GEOL. CROAT.	46/1	145 - 155	2 Figs.	6 Tabs.		ZAGREB 1993

UDC 553.3.072:553.685(497.13)

Original Scientific Paper

Heavy Metals in Liming Materials from NW Croatia: Possible Effect of Liming on Permissible Contents of Heavy Metals in Arable Soil

Goran **DURN**[1], Ladislav A. **PALINKAŠ**[1], Slobodan **MIKO**[1], Ferdo **BAŠIĆ**[2]
and Sanja **GRGIĆ-KAPELJ**[3]

Key Words: Heavy metals, Carbonate raw materials, Liming, Cadmium, Arable soil, Agroecological environment, NW Croatia

Ključne riječi: Teški metali, karbonatne mineralne sirovine, kalcifikacija, kadmij, obradivo tlo, agroekološki okoliš, sjeverozapadna Hrvatska

Abstract

The evaluation of the heavy metal discharge from liming materials into the arable soil in NW Croatia is based upon the contents of Fe, Mn, Pb, Cu, Zn, Cd, Co and Hg in the studied carbonate raw materials, obtained under simulated conditions of the lowest presumed acidity (pH>3) which can occur in the agroecological environment. From the agroecological viewpoint, the heavy metal contents of the analyzed liming materials are much lower than the permissible levels. Only cadmium contents indicate that a certain amount of care should be taken into account. Because cadmium is bound in labile forms (pH>3 soluble fraction), it has to be considered quite mobile and biologically available in limed arable soils that are affected by drastic pH changes in the agroecological environment.

Sažetak

Procjena unosa teških metala iz materijala za kalcifikaciju u obradivo tlo sjeverozapadne Hrvatske temelji se na rezultatima analiza Fe, Mn, Pb, Cu, Zn, Cd, Co i Hg iz proučavanih karbonatnih mineralnih sirovina pri simuliranim uvjetima najniže pretpostavljene kiselosti agroekološkog okoliša (pH>3). S agroekološkog stajališta, koncentracije teških metala u analiziranim materijalima za kalcifikaciju znatno su niže od tolerantnih vrijednosti. Odredenu pozornost neophodno je obratiti jedino udjelu kadmija jer su ustanovljene relativno povišene vrijednosti. S obzirom da je vezan za pH>3 topivu frakciju, kadmij se mora smatrati prilično mobilnim i biološki dostupnim u kalcificiranim obradivim tlima pogođenim drastičnim promjenama pH agroekološkog okoliša.

1. INTRODUCTION

Mineral fertilizers represent one type of the numerous sources of agricultural soil pollution by heavy metals and potentially toxic elements (term used by PATTERSON et al., 1990). The concentration of certain metals in mineral fertilizers and phosphate raw materials used in Croatia is presented in Table 1 (GRGIĆ, 1990). Phosphates and phosphorites very possibly are sources of high Cd concentrations in fertilizers. A significant enrichment of cadmium (with an average of 15 ppm) in marine phosphorites was shown by FÖRSTNER (1980). Furthermore, O'NEIL (1985) reported a high cadmium content in phosphate rocks (with an average of 100 ppm). According to MORTVEDT et al. (1981), cadmium contents in commercially important rock phosphate deposits in North America range from 3 to 130 ppm cadmium. As ROTHBAUM et al. (1986) stressed, phosphatic fertilizers made from these kinds of materials therefore add varying amounts of cadmium to agricultural soils.

Apart from mineral fertilizers, liming materials may also contribute to heavy metal pollution. Although the liming of soils could reduce the biological availability of heavy metals, long-term liming of agricultural soils may represent a possible source for the release of metals which have potentially harmful effects on agricultural products.

One of the main factors affecting the solubility and mobility of metals in soils, as well as the remobilization of metals from mineral fertilizers or liming materials, is acid precipitation. Because of its increased acidity (from the burning of fossil fuels etc.), water that enters the soil by precipitation is more capable of dissolving minerals. According to LIKENS et al. (1979), the average pH of rainwater in the eastern USA is about 3.5 in summer and 4.2 in winter. Soil properties can at times allow the percolation of pollutants, which can lead to the contamination of an aquifer. If, on the other hand, the polluting matter accumulates in the soil, plants become polluted and cause bioaccumulation in the food chain. These are the main reasons why the emission of heavy metals and other pollutants into the soil ecosystem needs to be controlled.

In order to obtain information on heavy metal contents in carbonate raw materials from NW Croatia, 49 samples of limestones and dolostones were investigat-

---

[1] Faculty of mining, geology and petroleum engineering, University of Zagreb, Pierottijeva 6, 41000 Zagreb, Croatia

[2] Faculty of the agricultural sciences, University of Zagreb, Svetošimunska cesta 25, 41000 Zagreb, Croatia

[3] Institute of Geology, Sachsova 2, 41000 Zagreb, Croatia

Type of fertilizer or phosphate raw material (PRM)	Cd	Cu	Pb	Co
NPK 14 - 14 - 14	20.3	0.2	2.9	0.8
NPK 7 - 20 - 30	25.0	0.8	2.1	0.2
NPK 10 - 30 - 20	20.3	1.1	2.6	0.2
NPK 8 - 26 - 26	20.8	1.3	2.4	0.4
NPK 15 - 15 - 15	42.1	0.9	2.2	0.6
NPK 13 - 10 - 20	72.6	0.8	2.6	0.3
PRM Marocco	43.7	1.5	3.5	0.5
PRM Senegal	218.7	2.4	3.5	2.0

Table 1 - Concentration of metals in some mineral fertilizers and phosphate raw materials (in ppm), according to GRGIĆ (1990).
Tablica 1 - Koncentracije metala u nekim umjetnim gnojivima i fosfatnim sirovinama (u ppm), prema GRGIĆ (1990).

ed. The results of both geochemical and mineralogical analyses are given in order to evaluate the discharge of heavy metals from the studied raw materials into the agroecological environment in NW Croatia.

