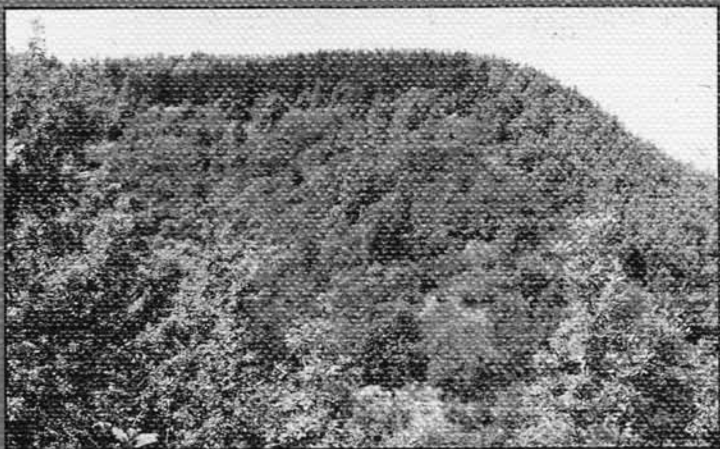
Miodrag Zlatic & Stanimir Kostadinov (Editors)

Challenges: Sustainable Land Management – Climate Change



ADVANCES IN GEOECOLOGY 43

IUSS – UISS - IBU

A Cooperating Series of the International Union of Soil Science (IUSS)

ISBN 978-3-923381-61-6 US ISBN 1-59326-265-5

Contents

Geoenvironmental Investigations at a Smelter Location in Bor (Serbia)

Petar Papić, Zvonimir Milijić, Jana Stojković, Jovana Milosavljević, Maja Todorović, Marina Ćuk and Željko Kamberović

Abstract

The goal of the geoenvironmental investigations was to identify and determine the degree of soil contamination present in the area of the plant planned for redevelopment. These investigations also included a determination whether the soil underlying below the investigated area should be considered a hazardous waste. The secondary goal was to determine the level of contamination in surface dust accumulated on the abandoned buildings being prepared for demolition. Soil samples from the investigated areas were analyzed for 15 different metals, fluoride and PHC concentrations, VOCs, PAHs, PCBs, pH, atrazine and simazine. In addition, samples of dust, waste and topsoil were analyzed. The results of these analyses showed that the main contaminants were heavy metals. Lead, mercury, arsenic and PCB were above Action level (The New Dutchlist) in many borehole soil samples. Contaminated soils should mainly remain *in situ* and undisturbed, since groundwater leaching would not appear to be a significant issue. According to TCLP (Toxicity Characteristic Leaching Procedure) there would be a potentially negative impact to workers during demolition and constructions activities. According to geochemical and geomechanical investigations consideration of the possibility for a new location of the wastewater treatment plant was recommended and excavations for foundations and services are required.

Keywords: Geoenvironmental investigations, heavy metals, groundwater

Introduction

All primary and secondary industries impact the environment to a greater or lesser extent, through the use of energy and raw materials. The main environmental impact is direct: as a result of emissions of pollutants into the air, water and soil. This impact may be local, transboundary or global, and it affects human health.

Soil is often seen as an inert medium and as something that only helps people in their activities. However, soil represents a complex system in which key

ISBN 978-3-923381-61-6, US ISBN 1-59326-265-5

peer reviewed paper

chemical and biochemical processes take place. In most European countries, reported soil data are qualitative in nature and the interpretation of such data requires specialized knowledge. Study and classification methods vary from country to country, and occasionally even within a single country. Information on soil and terrain properties, which affect environmental processes, is often lacking.

A broad range of diverse industries impact the environment. Some natural resources are often used in different ways by different manufacturing sectors. Table 1 contains a summary of the types of emissions generated by the non-ferrous metal industry.

Table 1: Summary of the types of emissions generated by the non-ferrous metal industry.

