Vulnerability of the karst area related to potentially toxic elements

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ABSTRACT

Soil samples from 31 locations in the Una river spring catchment were subject to chemical extraction analyses. The data were presented as distribution maps of potentially toxic elements (Al, Cu, Mn, Pb and Zn) in the surface soil of the area. To evaluate the vulnerability of the immediate spring zone of the karst catchment, the vulnerability map was derived from the application of the PI methodology proposed by the European COST Action 620. The PI method used to produce the vulnerability map takes into account the protective cover (P) and the infiltration conditions (I). It is based on the origin-pathway-target model. The π-factor (π = P × I) describes the vulnerability in the area, sub-divided into 5 classes: π-factor in the range 0-1 implies an area of extreme vulnerability, while π-factor in the range 4-5 implies an area of very low vulnerability. The extraction procedure for the elements Al, Cu, Mn, Pb and Zn, has been applied in order to determine the potential mobility and redistribution of elements that could influence the groundwater and affect its quality. The applied extraction was the second step of the sequential procedure proposed by TESSIER et al. (1979), i.e. extraction with 1 mol dm^{-3} CH$_3$COONa/CH$_3$COOH buffer (pH 5). The results provide information on the potential mobility of the studied elements, indicating the possibility of their mobilization through changes in pH. Lead shows the greatest amount of mobility, with a mean of 9% (max. 16%) extracted under an acidic condition. Manganese follows with a mean of 5% (max. 11%) and zinc, copper and aluminium show less than 1% (mean) mobility. The vulnerability map of the karst area was produced in order to predict potential problem areas of karst aquifers. The Una spring catchment area presents generally low to moderate vulnerability; 8% of the studied area can be considered as extremely vulnerable according to the PI-methodology. Based on these data it was possible to delineate areas with a low protection cover i.e. combining the vulnerability map of the karst area with the distribution maps of potentially toxic elements, areas considered extremely vulnerable could be identified.

Keywords: karst, vulnerability map, PI-method, soil, environmental geochemistry, Una River

1. INTRODUCTION

The study area lies in the Una River valley, east of the small town of Gračac, in the southern part of the Lika region. It is a part of a catchment of the Una spring and extends over 135 km^2 (Fig. 1).

The Una River spring surfaces near the village of Su-vaja, 399 m above sea level (BOGNAR, 2005), and is protected as a hydrogeological heritage site of Croatia. Typical karst landforms are observed here, including dolines, sink-holes and karst springs (vauclusian type). Sinkholes are covered, mostly by silt loam, and overgrown by vegetation.

The area is part of a high karst belt of the Outer Dinarides, the genesis of which is connected with the Adriatic Carbonate Platform (AdCP). The deposit can be very thick, in some areas surpassing 8000 m. The age of this carbonate succession ranges from Middle Permian, or even Upper Carboniferous to Eocene (VLAHOVIĆ et al., 2005). The area of investigation is part of a large carbonate aquifer system which accounts for 88% of Croatian ground water reserves, and is an important drinking water source (BIONDIĆ, 2009).

Karst aquifers are exceptionally vulnerable to contamination due to their heterogeneity, which results in huge variations in permeability, and enables poorly filtered, concentrated recharge to take place (ZWAHLEN, 2004). Since contaminants can easily reach the aquifer by bypassing filtration, it is important to know where such events might occur.

Predicting the path of possible pollutants in aquifers is more difficult in karst due to the fact that water often lacks a specific flow path.

The objective of this paper was to evaluate the vulnerability of the karst catchment immediate to the Una spring zone. To assess the vulnerability, a combined soil/geochemical approach with vulnerability mapping was applied.

Since the protection of groundwater is important not only from an ecological point of view, but also from an economic one, different approaches to ground water protection have been developed. Comparative studies have shown that the application of various methods often leads to different results (NGUYET & GOLDSCHEIDER, 2006; GOGU et al., 2003). In order to develop an approach that considers the specifics of karst formations, a special group, COST Action 620, was established. The group developed an approach to "vulnerability and risk mapping for the protection of carbonate (karst) aquifers" (ZWAHLEN, 2004; NGUYET & GOLDSCHEIDER, 2006), and proposed a new method of vulnerability mapping – the PI method – for mapping karst groundwater resources (ZWAHLEN, 2003; GOLDSCHEIDER, 2005). This approach was used in this study.