2. STUDY AREA

The study area is located in NW Croatia (Fig. 1). It is composed of Upper Paleozoic, Mesozoic, Tertiary and Quaternary rocks (ŠIMUNIĆ et al., 1981). The Upper Paleozoic rocks are situated along the northern slopes of Mt. Ivančica and are mainly composed of alternating coarse-grained, grey and dark-grey greywackes and black shales. The Lower Triassic rocks comprise reddish-brown, grey and yellow sandstones of subarkose and protoquartzite types, siltstones, shales and, rarely, oolitic limestones and marls. In the upper part of Lower Triassic, thin-bedded limestones with interbeds of shales and dolomites prevail. The most widespread Middle Triassic rocks are dolomites, overlain by dolomitized limestones and breccias. Subsidence of the sedimentary basin caused sedimentation of fine-grained clastic rocks, pelagic limestones, cherts, tuffaceous sediments and tuffs accompanied by basaltic rocks. These rocks are followed by the Upper Triassic, stromatolite type, medium-grained dolomites accompanied by rare interbeds of limestones and dolomite breccias. A shallow-water sedimentation, which continued up until the Liassic, was interrupted until the Tithonian. The sedimentary unit, which passes upward into the Lower Cretaceous volcanogenic-sedimentary complex, comprises thin-bedded limestones, radiolarian shales and cherts, as well as sandstones. The Paleogene sedimentary rocks are composed of carbonate breccias, limestones, claystones, and silty and sandy marls. The Lower and Middle Miocene rocks comprise gravels, sands, clays and marls, with coal interbeds. The presence of andesites and tuffs indicates intensive volcanic activity. Biogenic limestones are the most important lithological member of the Turonian. While the Upper Miocene comprises marls, sandy limestones, sandstones and sands, the Pliocene is composed of different types of unconsolidated clastic rocks. The Quaternary consists of various clastic deposits. A detailed overview of the geology of the study area is given by ŠIMUNIĆ et al. (1981).

Although quarries of carbonate raw material are quite widespread in the area, this study focused only on quarries situated south and southeast of Varaždin, and west of Mt. Ivančica (Fig. 1). Dolomitized limestones and, partly, dolomites and limestones of the Triassic age are exposed in the Špica quarry, and bituminous dolomites of the Triassic age are found in the Očura quarry. The quarry at Presečno consists of bioclastic limestones of Tortonian age.

3. SAMPLING

Thirty-seven samples of carbonate raw materials were collected from the investigated quarries (Špica - 15 samples, Očura - 15 samples and Presečno - 7 samples) at distances, inside each individual quarry, ranging between 20 and 100 meters. Twelve samples were taken from the drill core that had been drilled within the area of the Špica quarry. The distance between the core samples was approximately 10 meters. Roughly 0.5 kg of a carbonate raw material was collected for each sample. Only unweathered samples were collected. Red-staining noticed on some samples was washed, removed with an awl or carefully isolated prior to drying and grinding the samples.

4. ANALYTICAL PROCEDURES

Insoluble residues were extracted from the carbonate rocks by dissolving 2 g samples in 1N HCl (added dropwise, maintaining pH>3) and filtering. The remaining soluble fractions were analyzed for Fe, Mn, Pb, Cu, Zn, Cd and Co with a Pye Unicam SP 9 Atomic Absorption Spectrophotometer. Three samples, each

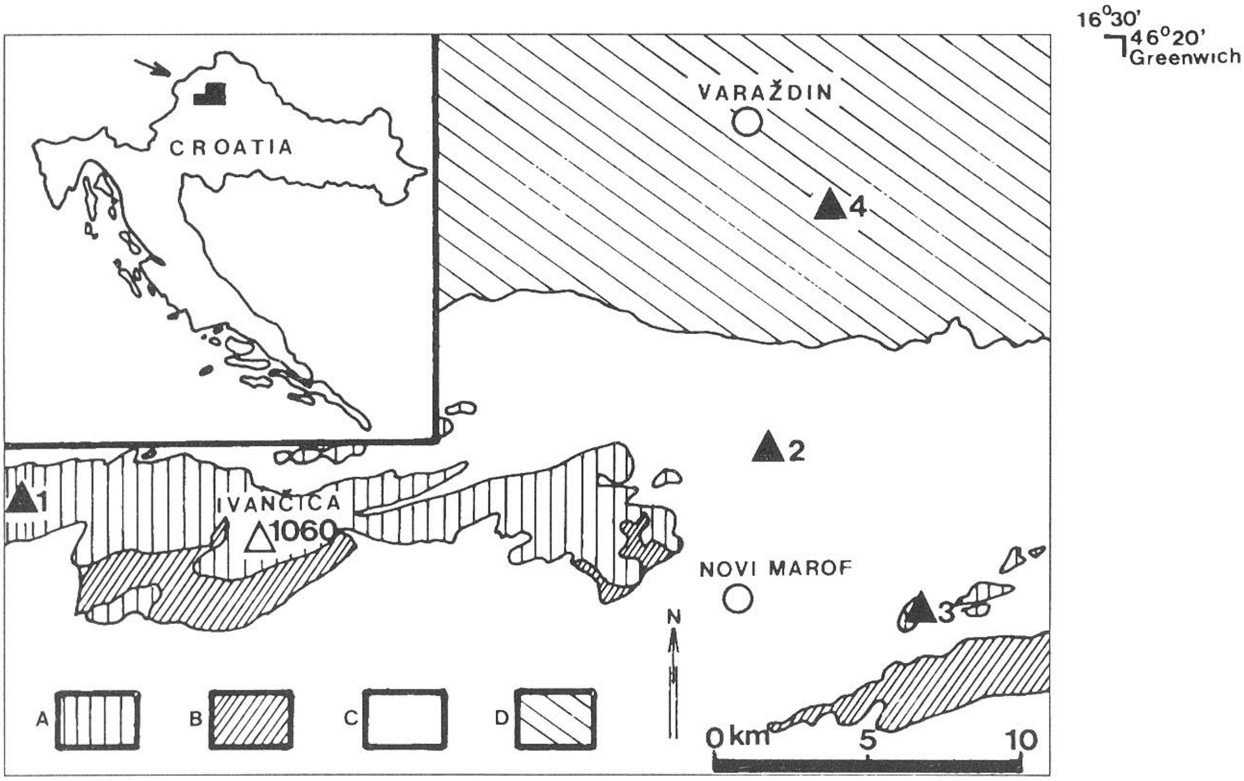

Fig. 1: Schematized geological map and positions of the investigated localities (modified from ŠIMUNIĆ et al., 1981): 1) Očura quarry; 2) Presečno quarry; 3) Špica quarry; 4. Brezje; A- Triassic; B- Jurassic and Cretaceous; C- Paleogene and Neogene; D-Quaternary.
Slika 1: Shematizirana geološka karta s položajem istraženih lokaliteta (modificirano prema ŠIMUNIĆ et al., 1981): 1) kamenolom Očura; 2) kamenolom Presečno; 3) kamenolom Špica; 4. Brezje; A- Trijas; B- Jura i Kreda; C- Paleogen i Neogen; D-Kvartar.

