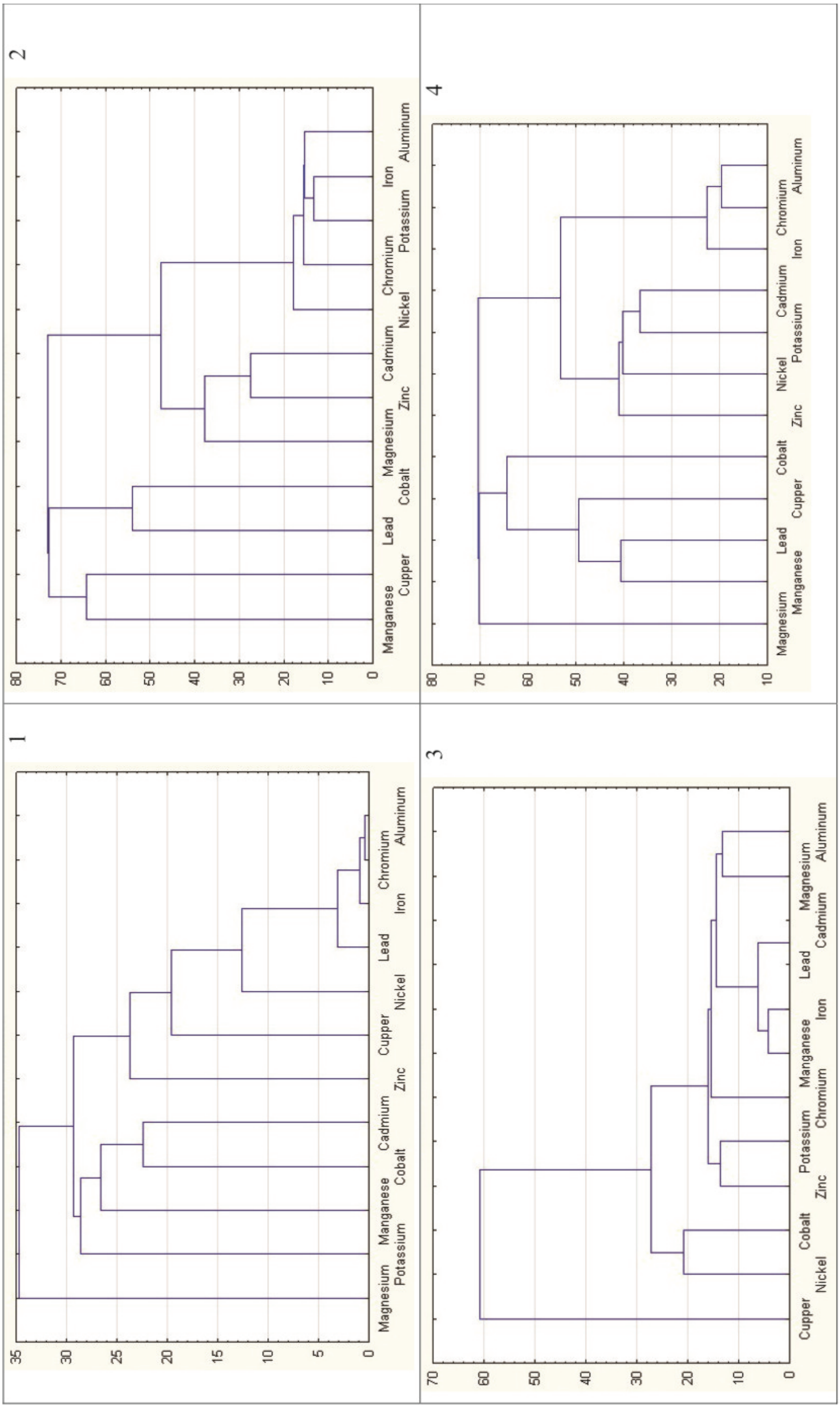

Figure 3. Dendrograms of percentage extracted in each BCR step.