Acidification of the topsoil cover may cause the mobilization of certain potentially toxic elements that accumulate in the soil and could be transported into aquifers, thus affecting the water quality. Therefore, topsoil can be considered a source of contamination, especially if possible changes in environmental conditions would lead to leaching of pollutants. With analysis of the soil for total elements and their mobile fraction, it is possible to distinguish between anthropogenic and geochemical sources of heavy elements (DUBE et al., 2001; FILGUEIRAS et al., 2002).

2. METHODS

2.1. Laboratory analysis

Topsoil (0−2 cm) and subsoil (40−50 cm) samples were collected at 31 locations. Some of the topsoil of each sample was used for granulometric analysis, which was performed on 29 samples, by wet sieving using ASTM standard stainless steel sieves. Due to an insufficient amount of samples, granulometric analysis could not be performed for three samples. Hydraulic conductivity for the 29 samples was defined by grain size composition of sediments using the Hydraulic Conductivity Software, SizePerm. All samples were analyzed for total (HF-HClO$_4$-HNO$_3$-HCl) and mobile
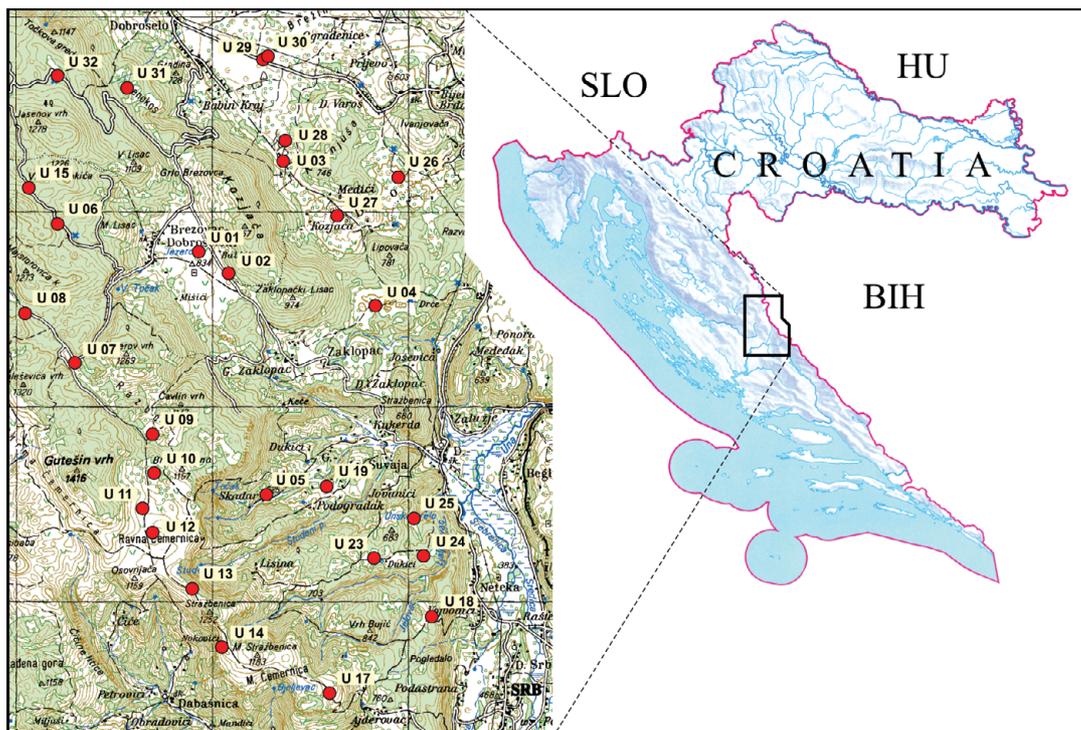

Figure 1: Geographic location of the studied area with the sampling sites.