representing one type of carbonate raw material (sample Č-2, Očura quarry, for dolomites; sample Š-10A, Špica quarry, for dolomitized limestones and P-3, Presečno quarry, for bioclastic limestones), were selected for the analysis of insoluble residue. Insoluble residues (obtained by dissolving 100 g carbonate sample in 1N HCl, pH>3) were prepared for the AAS analysis by digestion of 0.2 g samples in an autoclave (teflon bomb) with HF and HNO_3 at 150° C and 50 bars, and after that diluted to 250 ml. For the total decomposition of a sample, we used the procedure proposed by DYMOTT (1985) and PRICE & WHITESIDE (1977). The resulting solutions were analyzed for Fe, Mn, Pb, Cu, Zn, Cd and Co using the AAS. Total mercury content as well as the content of mercury in selected insoluble residues was analyzed by a modified soil vapor mercury analyzer (AGP-1) with a heating stage. The detection limit of the method is 0.5 ppb. The standard calibration solutions for each element were matched in calcium and hydrochloric acid content to those of the sample solutions (pH>3 soluble fraction solutions) to minimize any matrix effects that may occur during the analysis due to the high calcium content of the solutions (1.5 % Ca). The method of standard additions was also employed to check for interference effects (DYMOTT, 1985). Precision and accuracy based on the analyses (total acid digestion) of the reference geological sample GXR 5 (GOVINDARAJU, 1989) was of the order of ± 5-15 per cent. Thin sections as well as mineralogical analyses by X-ray diffraction and thermic analyses (DTA, TG and DTG) were used in defining the carbonate rock types and the composition of the insoluble residues.

5. RESULTS AND DISCUSSION

5.1. LIMING MATERIALS

GRAF (1960) stated that the concentrations of minor elements found in carbonate rocks are a function of their amounts present in solid solution in the carbonate minerals and of the kinds and amounts of present detrital minerals, accesory authigenic precipitates, noncarbonate skeletal material, organic matter, phases formed during diagenesis, and elements adsorbed upon all these materials. Concentrations of elements that can be obtained from carbonate rocks also depend on the analytical method employed. While some authors use total decomposition of samples and present their results as total element content, others apply various leaching methods (e.g. acid digestion in aqua regia), obtaining close to the total element content (aqua regia extractable content, WARREN & DELEVAULT, 1961). FÖRSTNER (1987) suggests that the extracting medium has to be designed to simulate the most extreme environmental conditions. Bearing this in mind, the dissolution of carbonate rocks was performed

LOCALITY		P	Šk	Šb	Č
GEOLOGICAL AGE		M	T	T	T
SAMPLE		7	15	12	15
Hg*	x_m	0.005	0.107	0.105	0.037
	x_{min}	0.003	0.014	0.003	0.012
	x_{max}	0.006	0.513	0.540	0.130
Cd	x_m	1.5	0.5	0.7	0.5
	x_{min}	0.9	0.07	0.07	0.07
	x_{max}	2.4	1.9	3.3	1.5
Cu	x_m	3.4	3.7	4.2	6.0
	x_{min}	1.9	0.6	0.9	1.3
	x_{max}	5.2	12.5	14.4	46.5
Pb**		<1	<1	<1	<1
Co	x_m	1.5	1.8	2.8	1.8
	x_{min}	0.8	1.0	1.3	1.1
	x_{max}	2.0	2.7	9.4	2.8
Zn	x_m	11	9	10	11
	x_{min}	8	3	4	6
	x_{max}	13	22	27	16
Mn	x_m	16	51	60	210
	x_{min}	6	13	5	139
	x_{max}	41	130	450	294
Fe	x_m	183	283	310	403
	x_{min}	64	115	64	162
	x_{max}	564	807	730	850
I.R.	x_m	1.6	1.33	1.52	0.26
	x_{min}	0.21	0.57	0.69	0.05
	x_{max}	2.53	2.31	2.7	0.9

P - Presečno (quarry); Šk - Špica (quarry); Šb - Špica (drill core); Č - Očura (quarry); M - Miocene; T - Triassic; * - total mercury content; ** - content of element below lower detection limit of the employed analytical method; x_m - mean value; x_{min} - minimum value; x_{max} - maximum value; I.R. - insoluble residue.

P - Presečno (kamenolom); Šk - Špica (kamenolom); Šb - Špica (bušotina); Č - Očura (kamenolom); M - Miocen; T - Trijas; * - totalni sadržaj žive; ** - sadržaj elementa niži od donje granice detekcije za primijenjenu analitičku metodu; x_m - srednja vrijednost; x_{min} - minimalna vrijednost; x_{max} - maksimalna vrijednost; I.R. - netopivi ostatak.