	Air	Water	Soil
NON-FERROUS METAL INDUSTRY	Emissions of SO_2, NO_x, Cd, Cr, Cu, Zn, Hg, As, PAH, F; HF and Ni aerosols	Wastewater loaded with metals and other solid particles, gases, fluoride, etc.	Sludge from raw material and wastewater treatment plants

Non-ferrous metal industry facilities release diverse pollutants into the atmosphere, resulting from various ore processing stages, as well as the production, smelting and purification of metals. The adverse impact of this industrial sector on the environment and human health has been relatively well studied and documented (World Health Organization). The air most often receives heavy metals, gases and other substances. Apart from mercury, heavy metals are generally not discharged into the atmosphere in their elemental form, but bound to dust particles. The deposition of these substances often leads to contamination of crops near smelters and to exposure of the local population to diverse toxic substances, depending on the type of ore processed. In the widest sense, pollutants generated by factories reach the environment in two ways: (1) by transportation of substances released into the air over small or large distances, and their subsequent deposition on the soil or water; and (2) by permeation of heavy metals and other substances through the soil into groundwater or surface water, due to improper storage of chemicals, runoff from solid waste landfills, and the like. The latter includes direct discharges of wastewater into surface water.

Many manufacturing companies have adapted their production processes to address environmental concerns. In practice, such changes are generally made in response to internal and external pressures.

One of the main and also the most difficult questions is: "Who is responsible for restoring the original state of, above all, the soil polluted by industry in the past?" Polluted soil is found in many areas where various chemicals had previously been discharged. In some countries there are hundreds of such sites where, notwithstanding the fact that the size of the individual sites is often small, pollutant concentrations are often extremely high. Some of these sites can be remediated, but remediation generally requires considerable spending.

Large industrial facilities, which were commissioned at the time when environmental issues were not addressed, are now generally obsolete. Industry is capable of developing the new processes and machinery needed to effectively reduce pollution, by introducing new technologies and modifying products, thereby also improving product quality and boosting productivity.

This paper presents the final results of geoenvironmental investigations on the locality of reconstructed smelter and sulfuric acid new factory, in the Copper Mining and Smelting Complex Bor (RTB Bor), in eastern Serbia. The goal of the geoenvironmental investigations was to identify and determine the degree of contamination present in the area of the plant planned for redevelopment. These investigations also included a determination whether the soil underlying beneath investigated area should be considered a hazardous waste. The secondary goal was to determine the level of contamination in surface dust accumulated on the abandoned buildings being prepared for demolition.

Methods

The analytical program reported in this paper was developed in accordance with a sampling program. There are three sites where new industrial projects are proposed, and they represented study areas for environmental pollution assessment. They include:

a) Study Area 1: site of existing smelter slated for reconstruction;
b) Study Area 2: site of new sulfuric acid plant;
c) Study Area 3: site of new wastewater treatment plant.

A number of sampling points were selected in each study area, including boreholes up to a depth of 10 m. The total number of these boreholes was 34, including three boreholes beyond the polluted zone, and there were only six observation wells (where groundwater was present). Most boreholes tested negative for groundwater, even during rainy periods.

The analytical program included: 101 analyses of metal concentrations (15 elements) in soil samples; 68 analyses of fluoride and PHC concentrations; 34 analyses of VOCs, PAHs, PCBs, pH, atrazine, and simazine; and analysis of hazardous waste applying the TCLP method. In addition, 74 samples of dust, waste and topsoil were analyzed applying the X-RFA method *in situ*, while 10 samples were tested for heavy metals by the TCLP method. Metal concentrations in the filtrate were compared with the filtrate quality criteria per the Canadian standard (Ontario, Canada).

Methodology: Sampling and mapping of soil, determination of coordinates (width, length and height), sampling of topsoil and subsoil, and sample homogenization. The following parameters were tested: humidity (%), pH level, fluorides, heavy metals, pesticides, PCBs, PAHs, PHCs, VOCs; TCLP method for the determination of hazardous waste. Equipment: GPS, dryer, analytical scale, furnace, pH meter, water bath, ultrasonic bath, centrifuge, ICP-OES, turbotherm, vapodest VAP, GC/FID/PTV GC 6890N, GC/MSD HP 6890 GC, HP 5793 MSD, NITON X-ray fluorescent analyzer.

Quality control: The recommendation was that 10% of all soil samples and 20% of all groundwater samples be control samples. The analytical laboratories, accredited by the relevant ministry, followed environmental quality control procedures.

Results

The geological makeup of the investigated terrain is comprised of the so-called Bor Andesitic Massif, largely hornblende-biotite andesites. They are generally covered with technogenic deposits of varying compositions.

Prior to the erection of the existing structures, a portion of the terrain designated as Study Area 1 (locations of Study Areas are shown on Figures 1 and 2) was excavated by cutting into a slope and creating a platform which holds the foundations. The thickness of the fill over this platform varies between 0.15 and 1.5 m. The locations of boreholes BH-5 and BH-2 are exceptions, as the bedrock was encountered at 2.5 m and 2.6 m, respectively, as a result of the fact that excavation was deeper within that zone for purposes of underground infrastructures. The technogenic deposits in Study Area 1 are generally comprised of sandy material combined with building debris, smelter slag and concrete.