(CH₃COONa / CH₃COOH, pH 5) contents of the elements of interest (Al, Cu, Mn, Pb and Zn). Analyses were carried out on the fraction <0.063 mm. Inductively coupled plasma atomic emission spectrometry (ICP-AES) was used for determination of the total content of elements in soils, for which samples were dissolved using 4-acid digestion (HF, HClO₄, HCl, HNO₃), by standard procedure (MIKO et al., 2000).

In order to determine the potential mobility and redistribution of the elements that could have an influence on the groundwater, the extraction procedure for elements Al, Cu, Mn, Pb, and Zn was also applied. The sequential extraction procedure provides more information, than the analysis of the total heavy metal content of soil, i.e. it is possible to determine preferential binding sites for observed elements, to evaluate the potential mobility of metals in the environment and to differentiate the lithological from the anthropogenic contributions of elements (TESSIER et al., 1979; PROHIĆ & KNIEWALD, 1987; AUBERT et al., 2004; KAASALAINEN & YLI-HALLA, 2003). For the purpose of the paper, only the second step of five-step sequential extraction procedures based upon TESSIER et al. (1979) was carried out, i.e. extraction with 1 mol dm⁻³ CH₃COONa / CH₃COOH buffer (pH 5), on the <0.063 mm size. The goal of this extraction was to observe the amount of the mobile fraction under specific pH conditions (5).

2.2. Intrinsic vulnerability mapping

The data for the vulnerability map were compiled from the digital topographic data (scale 1:25000), which included land-use data, sinkhole distribution data, a digital elevation model (DEM), soil map data, geological and hydrogeological digital maps, and a database of potential pollution sources (road infrastructure, settlements). The vulnerability map was the final result of different analyses and a few intermediate steps, which are briefly described in this paper. The vulnerability map is coloured according to π-factor, which is expressed by $\pi = P \times I$ (Table 1). The PI method takes into account the protective cover (P) and the infiltration conditions (I). Its goal is to describe how vulnerable the groundwater is. Extreme vulnerability is presented as a red colour, while very low vulnerability is presented in a blue colour (Tab. 1). In order to be able to compute the P factor (protective cover), the following information about the protective function was used: topsoil and subsoil thickness, precipitation regime, grain size, lithology, fissuring and karstification. The P-factor ranges from 1 to 5, with 1 presenting a very low protec-

tive function. The I-factor gives an insight into infiltration conditions and the degree to which the protective cover is by-passed as a result of lateral surface and subsurface flows. In order to compute the I-factor, information about the hydraulic conductivity, depth to low permeability layers, slope gradient and vegetation was used. The I factor ranges between 0.0 and 1.0, with 0 being the most permeable (GOLDSCHEIDER et al., 2000). Some of the information on vegetation and slope gradient were directly taken from digital data.

The vulnerability map was derived from application of the PI methodology proposed by the European COST Action 620; detailed information and a description of these methods can be found in ZWAHLEN (2004). According to this methodology, intrinsic vulnerability takes into account the geological, hydrological and hydrogeological characteristics of an area, but it is independent of the nature of the contaminants and the contamination scenario.

It is based on the origin-pathway-target model, and as final result, areas considered extremely vulnerable could be highlighted. The origin is the term used to describe the location of a potential contaminant release. The pathway includes the passage of potential contaminants, from its origin to the target (receptor). The target may be the groundwater surface in the aquifer (GOLDSCHEIDER et al., 2000).

3. RESULTS

Analyses for the total and mobile content of observed elements, (Al, Pb, Cu, Mn and Zn) are presented in Table 2. The analyses were used to display the percentage of mobile content for all topsoil samples. Results of soil texture classification, based on a granulometric analysis are also presented in Table 2.

Information about the hydraulic conductivity was needed to compute the I-factor of the PI method. This was calculated from granulometric analysis, with the software EasyPerm, and for all samples, values fall in the range of 10^{-8} cm/s to 10^{-9} cm/s.