Table 2 - Concentration of metals in pH >3 soluble fraction (in ppm) and insoluble residues (in wt.%).
Tablica 2 - Koncentracija metala u pH >3 topivoj frakciji (u ppm) i netopivi ostaci (u tež.%).

maintaining pH>3 to simulate the lowest presumed acidity of the agroecological environment. LIVINGSTON & THOMPSON (1971), indicated that a 4% acetic acid attack, apart from carbonates, also removes some ions adsorbed from clay minerals, as well as some ions associated with thin coatings or micronodules of hydrated ferromanganic oxides on the carbonate skeletons. On the basis of this and the extraction sequences for sediment characterization designed by ENGLER et al. (1977), we can tentatively conclude that the pH>3 soluble fraction is composed of the exchangable, carbonate and partly, reducible fractions. Table 2 gives the results of analyzed element concentrations in liming materials determined by digestion with 1N HCl as well as the average content of insoluble residues. Comparing our results with the total content of metals as given by various authors (Table 3), the following trends can be observed:

- Hg content varies considerably, from very low (as in Presečno) to relatively high (Špica and Očura) values;
- concentrations of Cd are much higher than the average concentrations;
- concentrations of Pb are significantly lower than the average ones;
- concentrations of Fe and Mn are slightly lower than the average ones;
- concentrations of Cu, Zn, and Co do not deviate from the average values.

Optical microscope studies of thin sections show

	CONNOR & SHACKLETE, 1975	HAWKES & WEBB, 1962	TUREKIAN & WEDEPOHL, 1961	GRAF, 1960	HORN & ADAMS, 1966
Hg	0.022-0.030	0.03	0.04	0.07	0.046
Cd	No data	No data	0.035	0.1-0.2(?)	0.048
Cu	0.84-12	5-20	4	5-23	4.44
Pb	4-18	5	9	4-12	16.5
Co	1.3-7.1	0.2-2	0.1	4.3	0.12
Zn	6.3-24	4-20	20	21-31	15.6
Mn	83-910	1300	1100	500(?)	842
Fe	1100-21000	13000	3800	No data	8190

Table 3 - Average concentration of metals in carbonate rocks (limestones and dolostones) as given in various publications (in ppm).
Tablica 3 - Srednje vrijednosti koncentracija metala u karbonatnim stijenama (vapnenci i dolomiti) prema literaturnim podacima (u ppm).

SAMPLE LOCALITY ROCK TYPE		Č-2 Č A	P-3 P B	Š-10A Šk C
I.R.		0.9	1.9	1.1
Hg	*	0.13	0.006	0.097
	2	1.22	0.015	0.011
Cd	1	1.0	2.4	0.5
	2	<2**	<2	<2
	3	<2	<0.83	<4
Cu	1	1.9	5.0	3.2
	2	40	52	25
	3	21	10.4	7.8
Pb	1	<1	<1	<1
	2	105	23	62
	3	>105	>23	>62
Co	1	2.8	1.7	1.6
	2	61	14	13
	3	21.8	8.2	8.1
Zn	1	13	13	16.5
	2	120	320	60
	3	9.2	24.6	3.6
Mn	1	200	9	32
	2	327	62	143
	3	1.6	6.9	4.5
Fe	1	807	564	397
	2	15,000	6,000	4,500
	3	18.6	10.6	14.6

1 - pH > 3 soluble fraction; 2 - insoluble residue; 3 - 2/1 ratio; Č - Očura (quarry); P - Presečno (quarry); Šk - Špica (quarry); * total mercury content; ** - content of element below lower detection limit of the employed analytical method; A - Late - diagenetic microcrystaline bituminous dolostone; B - Litothamnium limestone; C - Early-diagenetic stromatolite dolostone; I.R. - Insoluble residue.

1 - pH > 3 topiva frakcija; 2 - netopivi ostatak; 3 - 2/1 omjer; Č - Očura (kamenolom); P - Presečno (kamenolom); Šk - Špica (kamenolom); * - totalni sadržaj žive; ** - sadržaj elementa niži od donje granice detekcije za primijenjenu analitičku metodu; A - mikrokristalasti kasnodijagenetski bituminozni dolomit; B - litotamnijski vapnenac; C - ranodijagenetski stromatolitni dolomit; I.R. - netopivi ostatak.

Table 4 - Concentration of metals in pH > 3 soluble fraction and insoluble residue from selected samples of carbonate rocks (in ppm), and insoluble residue content (in wt.%)
Tablica 4 - Koncentracija metala u pH >3 topivoj frakciji i netopivom ostatku iz odabranih uzoraka karbonatnih stijena (u ppm) i udio netopivog ostatka (u tež. %)

that the late diagenetic dolomitized intrasparite/intrasparudite limestones and, partly, early diagenetic stromatolite dolomites and intrasparite/intrasparudite limestones are exposed in the Špica quarry. While late diagenetic bituminous dolomites are found in the Očura quarry, biosparite, biosparudite and biomicrite limestones have been recognized in the Presečno quarry. The presence of bituminous compounds was also confirmed by thermic analysis.

In order to compare the concentrations of elements in the soluble fraction with the same in the insoluble residues, three selected insoluble residues were totally digested and analyzed. Table 4 contains the weight percentages and element concentrations of the analyzed insoluble residue. Concerning the fact that detrital minerals are the principal sources of minor elements in many carbonate rocks (GRAF, 1960), the estimated mineralogical composition is given in Table 5. Sample P-3 consists of quartz, mica-type mineral, chlorite, smectite, plagioclase, K-feldspar, goethite and amorphous compounds. Sample Č-2 is enriched with bituminous compounds and mica-type mineral, and contains quartz, kaolinite, K-feldspar and pyrite. Sample Š-10A is composed of kaolinite, quartz, mica-type mineral, plagioclase, K-feldspar and amorphous compounds.