Table 4. Amount and percentage of nutrient extracted per step (step 1 – CH_3COOH; step 2 – $NH_2OH \times HCl$; step 3 – H_2O_2 + CH_3COONH_4; step 4 - aqua regia)

a - Aluminium	µg/g					%				
	step 1	step 2	step 3	step 4	sum extracted	step 1	step 2	step 3	step 4	sum extracted
G1	3.75	709	481	8336	9529	0.0394	7.44	5.04	87.5	100
G2	2.74	857	318	6712	7889	0.0347	10.9	4.03	85.1	100
G3	2.95	912	551	6336	7802	0.0378	11.7	7.07	81.2	100
G4	30.4	901	430	8417	9779	0.311	9.22	4.40	86.1	100
G5	1.39	565	284	5702	6552	0.0213	8.62	4.34	87.0	100
G6	10.7	680	217	7057	7965	0.134	8.54	2.73	88.6	100
G7	33.9	1543	1276	7881	10735	0.316	14.4	11.9	73.4	100
G8	42.4	1853	623	7455	9973	0.425	18.6	6.20	74.8	100
G9	89.4	972	1192	7609	9863	0.907	9.86	12.1	77.1	100
G10	1.19	926	349	9096	10372	0.0115	8.93	3.36	87.7	100

b - Cadmium	µg/g					%				
	step 1	step 2	step 3	step 4	sum extracted	step 1	step 2	step 3	step 4	sum extracted
G1	0.302	0.706	< LOD	1.05	2.06	14.7	34.3	0	51.0	100
G2	0.339	0.491	< LOD	0.684	1.51	22.4	32.4	0	45.2	100
G3	0.308	0.654	< LOD	0.639	1.60	19.2	40.9	0	39.9	100
G4	0.146	0.248	< LOD	1.13	1.53	9.58	16.2	0	74.2	100
G5	0.349	0.489	< LOD	0.681	1.52	23.0	32.2	0	44.9	100
G6	0.143	0.277	< LOD	0.926	1.35	10.6	20.6	0	68.8	100
G7	0.148	0.343	< LOD	1.14	1.63	9.04	21.0	0	69.9	100
G8	0.196	0.413	< LOD	1.44	2.05	9.57	20.1	0	70.3	100
G9	0.174	0.310	< LOD	0.765	1.25	13.9	24.8	0	61.3	100
G10	0.329	0.191	< LOD	1.26	1.78	18.5	10.8	0	70.7	100

c - Chromium	µg/g					%				
	step 1	step 2	step 3	step 4	sum extracted	step 1	step 2	step 3	step 4	sum extracted
G1	< LOD	0.930	< LOD	23.0	23.9	0	3.89	0	96.1	100
G2	< LOD	1.18	0.909	18.5	20.6	0	5.75	4.42	89.8	100
G3	< LOD	1.08	1.94	15.7	18.7	0	5.75	10.4	84.1	100
G4	0.0853	1.28	1.62	22.0	25.0	0.342	5.12	6.51	88.0	100
G5	0.0592	2.05	3.06	18.1	23.2	0.255	8.83	13.2	77.7	100
G6	0.00792	0.374	0.396	9.83	10.6	0.0747	3.53	3.73	92.7	100
G7	0.140	4.32	5.59	31.3	41.3	0.338	10.4	13.5	75.7	100
G8	0.303	10.1	10.4	42.6	63.4	0.478	15.8	16.5	67.2	100
G9	0.124	1.00	2.79	15.9	19.9	0.625	5.04	14.1	80.3	100
G10	0.0350	0.0507	0.606	29.0	29.6	0.118	0.171	2.04	97.7	100