From the geochemical analysis, colour scale maps were generated for the mobile fraction content of the topsoil cover in relation to the deeper layer (Figs. 2a–e). Maps indicate which part of the examined area is mostly exposed to migration of the mobile fraction of elements. Lead shows the highest probability of mobility, with a mean of 9% (max. 16%) extracted under acidic conditions. Manganese follows with a mean of 5% (max. 11%), and zinc, copper and aluminium

Table 1: Common legend for the vulnerability map, the P and the I map (GOLDSCHEIDER, 2005).

VULNERABILITY MAP Vulnerability of groundwater		P – MAP Protective function of overlying layers		I – MAP Degree of bypassing	
DESCRIPTION	π – FACTOR	DESCRIPTION	P – FACTOR	DESCRIPTION	I – FACTOR
EXTREME	0 – 1	VERY LOW	1	EXTREME	0.0–0.2
HIGH	>1 – 2	LOW	2	HIGH	0.4
MODERATE	>2 – 3	MODERATE	3	MODERATE	0.6
LOW	>3 – 4	HIGH	4	LOW	0.8
VERY LOW	>4 – 5	EXTREME	5	VERY LOW	1.0
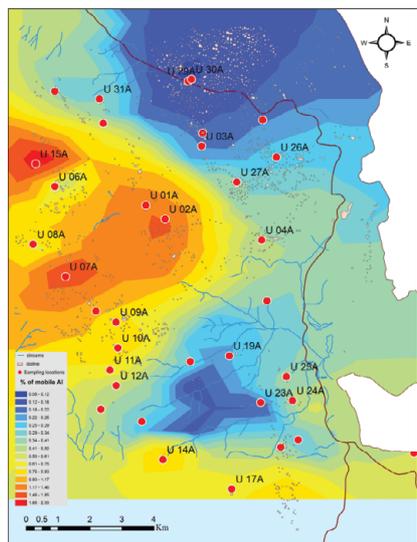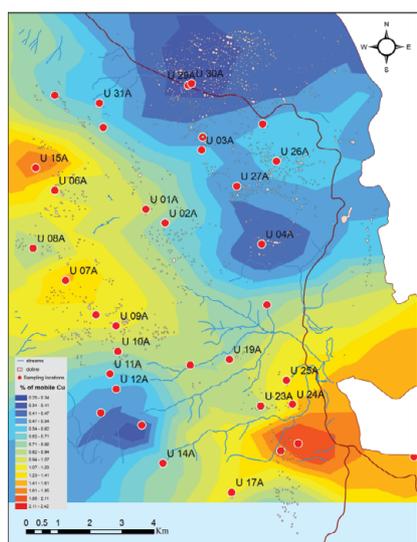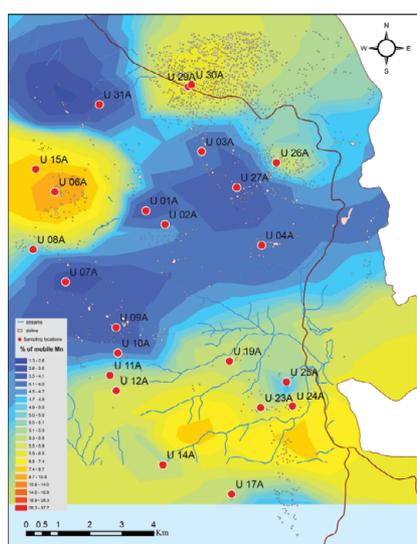
Figure 2: The maps of the content of mobile fraction of the topsoil cover in relation to the deeper layer for aluminium (a), copper (b), manganese (c), lead (d), zinc (e) and the PI vulnerability map (f).