Compared to the fossiliferous limestones (Presečno quarry), the late diagenetic bituminous dolomites (Očura quarry) and the late diagenetic dolomitized intrasparite/intrasparudite limestones and, partly, early diagenetic stromatolite dolomites and intrasparite/intrasparudite limestones (Špica quarry) are highly enriched with Hg (Table 2). The highest variability of Hg content was observed in the samples from the Špica quarry. This is probably connected with observed heterogeneous carbonate rock types that we observed there. It seems that the highest values (0.513 and 0.540 ppm) are related with the late diagenetic dolomitized intrasparite/intrasparudite limestones. Although the reason for such a high Hg content in these rocks is not clear, the observed Hg accumulation in dolomites from the Očura quarry can be explained. Namely, the thin section analyses as well as the DTA of insoluble residues showed that the dolomites contain bituminous compounds. In addition, we observed that the Hg content in the insoluble residue was ten times higher than the whole rock content (Table 4, sample Č-2). MAROWSKY & WEDEPOHL (1971) noticed that the Devonian limestone composite, with 0.29 ppm Hg, had a lower clay proportion but a higher concentration of bituminous compounds compared to the Cretaceous limestone composite, which had only 0.029 ppm Hg. This undoubtedly indicates a possible connection between the bituminous compounds and the accumulation of Hg. McNEAL & ROSE (1974) concluded that the main factors controlling the concentrations of Hg in sedimentary and metasedimentary rocks are the presence or absence of vulcanism in the source areas of deposition, the amount of iron or manganese oxides in oxidizing environments or the amount of organic material and sulfur in reducing environments, the thermal history of the rock, the intensity of regional hydrothermal activity and the effect of diagenesis. The variation of Hg content in carbonate rocks of different ages in the Dinarids has been noticed by PALINKAŠ et al. (1992), who determined generally low values in the carbonates of the Jurassic age and the Miocene age, and higher values in the carbonate rocks of the Triassic and Cretaceous ages.

Compared to the available data from the literature (Table 3), concentrations of Cd are highly enriched in all the investigated samples. GONG et al. (1977) concluded that organicaly rich sedimentary rocks, such as dark shales, are enriched with Cd, while others, such as red shales, sandstones and limestones, have depleted Cd content in comparison with igneous and metamorphic rocks and the crust. According to MAROWSKY & WEDEPOHL (1971), due to the crystal chemical properties, the Cd concentrations in limestones are expected to be controlled by their clay fraction. This can explain the relatively large differences in the average values for Cd in limestones (FÖRSTNER, 1980). MULLIN & RILEY (1956) showed that a marine calcareus ooze contained 0.574 ppm Cd. FÖRSTNER (1987) emphasized a significant shift of Cd to higher percentages in the carbonate fraction of solid waste, street dust and sewage sludge samples. HICKEY & KITTRICK (1984) pointed out that 83 % of the total Cd content in four samples (3 soil samples and 1 sediment sample) was associated with the exchangable, carbonate and Fe-Mn oxide fractions. The relation of Cd

SAMPLE	Q	K	M	C	S	AC	P	KF	Py	Ge
P-3	++		+	+	+	+	T	T		T
Č-2	+	T	++			++		T	T	
Š-10A	+	++	+			+	T	T		

Q - Quartz; K- Kaolinite; M - Mica (muscovite and illite); C - Chlorite; S - Smectite; Ac - Amorphous components; P - Plagioclase; KF - K-feldspar; Py - Pyrite; Ge - Goethite; ++ - 25-50%; + - 5-25%; T - < 5%.

Q - Kvarc; K - Kaolinit; M - Tinjac (muskovit i ilit); C - Klorit; S - Smektit; Ac - Amorfna komponenta; P - Plagioklas; KF - K - feldspat; Py - Pirit; Ge - Getit; ++ - 25-50%; + - 5-25%; T - <5%.

Table 5 - Mineral estimates from XRD and thermic analysis.
Tablica 5 - Procijenjeni mineralni udjeli na temelju XRD i termičke analize.

with the carbonate fraction was also observed by PROHIĆ & KNIEWALD (1987). The observed high content of Cd in soluble fractions indicate that Cd is either weakly adsorbed on clay fractions and leached during the 1N HCl digestion, or is associated with the carbonate and partly with the reducible fraction. Although the concentrations of Cd in the insoluble residues are below the detection limit (Table 4), the fact that, compared to the majority of analyzed elements, concentrations of Cd in the insoluble residues are not increased may also indicate Cd enrichment in the pH >3 soluble fraction.

Relatively low Pb values (Table 2) compared to the data available from the literature (Table 3) indicate that Pb is connected with insoluble residues. This has been confirmed by the results obtained by total decomposition of the selected insoluble residues (Table 4). The highest Pb content was obtained in the Č-2 sample (Očura quarry), which also contains bituminous compounds and pyrite (Table 5). Investigations performed by WEDEPOHL (1956) indicated that the insoluble residue of carbonate rock samples, averaging 10 per cent of the rock, contained about a third of the total Pb. WEDEPOHL (1974) stated that the higher lead content in bituminous shales, compared with non-bituminous shales, might be connected with the organic residues and/or the pyrite fraction. WAMPLER & KULP (1964) found that the Pb content of both sedimentary and metasedimentary pyrite varies from less than 5 ppm to hundreds of ppm. On the basis of chemical fractionation of Pb in solid waste particles, street dust and sewage sludge, FÖRSTNER (1987) concluded that Pb is typically enriched in the organic/sulphidic and residual forms.

Although they display concentrations within the average values presented in Table 3, Cu, Zn and Co are highly enriched in the selected insoluble residues (Table 4). The highest *insoluble residue concentration / pH>3 soluble fraction concentration* ratios for Cu and Co were observed in the insoluble residue of sample Č-2, which contains bituminous compounds and pyrite.

Compared to the average pH >3 soluble Mn and Fe contents in carbonate rocks from the Špica and Presečno quarries, dolomites from the Očura quarry are significantly enriched with Mn and slightly enriched with Fe. Although the higher average Mn content can be attributed to regional geochemical processes which were active during the carbonate formation, it is important to stress that, according to WEDEPOHL (1978), many of the higher Mn contents in carbonate rocks are probably derived from diagenetic mobilization of Mn under reducing conditions. Investigations of coexisting dolomite and calcite, performed by ATWOOD & FRY (1967), showed that the Mn is concentrated in the dolomite phase. *Compared to the insoluble residue con-*