d - Cobalt	µg/g					%				
	step 1	step 2	step 3	step 4	sum extracted	step 1	step 2	step 3	step 4	sum extracted
G1	0.554	3.27	0.598	0.135	4.55	12.2	71.7	13.1	2.96	100
G2	0.527	2.17	0.599	0.0821	3.38	15.6	64.3	17.7	2.43	100
G3	0.579	2.60	1.33	0.0777	4.58	12.6	56.7	29.0	1.70	100
G4	0.707	3.48	0.699	0.0738	4.96	14.3	70.2	14.1	1.49	100
G5	0.355	3.26	0.888	0.0612	4.56	7.79	71.4	19.5	1.34	100
G6	0.753	2.02	1.19	0.0682	4.03	18.7	50.2	29.5	1.69	100
G7	0.679	12.0	1.30	0.210	14.2	4.78	84.6	9.13	1.48	100
G8	0.950	11.8	1.64	< LOD	14.4	6.61	82.0	11.4	0	100
G9	0.905	4.95	1.24	0.0663	7.16	12.6	69.1	17.3	0.926	100
G10	1.27	3.36	0.0905	0.159	4.88	26.0	68.9	1.85	3.25	100

Table 4. (Continued)

e - Copper	µg/g					%				
	step 1	step 2	step 3	step 4	sum extracted	step 1	step 2	step 3	step 4	sum extracted
G1	< LOD	3.63	0.408	8.16	12.2	0	29.8	3.35	66.9	100
G2	< LOD	4.67	5.99	7.57	18.2	0	25.6	32.9	41.5	100
G3	< LOD	3.30	9.40	6.48	19.2	0	17.2	49.0	33.8	100
G4	< LOD	6.14	0.101	4.00	10.2	0	59.9	0.991	39.1	100
G5	< LOD	1.72	15.1	9.48	24.8	0	6.90	60.9	38.2	100
G6	< LOD	4.00	< LOD	4.00	8.00	0	50.0	0	50.0	100
G7	< LOD	7.43	< LOD	4.80	12.2	0	60.7	0	39.3	100
G8	2.94	7.93	0.307	6.52	14.8	19.9	53.7	2.08	44.2	100
G9	< LOD	4.94	0.103	2.49	7.53	0	65.6	2.00	33.1	100
G10	3.10	66.1	34.1	56.1	156	1.98	42.3	3.00	35.9	100

f - Iron	µg/g					%				
	step 1	step 2	step 3	step 4	sum extracted	step 1	step 2	step 3	step 4	sum extracted
G1	5.45	3073	320	25490	28889	0.0189	10.6	1.11	88.2	100
G2	3.51	2569	483	19607	22663	0.0155	11.3	2.13	86.5	100
G3	5.23	4010	1200	18067	23282	0.0225	17.2	5.16	77.6	100
G4	5.26	2252	590	28976	31823	0.0165	7.08	1.85	91.1	100
G5	2.17	2587	527	17365	20481	0.0106	12.6	2.57	84.8	100
G6	4.11	2594	341	25939	28878	0.0142	8.98	1.18	89.8	100
G7	1.62	3053	942	28418	32415	0.00501	9.42	2.90	87.7	100
G8	2.42	2987	511	33040	36540	0.00661	8.17	1.40	90.4	100
G9	5.75	4201	1048	20888	26143	0.0220	16.1	4.01	79.9	100
G10	0.922	1147	260	14822	16230	0.00568	7.07	1.60	91.3	100

g - Lead	µg/g					%				
	step 1	step 2	step 3	step 4	sum extracted	step 1	step 2	step 3	step 4	sum extracted
G1	< LOD	41.7	< LOD	7.83	49.5	0	84.2	0	15.8	100
G2	< LOD	39.0	< LOD	6.57	45.6	0	85.6	0	14.4	100
G3	< LOD	40.9	< LOD	7.09	48.0	0	85.2	0	14.8	100
G4	< LOD	19.9	< LOD	7.83	27.8	0	71.8	0	28.2	100
G5	< LOD	29.1	< LOD	9.49	38.6	0	75.4	0	24.6	100
G6	< LOD	24.9	< LOD	3.92	28.8	0	86.4	0	13.6	100
G7	< LOD	36.5	< LOD	9.64	46.2	0	79.1	0	20.9	100
G8	< LOD	34.9	< LOD	13.2	48.1	0	72.5	0	27.5	100
G9	< LOD	15.5	< LOD	5.11	20.6	0	75.2	0	24.8	100
G10	0.503	11.3	< LOD	4.34	16.1	3.12	70.0	0	26.9	100