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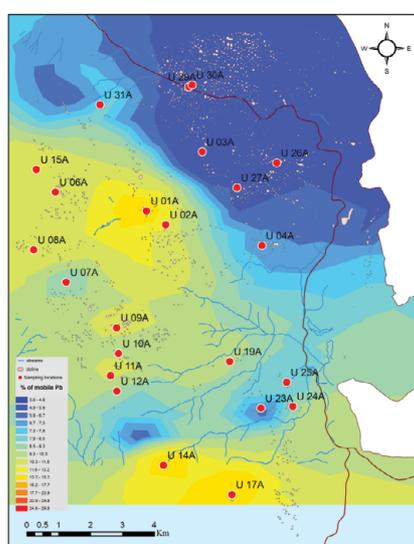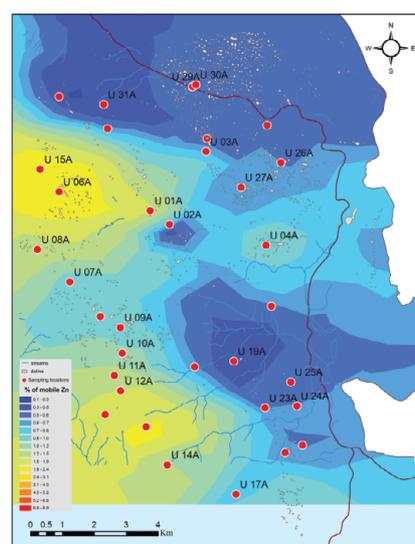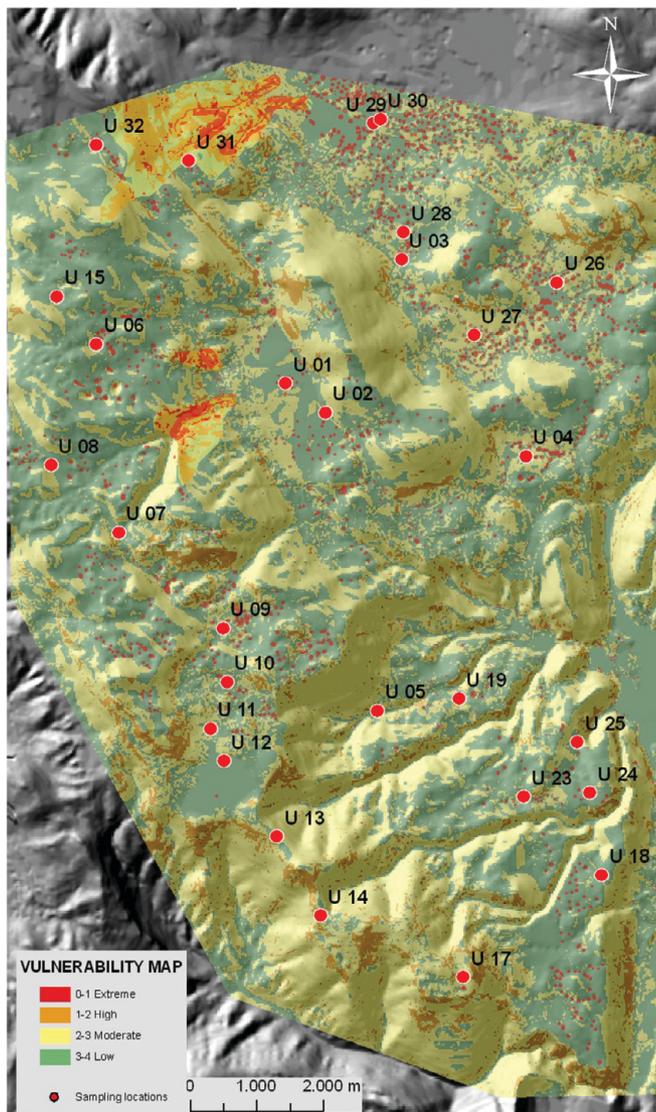**Table 2:** Mobile portion rate as a proportion of mobile (1 mol dm^{-3} CH$_3$COONa) (pH 5/CH$_3$COOH) and total (HF-HCl-HNO$_3$-HClO$_4$) element concentration in the soil.