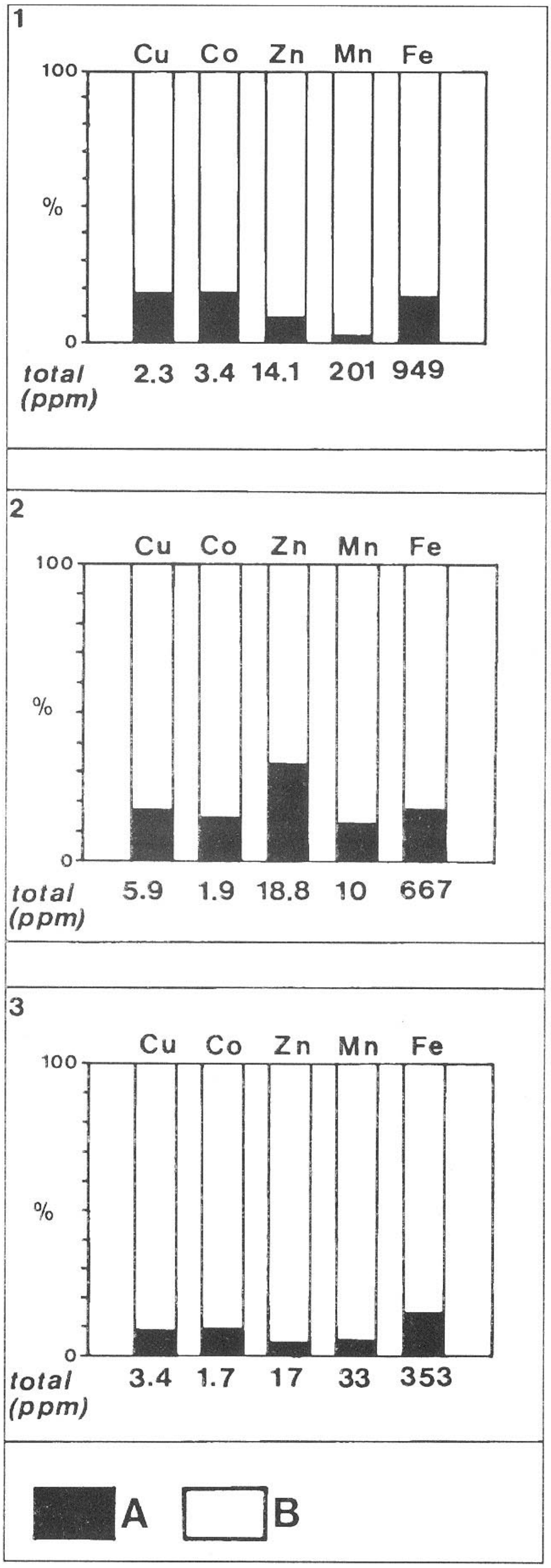

Fig. 2 - Partition of metals in the pH>3 soluble fraction and insoluble residue in relation to the total metal content: 1 - sample Č-2; 2 - sample P-3; 3 - sample Š-10A; A - insoluble residue; B - pH>3 soluble fraction.

Slika 2 - Raspodjela metala u pH>3 topivoj frakciji i u netopivom ostatku u odnosu na ukupni sadržaj metala: 1 - uzorak Č-2; 2 - uzorak P-3; 3 - uzorak Š-10A; A - netopivi ostatak; B - pH>3 topiva frakcija.

			Zn	Cu	Pb	Cd
Brezje, content in soil (ppm)			9.7	1.4	20.5	0.3
Brezje, content to 30 cm depth (kg/ha)			43.6	6.3	92.2	1.35
Maximal permissible content (kg/ha)			900	225	225	3.6
Difference (tolerable intake) to 30 cm depth (kg/ha)			-856	-219	-133	-2.3
Intake in kg/ha of liming material	Šk	x_m	0.153	0.055	-	0.007
		x_{max}	0.330	0.187	0.015	0.028
	Šb	x_m	0.150	0.063	-	0.010
		x_{max}	0.405	0.216	0.015	0.049
	P	x_m	0.165	0.051	-	0.022
		x_{max}	0.195	0.078	0.015	0.036
	Č	x_m	0.165	0.090	-	0.007
		x_{max}	0.240	0.697	0.015	0.165
Tolerant annual intake during 100 years (kg/ha)			8.56	2.19	1.33	0.023
Tolerant annual intake according to PETRUZZELI (1989) (kg/ha)			2.5	0.5	0.6	0.001

x_m - mean value; x_{max} - maximum value; Šk, Šb, P, and Č - as on Table 2.
x_m - srednja vrijednost; x_{max} - maksimalna vrijednost; Šk, Šb, P, i Č - kao na Tablici 2.

Table 6 - Intake of some metals in arable soil by liming.
Tablica 6 - Unos nekih metala u obradivo tlo kalcifikacijom.

centration / pH>3 soluble fraction concentration ratios of Cu, Co, Pb, Zn and Fe, Mn is the least enriched in the selected insoluble residues (Table 4). According to WEDEPOHL (1978), Mn is one of the few minor elements which is more abundant in the carbonate than in the detrital fraction of carbonate rocks. Apart from the previously mentioned relationship with bituminous compounds and pyrite, no specific regularity was noticed between the observed minerals in the selected insoluble residues and metal content.

Analyzed carbonate rocks contain, on the average, quite a low percentage of insoluble residue (Table 2). If we assume that the contribution of each metal from the insoluble residue to the total carbonate rock content equals the metal concentration multiplied by the insoluble residue weight percentages, and that the contribution of each metal from the pH>3 soluble fraction equals the metal concentration multiplied by the soluble fraction weighht percentage, the diagrams shown on Fig. 2 can be constructed. They show that heavy metals are much more bound in the pH >3 soluble fraction. Bearing in mind the fact that the analyzed carbonate rocks are pure with respect to the content of insoluble residue, it is obvious that the total heavy metal concentrations (especially of Fe, Co and Cu) strongly depend on the insoluble residue content in the samples as well as its composition (e.g. sample Č-2).

5.2. ESTIMATED PERMISSIBLE EMISSION OF HEAVY METALS IN THE ARABLE SOIL FROM NW CROATIA

Continual liming of agriculture soils may represent a long-term source for the release of heavy metals. The maximum limit values of tolerant contents of heavy metals and potentially toxic elements in soils are mainly related to both the total content and the amount of exchangable, water-soluble elements available for plants. The rigid criteria such as those proposed by HEINZ (1987), VEREMES (1990) and PETRUZZELLI (1989) should be applied in practice. Due to the serious danger of accumulation in the soil, the delicate question is this: what would the permissible annual emission be, and what percentage of the dose is contributed by liming materials. PETRUZZELLI (1989) uses the difference between the permissible and actual content within 100 years as the criterium for heavy metal intake, because this is a period during which it is possible to reach the maximum permissible content.