h - Magnesium	µg/g					%				
	step 1	step 2	step 3	step 4	sum extracted	step 1	step 2	step 3	step 4	sum extracted
G1	3382	4832	597	5340	14150	23.9	34.1	4.22	37.7	100
G2	3554	5329	440	3818	13142	27.0	40.5	3.35	29.1	100
G3	3747	4449	729	3700	12624	29.7	35.2	5.77	29.3	100
G4	499	398	324	3226	4446	11.2	8.94	7.28	72.6	100
G5	3364	6485	2149	2451	14449	23.3	44.9	14.9	17.0	100
G6	2400	2956	172	4227	9754	24.6	30.3	1.76	43.3	100
G7	499	398	324	3226	4446	11.2	8.94	7.28	72.6	100
G8	2193	1089	318	2861	6461	33.9	16.9	4.92	44.3	100
G9	320	1285	385	2999	4990	6.40	25.8	7.71	60.1	100
G10	6731	6916	1068	2537	17252	39.0	40.1	6.19	14.7	100

Table 4. (Continued)

i - Manganese	µg/g					%				
	step 1	step 2	step 3	step 4	sum extracted	step 1	step 2	step 3	step 4	sum extracted
G1	88.2	191	6.84	113	400	22.0	47.9	1.71	28.4	100
G2	84.4	123	3.79	105	316	26.7	38.9	1.20	33.3	100
G3	89.5	143	7.36	89.3	329	27.2	43.4	2.24	27.2	100
G4	84.7	172	5.07	107	369	23.0	46.7	1.38	28.9	100
G5	76.7	204	6.81	82.9	370	20.7	55.0	1.84	22.4	100
G6	65.6	70.6	2.77	88.8	228	28.8	31.0	1.22	39.0	100
G7	78.3	305	8.01	186	577	13.6	52.8	1.39	32.2	100
G8	91.3	324	8.80	213	637	14.3	50.8	1.38	33.5	100
G9	113	436	19.8	132	700	16.1	62.2	2.83	18.8	100
G10	54.9	152	11.8	134	353	15.6	43.2	3.35	37.9	100

j - Nickel	µg/g					%				
	step 1	step 2	step 3	step 4	sum extracted	step 1	step 2	step 3	step 4	sum extracted
G1	1.11	5.08	3.39	25.4	34.9	3.18	14.5	9.70	72.6	100
G2	1.01	3.56	4.29	15.6	24.4	4.15	14.6	17.6	63.7	100
G3	1.13	4.54	6.03	14.5	26.2	4.33	17.3	23.0	55.3	100
G4	0.786	2.84	4.29	19.1	27.1	2.91	10.5	15.9	70.7	100
G5	1.12	3.82	3.65	15.4	24.0	4.66	15.9	15.2	64.3	100
G6	0.721	3.21	3.67	22.0	29.6	2.44	10.9	12.4	74.3	100
G7	2.48	10.7	7.09	30.2	50.5	4.90	21.2	14.0	59.9	100
G8	3.59	18.4	8.60	69.2	99.7	3.60	18.4	8.62	69.4	100
G9	1.74	2.00	5.99	16.4	26.1	6.64	7.65	22.9	62.8	100
G10	2.67	5.63	1.99	34.9	45.1	5.91	12.5	4.41	77.2	100

k - Potassium	µg/g					%				
	step 1	step 2	step 3	step 4	sum extracted	step 1	step 2	step 3	step 4	sum extracted
G1	1039	310	< LOD	1410	2759	37.7	11.2	0	51.1	100
G2	685	261	52.0	1078	2076	33.0	12.6	2.51	51.9	100
G3	607	261	82.0	1058	2008	30.2	13.0	4.08	52.7	100
G4	605	272	< LOD	690	1567	38.6	17.4	0.00	44.1	100
G5	297	135	217	443	1091	27.2	12.4	19.9	40.5	100
G6	301	153	< LOD	1010	1464	20.6	10.4	0	69.0	100
G7	171	90.0	< LOD	1010	1271	13.5	7.08	0	79.5	100
G8	280	115	< LOD	725	1120	25.0	10.2	0	64.7	100
G9	178	118	< LOD	575	871	20.4	13.6	0	66.0	100
G10	542	320	46.2	1562	2470	22.0	12.9	1.87	63.2	100