The portion of the terrain designated as Study Area 2 is also largely (southwest part) a platform created by cutting into a slope. The andesite bedrock was encountered at depths ranging from 0.15 and 1.3 m, except for the location of borehole BH-E15 where beyond filled sand with building debris, drilling was conducted in reinforced concrete for nearly 2 m. Technogenic deposits in this part of Study Area 2 are generally comprised of concrete and filled materials with building debris and slag. In another, northeastern, part of this area, towards an abandoned mining site, there are thicker deposits of smelter slag, such that the bedrock was encountered at depths between 5.5 and 9.0 m. Borehole BH-E16 is located within the border zone between the SW and NE parts of Study Area 2.

Study Area 3 is the lower part of a previously natural slope or one of the top benches of an abandoned open pit mine. While drilling to a depth of 12 m, no bedrock was encountered. From the ground surface to a depth of 5.4-9.2 m, an unconsolidated and unformed fill was found, underlain by smelter slag.

The surface of the andesite bedrock was found to be generally degraded up to the depth investigated. The degree of degradation varied, from total grussification, where the characteristics of the rock were almost sand-like, to relatively solid rock. The effects of degradation were found to be governed by the composition and structure of the rock, as well as its depth relative to the previous natural surface of the terrain.

Upon completion of investigations at the site of the smelter which is to be reconstructed and the site of the new sulfuric acid plant (which involved the determination of more than 4000 inorganic and organic geochemical and hydrogeochemical parameters), soil pollutants were identified and quantified. The results were compared with Serbian national standards, the new Dutchlist (The Netherlands) and the Leachate Quality Criteria (Ontario, Canada), and are shown, in part, in Table 2.

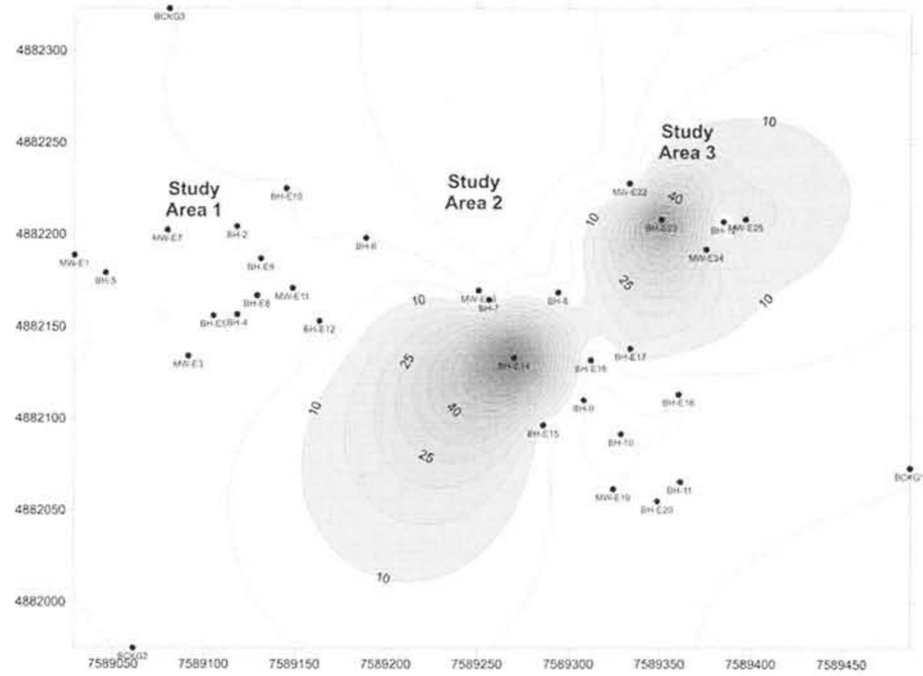


Fig. 1: Geochemical map of mercury concentrations [mg/kg].