A brown soil to the depth of 30 cm, from the vicinity of Varaždin (Brezje, Fig.1) was used for the performed calculations (BAŠIĆ et al., 1990) To follow the intake of heavy metals and toxic elements in the analyzed carbonate rocks, a dose of 15 tons per ha of liming material was taken on account of its content of Cu, Pb, Zn and Cd (Table 6). The criteria proposed by HEINZ (1987) were used. The intake of heavy metals, even with these large doses of material, was very small. Only cadmium contents indicate that a certain amount of care should be taken into account. Cadmium is easily adsorbed up by plants, and its concentrations in plants are much closer to soil levels (O'NEIL, 1985). Because Cd is bound in labile forms (pH>3 soluble fraction), it has to be considered quite mobile and biologically available in limed arable soils that are affected by drastic changes in the agroecological environment. Since the average content of cadmium is relatively very high only at the Presečno locality, and even there it is bellow the tolerated level of annual intake (Table 6), the analyzed materials can be used as raw material for liming. Mineral fertilizers undoubtedly cause much higher pollution of soils (Table 1). PETRUZZELI (1989) presented results for the permissible annual intake of heavy metals in Italian soils (Table 6). Compared to his results, the calculated tolerable annual intake of heavy metals for the arable soil is significantly higher indicating favourable conditions in arable soils in NW Croatia.

Acknowledgments

The authors acknowledge the Ministry of Science of the Republic of Croatia and the IGM Lepoglava Company, which financially supported the research. Thanks also go to Prof. J. TIŠLJAR for his help in the thin section analyses, to V. BABIĆ for the DTA determinations and to K. MARIĆ for help in the field work and organization.

6. REFERENCES

ATWOOD, D.K. & FRY, H.M. (1967): Strontium and manganese content in some coexisting calcites and dolomites.- American Mineralogist, 52, 1530-1535.

BAŠIĆ, F., BUTORAC, A., VAJNBENGER, A., MALBAŠIĆ, D., BERTIĆ, B. & MESIĆ, M. (1990): The effect of liming on the yield of some field crops and chemical properties of soil.- 10th World Fertilizer Congress of C.I.E.C., Nicosia, Spec. Publ., 12p.

CONNOR, J.J. & SHACKLETTE, H.T. (1975): Background geochemistry of some rocks, soils, plants and vegetables in the conterminous United States.- U.S. Geol. Survey Profess. Papers, 574-F, 168p.

DYMOTT, T.C. (1985): Atomic absorption with electrothermal atomisation.- Pye Unicam Ltd., Cambridge, 85p.

ENGLER, R.M., BRANNON, J.M., ROSE, J. & BIGHAM, G. (1977): A practical selective extraction procedure for sediment characterization.- In: YEN, T.F. (ed.): Chemistry of marine sediments. Ann Arbor Sci Publ., 163-171.

FÖRSTNER, U. (1980): Cadmium.- In: HATZINGER, O. (ed.): Handbook of Environmental Chemistry, Vol.3, Part A. Springer Verlag, Berlin, Heidelberg, New York, 59-107.

FÖRSTNER, U. (1987): Metal speciation in solid wastes-factors affecting mobility.- In: LANDER, L. (ed.): Speciation of metals in water, sediment and soil systems. Springer-Verlag, Berlin, Heidelberg, New York, 13-42.

GONG, H., ROSE, A.W. & SUHR, N.H. (1977): The geochemistry of cadmium in some sedimentary rocks.- Geochimica et Cosmochimica Acta, 41, 1687-1692.

GOVINDARAJU, K. (1989): Compilation of working values and sample description for 272 geostandards.- Geostandards Newsletters, XIII, 1-28.

GRAF, D.L. (1960): Geochemistry of carbonate sediments and sedimentary carbonate rocks I-IV.- Illinois State Geol. Surv., Circ. 301, 71 p.

GRGIĆ, S.(1990): Influence of agrochemicals on the heavy metal content in the ground water and soil of the Eastern Slavonian region (in Croatian).- M.Sc. Thesis, University of Zagreb, 145p.

HAWKES, H.E. & WEBB, J.S.(1962): Geochemistry in mineral exploration.- Harper and Row, New York, 351 p.

HEINZ, H. (1987): Richtwerte fur Schadstoffe des Bodens Materialen.- Kongress Bodenschutz, 13-14 Oktober, Bayerisches Staatsministerium furLändesentwicklung und Umweltfragen, München, 52, 157-164.

HICKEY, M.G. & KITTRICK, J.A. (1984): Chemical partitioning of cadmium, copper, nickel and zinc in soils and sediments containing high levels of heavy metals.- Journal of Environmental Quality, 13, 372-376.

HORN, M.K. & ADAMS, J.A.S. (1966): Computer-derived geochemical balances and element abundances.- Geochimica et Cosmochimica Acta, 30, 279-298.

LIKENS, G.E., WRIGHT, R.F., GALLOWAY, J.N. & BUTLER, T.J. (1979): Acid rain.- Scientific American, 241, 43-51.

LIVINGSTON, H.D. & THOMPSON, G. (1971): Trace element concentrations in some modern corals.- Limnol. Oceanogr., 16, 786-796.

MAROWSKY, G. & WEDEPOHL, K.H. (1971): General trend in the behavior of Cd, Hg, Tl and Bi in some major rock forming processes.- Geochimica et Cosmochimica Acta, 35, 1255-1268.

McNEAL, J.M. & ROSE, A,W. (1974): The geochemistry of mercury in sedimentary rocks and soils in Pennsylvania.- Geochimica et Cosmochimica Acta, 38, 372-376.

MORTVEDT, J.J., MAYS, D.A. & OSBORN, G. (1981): Uptake by wheat of cadmium and other heavy metal contaminants in phosphate fertilizers.- Journal of Environmental Quality, 10, 193-197.

MULLIN, J.B. & RILEY, J.P. (1956): The occurence of cadmium in in seawater and marine organisms and sediments.- Journal of Marine Research, 15, 103-115.