l - Zinc	µg/g					%				
	step 1	step 2	step 3	step 4	sum extracted	step 1	step 2	step 3	step 4	sum extracted
G1	16.9	50.9	< LOD	72.0	140	12.1	36.4	0	51.5	100
G2	16.9	42.8	4.69	47.7	112	15.1	38.2	4.19	42.5	100
G3	25.4	56.8	7.26	47.2	137	18.6	41.6	5.31	34.6	100
G4	2.87	16.9	0.304	50.2	70.3	4.07	24.1	0.432	71.4	100
G5	12.0	42.2	45.0	46.0	145	8.26	29.1	31.0	31.7	100
G6	7.16	26.5	< LOD	57.9	91.6	7.82	29.0	0	63.2	100
G7	8.79	32.3	6.49	47.3	94.8	9.27	34.0	6.84	49.9	100
G8	6.36	42.7	< LOD	65.1	114	5.57	37.4	0	57.0	100
G9	0.149	5.91	1.14	31.5	38.7	0.385	15.3	2.94	81.4	100
G10	< LOD	5.31	< LOD	61.1	66.4	0	7.99	0	92.0	100

ranged from 1.2 up to 2.1 µg/g and correspond to values in literature: Cd levels were found in the Yozgat region (Turkey) below 1 µg/g,[16] in the Incesu-Kayseri region (Turkey) 1–4 µg/g,[17] from < 0.1 µg/g to 1.5 µg/g for horticultural soils in New Zealand,[18] a study on agricultural soils in USA led to Cd concentrations of < 0.01 µg/g to 2.0 µg/g.[19] In orchard soils in China total Cd amounts of 0.7 up to 1.8 µg/g were found by Li *et al.*[20] In Algeria in a study on agricultural soils Cd level of 0.30 µg/g (median) was obtained.[21] Cadmium levels in horticultural and agricultural soils depend on the continued use of phosphate-fertilizers and zinc containing agrichemicals, where cadmium is present as impurity.[15] The total amounts of cadmium in garden soils were expected to be lower than those reported for plants grown commercially. Cadmium contamination limits agricultural use of soil, thus critical soil Cd concentration has been proposed in various countries, *e.g.* 0.3 µg/g in China.[3] According to French regulation maximum Cd soil level is 2 µg/g.[14] In Canada the limit concentration is 1.4 µg/g.[2]

Regarding the extractability of cadmium, 30–60 % were extracted in the first two steps (10–20 % and 20–40 %, resp.) and the remaining 40–70 % were found in the residue (step 4).

Chromium

Chromium is ubiquitous in the environment, like soil, water and air, and occurs in two forms, as Cr(III) and Cr(VI). The latter is more toxic and, in plants affects negatively leaf and root growth, inhibits certain enzymes and may cause mutagenesis.[22] High chromium levels in soil are caused by anthropomorphic activities. The amounts found in the analysed soils samples ranged from 10 up to 63 µg/g with 70 % between 19 and 30 µg/g. The exceptions are G6 11 µg/g, G7 41 µg/g and G8 63 µg/g. The entire range is reported by Adriano[4] as normal chromium soil level, namely 10 to 50 µg/g depending on the bedrock concentration. In Algeria (Anaba region) the median total chromium level in agricultural soil was found to be 28.3 µg/g (Ref. 21) and in the Incesu-Kayseri region (Turkey) 0.5–38 µg/g.[17] Even the outlier G8 is below the permissible concentration of toxic elements for agricultural soils of China (200 µg/g),[3] French regulatory limit of 150 µg/g (Ref. 14) and the Canadian limit of 64 µg/g for total chromium.[2] Regarding the extractability of chromium from soil it was found that 1 % was extracted in step 1 and up to 10 % in steps 2 and 3. As expected, the highest amounts were found in samples G7 and G8.