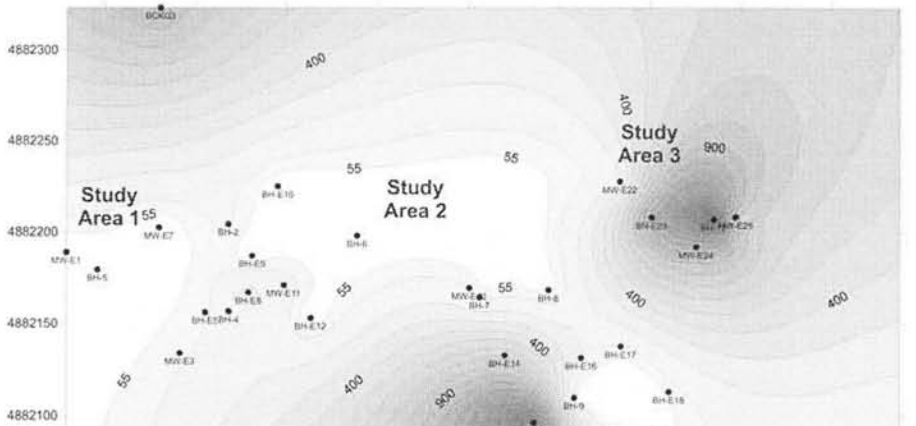


Fig. 2: Geochemical map of arsenic concentrations [mg/kg].

Table 2: Concentrations of heavy metals in soil sampled from boreholes (mg/kg), along with optimal and action concentrations, according to the Dutchlist (bolded values require action).

Parameter	pH	Pb	Cd	Zn	Cu	Cr	Ni	Hg	As	Ba
BH-8	6.6	186	1.3	95	**806.4**	10.4	14.9	0.5	28	126
BH-9	7.9	19.5	<0.2	16.8	120.7	1.5	0.8	<0.2	3.2	25.3
BH-10	4.63	13.6	<0.2	38.4	**1582**	9.9	50.5	<0.2	5.4	54.2
BH-11	7.26	**677.2**	4.8	139.1	**2929.8**	14.6	14.9	1.9	**155**	355.7
BHE-14	6.93	**6518.4**	11	558.9	**24304**	8.3	46.8	**98.6**	**697.8**	244.2
BHE-16	7.28	247.5	1.5	113	**4181**	8.3	18	0.4	**203.4**	271.2
BHE-17	8.16	**2904**	0.9	112.2	**3047**	13.2	6.7	**14.3**	**85.7**	**724.9**
BHE-18	9.16	**2024**	3.1	75.7	**1122.4**	12.9	5.7	<0.2	**69.7**	92.8
BHE-20	8.19	**619.9**	4.5	347.8	**3661.2**	98.1	31.6	0.5	**400.7**	129.6
BHE-15	4.42	**6802.6**	5.6	314.3	**9751.9**	**505.1**	35.2	7	**1717.6**	331.1
BH-7	7.27	21.7	0.7	25.9	**470.9**	1.1	1.5	<0.2	**58.5**	37.4
BH-2	4.69	468.2	9.7	**1285.2**	**127806**	5.3	160.1	<0.2	**116.3**	64.3
BHE-9	7.3	37.7	1.6	96.9	**10647.6**	1.4	18	<0.2	5.9	12.8
MWE-11	6.36	**1155.4**	10.1	**2289**	**334521**	7.6	**68670**	<0.2	**152.6**	8.4
BHE-12	6.9	25	0.4	192	**4820**	2.7	11.9	<0.2	7.5	12.6
MWE-22	3	268.4	1.1	122.1	**2013**	3.5	5.9	<0.2	**154**	71.6
BHE-23	6.53	**20790**	6.16	426.8	**9614**	25.6	21.7	**79.3**	**1188**	145.2
MWE-24	5.02	**4036.5**	4.7	334.6	**22310**	**418.6**	23.3	**17.9**	**1055.7**	162.1
BCKG 1	5	33.1	<0.2	61.3	**223.7**	0.8	1.2	<0.2	45.3	73.7
BH 4	7.73	81.3	2.8	327.5	**7941.3**	8.9	11.9	<0.2	**153.4**	34.8
BHE 5	7.9	36.7	**20**	**769.6**	**8340.8**	20.2	20	<0.2	**85.5**	23.8
BH 6	4.26	13.5	2.2	196.5	**4018.2**	1	8.1	<0.2	2.4	11.4
BHE 8	5	208.4	10.4	283	**22680**	7	**211.4**	<0.2	**238.9**	37.7
BHE 10	6.68	33	1.1	252	**2200**	2.25	17.2	<0.2	7.1	34.4
BH 12	4.85	**1523.2**	9.6	**972.2**	**28560**	50.1	27.7	2	**1792**	157
MWE 25	7.67	**5456**	**14.8**	**959.8**	**34100**	121.6	67.9	**18.5**	**798.6**	389.4
BCKG 3	5.6	38.7	<0.2	40.1	**762.4**	8.4	2.9	<0.2	**1017.7**	400.2
BCKG 2	7.49	13.9	<0.2	114.7	**1120.9**	8.9	10	<0.2	13.1	81.7
MWE 13	6.1	185.3	0.8	35.5	**558.2**	1.9	0.8	0.3	**105.1**	59.5
BH 5	8.9	22.6	5.2	284.6	**2131.8**	3.6	6.1	<0.2	37	34.5
MWE 1	7.5	4.1	6.7	262.6	**445.4**	0.4	2	<0.2	8.9	21.3
MWE 3	6.53	58.7	11.6	357	**2896.8**	2.9	5.9	<0.2	**89.1**	41.1
MWE 19	8.75	203.5	1.8	125.4	**4004.5**	84.7	34.6	<0.2	**468.6**	237.6
MWE 7	9.16	10.2	0.2	63.5	**711.4**	1.8	10.4	<0.2	5.1	15.7
Optimum		85	0.8	140	36	100	35	0.3	29	200
Action		**530**	**12**	**720**	**190**	**380**	**210**	**10**	**55**	**625**