O'NEIL, P. (1985): Environmental Chemistry.- George Allen & Unwin, London, Boston, Sydney, 232p.

PALINKAŠ, L., ŠINKOVEC, B., MIKO, S. & DURN, G. (1992): Mercury in bauxites as an indicator of subaerial volcanic activity in the Tethyan history.- 7th International Congress of ICSOBA, Balatonalmadi, Abstracts, 96.

PATTERSON, E., BERROW, M.L. & WILSON, M.J. (1990): Soil Protection.- MLURI, Annual Report, Aberdeen, 14-23.

PETRUZZELLI, G. (1989): Recycling waste in agriculture, heavy metal bioavailability.- Agricultural ecology and environment, Amsterdam, New York, Oxford, Tokio, 505 p.

PRICE, W.J. & WHITESIDE, P.J. (1977): General method for analysis of siliceous materials by atomic-absorption spectrophotometry and its application to macro and micro samples.- The Analyst, 102, 664-671.

PROHIĆ, E. & KNIEWALD, G. (1987): Heavy metal distribution in recent sediments of the Krka River estuary - an example of sequential extraction analysis.- Marine chemistry, 22, 279-297.

ROTHBAUM, H.P., GOGUEL, R.L., JOHNSTON, A.E. & MATTINGLY, G.E.G. (1986): Cadmium accumulation in soils from long-continued applications of superphosphate.- Journal of Soil Science, 37, 99-107.

ŠIMUNIĆ, An., PIKIJA, M., HEČIMOVIĆ, I. & ŠIMUNIĆ, Al. (1981): Osnovna geološka karta SFRJ 1:100 000. Tumač za list Varaždin (L 33-69).- Geološki zavod, Zagreb (1982), Savezni geološki zavod, Beograd, 74 p.

TUREKIAN, K.K. & WEDEPOHL, K.H. (1961): Distribution of the elements in some major units of the earth's crust.- Bull. Geol. Soc. Am., 72, 175-191.

VEREMES, L. (1990): The system of conditions and regulations concerning land aplication of wastes.- 10th World Fertilizer Congress of C.I.E.C., Nicosia, Spec. Publ., 8p.

WAMPLER, J.M. & KULP, J.L. (1964): An isotopic study of lead in sedimentary pyryte.- Geochimica et Cosmochimica Acta, 28, 1419-1458.

WERREN, H.V. & DELEVAULT, R.E. (1961): The lead, copper, zinc and molybdenum content of some limestones and related rocks in southern Ontario.- Economic Geology, 56, 1265-1272.

WEDEPOHL, K.H. (1956): Investigations on the geochemistry of lead (in German).- Geochimica et Cosmochimica Acta, 10, 69-148.

WEDEPOHL, K.H. (1974): Lead - Behavior during weathering and rock alteration (82-G).- In: WEDEPOHL, K.H. (ed.): Handbook of geochemistry. Springer-Verlag, Berlin, Heidelberg, 82-G1-82-G3.

WEDEPOHL, K.H. (1978): Manganese - Abundance in common sediments and sedimentary rocks (25-K).- In: WEDEPOHL, K.H. (ed.): Handbook of geochemistry, Springer-Verlag, Berlin-Heidelberg, 25-K1-25-K17.

Teški metali u materijalima za kalcifikaciju iz sjeverozapadne Hrvatske: mogući utjecaj kalcifikacije na dopustivi sadržaj teških metala u obradivom tlu

G. Durn, L.A. Palinkaš, S. Miko, F. Bašić i S. Grgić-Kapelj

U karbonatnim mineralnim sirovinama iz tri kamenoloma (Presečno, Špica i Očura, slika 1) analizirani su teški metali u svrhu procjene njihova tolerantnog unosa u obradivo tlo sjeverozapadne Hrvatske. Sa ciljem simuliranja najniže pretpostavljene kiselosti agroekološkog okoliša, uzorci karbonatnih stijena otapani su pomoću 1N HCl održavajući pH>3. U svrhu usporedbe koncentracija teških metala u pH>3 topivoj frakciji s koncentracijama u netopivom ostaku, tri odabrana netopiva ostatka pripremljena su za analizu totalnom dekompozicijom pomoću HF i HNO_3 u autoklavu (teflonska bomba) kod 150° C i 50 bara. Metodom AAS analizirani su Fe, Mn, Pb, Cu, Zn, Cd i Co. Ukupni sadržaj Hg u karbonatnim mineralnim sirovinama i odabranim netopivim ostacima dobiven je pomoću modificiranog analizatora žive u zraku tla (AGP-1). Mineralni sastav netopivog ostatka određen je pomoću rendgenske difrakcije na prahu i termički.

Koncentracije Fe, Mn, Pb, Cu, Zn i Co u analiziranim materijalima za kalcifikaciju (pH>3 topiva frakcija, tablica 2) niže su ili na razini, a Cd znatno iznad prosječnih koncentracija metala u karbonatnim stijenama (tablica 3). Koncentracije Fe, Mn, Pb, Cu, Zn i Co u analiziranim netopivim ostacima znatno su povišene u odnosu na iste u pH>3 topivoj frakciji (tablica 4). Odnos koncentracije u netopivom ostatku i koncentracije u pH>3 topivoj frakciji za Cd niži je od odnosa za Fe, Mn, Pb, Cu, Zn i Co što ukazuje na povezanost Cd s pH>3 topivom frakcijom. Ukupni sadržaj Hg u analiziranim karbonatnim materijalima (tablica 2) varira od niskih (Presečno) do relativno povišenih vrijednosti (Špica i Očura). S agroekološkog stajališta, koncentracije teških metala u analiziranim materijalima za kalcifikaciju znatno su niže od tolerantnih vrijednosti. Određenu pozornost neophodno je posvetiti jedino udjelu Cd jer su utvrđene relativno povišene vrijednosti. S obzirom da je vezan za pH>3 topivu frakciju, Cd se mora smatrati prilično mobilnim i biološki dostupnim u kalcificiranim obradivim tlima pogođenim drastičnim promjenama pH agroekološkog okoliša.

Manuscript received November 5, 1992.
Revised manuscript accepted March 5, 1993.