Cobalt

The French regulations' limit of cobalt in soil is 30 µg/g (Ref. 14) and in Canada 40 µg/g.[2] All soils analysed contain Co in lower concentration. In the investigated soil samples six of ten had cobalt levels between 4 and 5 µg/g. Higher levels were found in G9 (7.2 µg/g) and in G7 and G8 (approx. 14 µg/g). G2 has less Co, namely 3.4 µg/g. Three Turkish studies came to similar results. In the soil samples from Kayseri region the concentration of cobalt is found to be less than 3 µg/g,[23] in the Incesu-Kayseri region 0.5–38 µg/g (Ref. 17) and in the Yozgat region 4–8 µg/g.[16] The China National Environmental Monitoring Centre reported cobalt levels of 15 µg/g and 26 µg/g.[24] In plants cobalt is required by the urease enzyme. Cobalt has only a low affinity to humic substances,[12] and it is adsorbed to clay minerals in soil and geological origin by specific reactions.[25] This is reflected in its extraction behaviour: 50–70 % of Co is extracted in step 2, approx. 10 % in step 1 and up to 30 % in step 3. Only 3 % of the total cobalt were detected in the residue (step 4).

Copper

Copper is essential for plants but is toxic at higher levels. The total copper levels in the soil samples analysed ranged from 10 to 25 µg/g, except for G10 containing 156 µg/g. Similar levels were reported for Turkish soil samples, namely 12–27.5 µg/g from Kayseri region[23] and ranging from 16–26 µg/g in Incesu-Kayseri region,[7] and even slightly higher than in samples from the Yozgat region (4–14 µg/g),[16] and below those reported for agricultural soils (40 µg/g in market garden and 58 µg/g orchard),[18] what can be explained by the minor use of copper-based fungicides in private gardens than in horticulture. In agricultural soils in the USA levels from 0.3 up to 495 µg/g were found with a median of 18.5 µg/g.[19] Algerian agricultural soils had a median copper level of 23.8 µg/g,[21] while higher copper levels were found in Italian vineyard soils (945 µg/g).[26] Chinese and French regulations stipulate maximum copper level in soil of 100 µg/g.[3,14] The Canadian Ministry of Environment limits Cu in agricultural soil to 63 µg/g.[2] Copper plays a role in plants' growth. Common garden plants, like tomatoes and strawberries need Cu up to 20 µg/g, thus all soils of this study met these needs.[5]

Regarding the extractability it was found that copper was leached mainly from soil in step 2 (reducible fraction). A similar finding was reported by Whalley and Grant.[27] In step 1, only extracts of G10 was the copper level above the LOD, which could be a result of the high total concentration in the sample. Cu has a high affinity for humic substances.[12]

Lead

The total lead content found ranged from 16–50 µg/g. A wide range of its concentrations are reported for soils in New Zealand,[15] namely 11–251 µg/g and in the Kayseri region (Turkey) 16–83 µg/g (Ref. 23) and in the Incesu-Kayseri region (Turkey) 13–34 µg/g.[16] Elevated lead levels are attributed to the usage of lead arsenate as insecticides especially in orchards. Similar levels were found for American agricultural soils, namely < 1–135 µg/g.[19] In Algeria (Anaba region) lead levels of approx. 40 µg/g were found,[21] whereby the highest values were found in soils of the city centre. Due to lead-free gasoline the lead concentration in soil decreased during the last decades. Levels up to 720 µg/g were found in soils in the USA.[28] At present lead originates as contaminant of certain fertilisers ans sewage sludge. French regulations limit lead levels in soil at 100 µg/g.[14] The Canadian Ministry of Environment[2] limits in agricultural soils the lead level to a maximum of 70 µg/g. In China the limit is 300 µg/g.[3]