	Al (mob)	Al (tot)	% Al mob	Pb (mob)	Pb (tot)	%Pb mob	Cu (mob)	Cu (tot)	% Cu mob	Mn (mob)	Mn (tot)	% Mn mob	Zn (mob)	Zn (tot)	% Zn mob	texture classification
	mg/kg	mg/kg	%	mg/kg	mg/kg	%	mg/kg	mg/kg	%	mg/kg	mg/kg	%	mg/kg	mg/kg	%	
U 01A	1018	73100	1.39	5.935	37.9	15.66	0.26	26.6	0.98	13	358	3.63	1.7	102	1.67	silt loam
U 01B		85700			31.2			37			168			88		
U 02A	1043	64600	1.61	3.336	30.2	11.05	0.16	23.6	0.68	29	617	4.7	0.3	97	0.31	silt loam
U 02B		76700			24.4			27			845			108		
U 03A	41	74000	0.06	1.389	38.5	3.61	0.19	27.3	0.7	55	1087	5.06	1.2	104	1.15	silt loam
U 03B		84200			34.9			28.9			969			104		
U 04A	309	79300	0.39	2.744	39.6	6.93	0.12	30.3	0.4	43	999	4.3	1.1	120	0.92	silt clay loam
U 04B		83400			34.1			29.4			993			116		
U 05A	101	75800	0.13	3.504	33.2	10.55	0.24	26.4	0.91	29	545	5.32	0.6	106	0.57	silt loam
U 05B		N.A.			N.A.			N.A.			N.A.			N.A.		
U 06A	121	56100	0.22	4.994	47.3	10.56	0.23	24.4	0.94	78	668	11.68	4	171	2.34	silt loam
U 06B		84000			35.5			30.6			990			206		
U 07A	1464	80400	1.82	3.467	41.8	8.29	0.43	29.4	1.46	40	1309	3.06	1.3	149	0.87	silt loam
U 07B		82700			40			32.7			1119			158		
U 08A	503	834 00	0.6	7.33	62.3	11.77	0.19	25.3	0.75	56	1222	4.58	1.9	144	1.32	silt loam
U 08B		85600			49.9			26			1262			128		
U 09A	624	76400	0.82	4.674	41.2	11.34	0.23	19.9	1.16	30	828	3.62	1	108	0.93	silt loam
U 09B		81000			39			21			907			95		
U 10A	896	83100	1.08	6.576	84.2	7.81	0.33	32.8	1.01	59	1903	3.1	1.2	175	0.69	silt clay loam
U 10B		87800			84.2			30.9			2021			169		
U 11A	595	77800	0.76	5.857	46.3	12.65	0.18	32.3	0.56	44	774	5.68	1.9	140	1.36	silt loam
U 11B		85200			40.1			31.2			931			119		
U 12A	152	73800	0.21	2.855	37.8	7.55	0.12	27.7	0.43	68	1063	6.4	1.9	116	1.64	silt loam
U 12B		78000			35			29.1			1153			112		
U 13A	157	72900	0.22	3.442	66.1	5.21	0.12	39.7	0.3	69	1352	5.1	3.1	145	2.14	silt loam
U 13B		N.A.			N.A.			N.A.			N.A.			N.A.		
U 14A	704	70900	0.99	4.942	33	14.98	0.18	25.9	0.69	31	599	5.18	1.3	112	1.16	silt loam
U 14B		84100			29.2			31.7			661			119		
U 15A	1672	71700	2.33	5.012	42.4	11.82	0.46	23.8	1.93	56	718	7.8	2.9	130	2.23	clay loam
U 15B		83100			37.4			24.1			613			123		
U 16A	51	72000	0.07	3.583	41.7	8.59	0.31	29.6	1.05	86	976	8.81	1.7	108	1.57	
U 16B		82600			33.4			27.2			837			95		
U 17A	719	68100	1.06	4.422	38.7	11.43	0.1	24.7	0.4	29	759	3.82	1.1	105	1.05	loam
U 17B		77900			30.9			21.8			776			95		
U 18A	124	70600	0.18	2.751	28.6	9.62	0.72	29.8	2.42	33	394	8.38	0.5	94	0.53	silt clay loam
U 18B		N.A.			N.A.			N.A.			N.A.			N.A.		
U 19A	183	70600	0.26	4.781	48.3	9.9	0.14	19	0.74	35	665	5.26	0.3	106	0.28	silt loam
U 19B		76300			46.6			19.1			783			114		
U 20A	263	65000	0.4	3.087	29.7	10.39	0.12	15.1	0.79	20	403	4.96	0.6	82	0.73	clay loam
U 20B		67500			28.7			13.2			356			83		
U 22A	408	66100	0.62	6.149	38.3	16.05	0.19	15.2	1.25	31	594	5.22	0.5	75	0.67	
U 22B		67400			41.2			14.6			785			76		
U 23A	123	79400	0.15	2.418	39.7	6.09	0.24	29.8	0.81	39	703	5.55	0.7	112	0.63	silt clay loam
U 23B		77000			40.4			26.9			818			103		
U 24A	512	68300	0.75	4.285	35.7	12	0.33	21.2	1.56	51	608	8.39	0.8	99	0.81	silt clay loam
U 24B		75600			31.5			21			712			104		