Lead is mainly extracted in steps 2 and 4 while in the solutions after step 1 and 3 the lead concentrations were below the LOD. Exception is G10 having the lowest lead content, but with 3 % extracted in step 1. Pb is readily complexed by humic substances.[12]

Manganese

In soils from Algeria Maas and colleagues[21] found Mn content ranging from 34 to 636 µg/g, the median being 400 µg/g. Similar values were found in Turkey, namely, in the Incesu-Kayseri region 130–2600 µg/g,[16] in the Yozgat region 280–360 µg/g,[17] and in the Kayseri region 500 µg/g.[23] The last two findings were in roadside soils. In both cases there was no correlation found between Mn content in soil and distance to the road. Manganese is not easily bound to humic substances.[12] The total manganese contents in the analysed garden soils ranged from 300 to 400 µg/g. Less Mn was found in G6 (228 µg/g) and 600 to 700 µg/g in G7–G9. No regulations exist for manganese content in agricultural soils.[2,14] Manganese is involved carbohydrate and nitrogen metabolism, but deficiency is not likely to occur in private gardens. Levels up to 500 µg/g are needed by some garden plants.[5]

Most manganese is extracted in step 2, 30 up to 50 %. In G9, 60 % were extracted and 20 to 40 % were found in the residue (step 4). In the oxidisable fraction only up to 3 % of the total Mn amount were found.

Nickel

For nickel similar extraction behaviour was reported in literature[27] with the highest extraction yields in the first two steps. The soils analysed in the present were different, since less than 10 % were extracted in step 1, and up to 20 % in step 2, while the rest remained unextracted. Not only can the different soil composition determined by the parent rock be considered as reason for this, but also in the diverse experimental set up. Whereas Whalley and colleague[27] first let the metals adsorb to the soil, real soil samples were used in the present investigation. The nickel content found in the present study ranged from 24 up to 35 µg/g, except for G10 (45 µg/g), G7 (51 µg/g) and G8 (100 µg/g). Holmgren *et al.*[19] reported a soil in a similar range, namely with Nickel from 0.7 up to 269 µg/g, with a median of 18.2 µg/g. They found higher Ni levels in serpentine soils and in glaciated areas. Nickel amount in to the soil samples from Kayseri region (Turkey) is 43–82 µg/g,[23] in the Incesu-Kayseri region (Turkey) 12–41 µg/g (Ref. 16) and in the Yozgat region (Turkey) 8–29 µg/g,[17] in all cases similar to the obtained results. According to French regulations the allowed maximum Ni soil level is 50 µg/g.[14] The same limit value is applied to Chinese agricultural soils.[3]

Zinc

Agrochemicals, such as fungicides and fertilisers, are a potential source of zinc in agriculture. Zinc levels in soils ranged from 64–108 µg/g in New Zealand,[15] in the Kayseri region (Turkey) from 15–25 µg/g,[23] in the Incesu-Kayseri region (Turkey) from 26–51 µg/g,[16] in the Lower Fraser Valley of British Columbia from 43–107 µg/g,[29] and in rural soils in Netherlands from 7–95 µg/g.[30] The results of the present study are in the same order of magnitude, namely from 40–145 µg/g. Zinc levels up to 560 µg/g (median 65 µg/g) were found in Algeria.[21] Regulations limit Zn levels in soil to 300 µg/g in France[14] and to 250 µg/g in China.[3] Zinc is involved in carbohydrate metabolism and in enzymatic systems regulating plant growth. Up to 100 µg/g zinc is needed by tomatoes,[5] and 5–30 µg/g by strawberries, blueberries and grapes.

Zinc is leached mainly in step 2 while small amounts were extracted in steps 1 and 3.

CONCLUSIONS

All soils analysed contained the studied elements at levels reported for other geographical regions worldwide and the levels did not exceed the limits imposed by different jurisdictions. The three soil samples taken from the city of Zagreb contained higher levels of pollutants. A similar observation was made in twelve cities in China.[31] The nutrient supply of elements was found to be adequate in all tested soil samples.

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