Table 2: Mobile portion rate as a proportion of mobile (1 mol dm^{-3} CH$_3$COONa) (pH 5/CH$_3$COOH) and total (HF-HCl-HNO$_3$-HClO$_4$) element concentration in the soil.

	Al (mob)	Al (tot)	% Al mob	Pb (mob)	Pb (tot)	%Pb mob	Cu (mob)	Cu (tot)	% Cu mob	Mn (mob)	Mn (tot)	% Mn mob	Zn (mob)	Zn (tot)	% Zn mob	texture classification
	mg/kg	mg/kg	%	mg/kg	mg/kg	%	mg/kg	mg/kg	%	mg/kg	mg/kg	%	mg/kg	mg/kg	%	
U 25A	224	76400	0.29	2.164	31.8	6.81	0.3	25.7	1.17	18	515	3.5	0.4	97	0.41	silt clay loam
U 25B		79500			32.9			24.3			653			100		
U 26A	237	86500	0.27	2.301	39.3	5.85	0.19	31.1	0.61	53	941	5.63	0.7	121	0.58	silt clay loam
U 26B		85200			38.9			31.1			897			120		
U 27A	229	75800	0.3	1.994	36.9	5.4	0.12	28.6	0.42	25	936	2.67	0.6	108	0.56	silt clay loam
U 27B		73500			31.4			23.6			939			94		
U 28A	216	85800	0.25	1.748	37	4.72	0.16	38	0.42	33	957	3.45	0.2	126	0.16	silt clay loam
U 28B		N.A.			N.A.			N.A.			N.A.			N.A.		
U 29A	80	82700	0.1	4.939	79.7	6.2	0.18	36.8	0.49	94	1357	6.93	1.3	179	0.73	silt loam
U 29B		92100			37.4			40.8			1010			133		
U 30A	106	87500	0.12	4.063	79.9	5.09	0.08	31.4	0.25	83	1313	6.32	0.6	161	0.37	silt loam
U 30B		N.A.			N.A.			N.A.			N.A.			N.A.		
U 31A	299	87800	0.34	6.307	73	8.64	0.2	33.9	0.59	46	1288	3.57	0.6	166	0.36	silt clay loam
U 31B		84700			60.1			29.2			1296			141		
U 32A	205	79800	0.26	1.962	35.8	5.48	0.16	27.4	0.58	18	1010	1.78	0.2	98	0.2	silt loam
U 32B		N.A.			N.A.			N.A.			N.A.			N.A.		

show less than 1% (mean) of mobile content. It is important to note that the same colour on these maps, for different elements, do not hold the same value. The colour scale was made separately for each map according to its minimum and maximum values. For instance, orange colour on the map represents 1.46% mobile content for aluminium, but 11.68% for manganese.

The vulnerability map of the karst area was compiled by combining a digital topographic map (scale 1:25000) and values of P and I factor (Fig. 2f). It was made to predict potential problem zones where the karst aquifer might be easily contaminated. The Una spring catchment area has low to moderate vulnerability in most parts, but 8% of the studied area could be considered as extremely vulnerable according to the PI-methodology. The steps preceding the creation of the vulnerability map are not displayed here, but details needed to produce a vulnerability map can be found in the Cost Action 620 Report (ZWAHLEN, 2004).

4. DISCUSSION AND CONCLUSION

Two types of maps, the PI-map (or vulnerability map), and maps of the mobile fraction content of the topsoil cover in relation to the deeper layer, were combined in order to assess the potential hazard to groundwater. Maps of the mobile fraction content for observed elements (Al, Mn, Pb, Cu, Zn) provide information about their potential mobility, indicating the possibility of mobilization through changes in pH. On these maps, the area with the highest content of mobile fraction is shown in red. It is important to be aware of well-connected environmental processes, in which acidification of the terrain as a result of climate change or anthropogenic impact may lead to increased levels of metals in the aquifer (DUBE et al., 2001). Extraction analysis, used for making these maps, is a common procedure when the goal is to indicate potential risk of toxic species entering the groundwater (RAO et al., 2008). Depending on the type of soil, and the pH used in the extraction procedure, heavy metals can be retained in a soil sample, but some amount can be observed as mobile content (LAFUENTE et al., 2008; RAO et al., 2008; FILGUEIRAS et al., 2002). Not all the mobile content will dissolve in water. Heavy metals may interact, chemically or physically, with the natural compounds found in the water and, in general, may react with particular species, change oxidation states and precipitate out (DUBE et al., 2001). However, one part will dissolve in the water, while the other could be found in colloidal fractions or associated with colloids (JENSEN et al., 1999; CHRISTENSEN et al., 2001). In the same aquatic environmental condition, dissolution of mobile elements will increase the higher the content of mobile elements. Further, due to features of

Table 3: The highest measured content of the mobile fraction for observed area and the maximum allowed concentration of elements of interest in drinking water.

	Al	Cu	Pb	Mn	Zn
Maximum allowed concentration of elements in drinking water (mg/l); N.N. 56/08	0.2	1	0.01	0.05	3
The highest measured concentration of mobile fraction (mg/l)	2330	1930	16050	11680	2340

karst hydrogeology, contaminants can quickly appear in areas distant from the source, and affect the quality of the aquifer.

If the protective cover is by-passed due to karst features, potential pollution can reach the aquifer in a short time. In order to prevent such scenarios, it is important to know which area is the most vulnerable. The PI-map provides such information. The red-coloured areas of the PI-map represent the zones with the lowest protection function of the aquifer. According to the PI-methodology, as shown in results, 8% of the studied area can be considered extremely vulnerable (Fig. 2f). By combining the aforementioned maps, it is possible to discuss potential scenarios that could lead to contamination of groundwater, and use the composite map as a decision-making tool in a sanitation or pollution-prevention process. The worst-case scenario would be if the red areas of both types of maps overlap. That would imply the absence of a suitable efficient barrier between the possible contaminant and the groundwater, and should lead to protective measures. Luckily, in the investigated area presented in this paper, red zones from the maps do not entirely coincide. As the red zones do not overlap, the question arises of which type of map should have preference as decision-making tool, (the PI map, or the mobile content map). Each situation should be considered separately, depending on the observed conditions. By considering both variables, it is possible to identify areas that must be prioritized in terms of protection, or monitoring and restriction of use (NOBRE et al., 2007). In such assessment, the areas of the highest proportion of mobile elements and those of extreme vulnerability are to be considered as important guidelines. For instance, if a red area of the PI-map (extremely vulnerable) overlapped with a low proportion of mobile elements (blue), then that area would have a lower priority than a yellow area of the PI-map (medium vulnerability) overlapping with an extremely high proportion of mobile elements (red). Such conclusions could be a helpful guide for investors, e.g. a water bottling branch. The main information that can be obtained from the maps in the paper is that the groundwater would not be seriously affected if environmental conditions changed to pH 5.

ACKNOWLEDGMENTS

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