The most significant soil contaminants detected in the boreholes (up to a depth of 1m) relative to the Dutchlist are bolded in the table and include: lead up to 20,790 mg/kg; zinc up to 2,290 mg/kg; cooper as much as 334,000 mg/kg; mercury up to 98,9 mg/kg and arsenic up to 1,800 mg/kg (Figures 1 and 2). Among other elements not included in this list, elevated concentrations were detected of selenium, vanadium and antimony. These are generally considered to be toxic elements. Mercury and arsenic concentrations were found to decline with depth, up to 3 m.

The Canadian standard (TCLP, Toxicity Characteristic Leaching Procedure) was applied to assess the toxic threat due to leaching. This procedure was used to determine the mobility of inorganic and organic analytes present in the soil. The test does not address non-dispersive forms of metals. The procedure simulates soil conditions. Over time, water and other fluids percolate into the soil and react with solid waste, potentially impacting the environment and creating a risk to human health, due to contaminant absorption. These analyses determine which contaminants have been identified and in which concentrations. If solid waste is characterized by one or several pollutants, it is considered to be characteristic hazardous waste.

The heavy metal concentrations, following TCLP and comparison with standards, show that there is no threat from potential activity of acidic agents, whereby some of the heavy metals would be transferred into solution. Exceptions were noted at several boreholes, where lead was detected in concentrations of up to 41.7 mg/L (the quality criterion is 5 mg/L). The concentrations of the other metals (Cd, Cr, Hg, As, Ba, Se and Ag) were far below respective criteria (µg/L magnitude).

With regard to organic micropollutants in the soil sampled from the boreholes, total PCBs were detected in concentrations of up to 6.63 mg/kg and they necessitate action. In nearly all the samples the presence of PHCs was recorded in excess of the optimal concentration of 50 mg/kg, ranging up to 2893 mg/kg, meaning that action needs to be taken with regard to the PCBs, being persistent organic pollutants or the so-called POPs.

Fig. 3: Field determination of heavy metal content with NITON X-ray fluorescence analyzer.

Topsoil samples were analyzed to determine the presence of 15 chemical elements, applying the XRFA method (Figure 3). The samples included dust rich in Fe and Cu, less represented elements Pb, Zn, V, Se, Sb and As, and slag with CaO and SiO_2. Heavy metal concentrations in post-TCLP extracts, applying Canadian criteria, showed that the concentrations of cadmium were elevated in several samples. Other concentrations were far below the respective criteria (Ontario, Canada).

The analyses showed that the main elements detected in the dust and waste on the ground surface were Fe, Cu, Pb and Zn. The concentrations of copper were up to 46%, of iron up to 56%, of zinc up to 4.4%, of lead up to 3.8%, of antimony up to 1%, of chromium up to 0.2%, of selenium up to 0.2% and of arsenic up to 0.3%. As such, the surface is contaminated to a certain degree. The test results indicate that the elements present in the surface samples of dust and slag belong to the group of toxic elements.

Six samples of groundwater were analyzed, including one QC sample. They were collected from four boreholes in Study Area 1 and two boreholes in Study Area 2. Borehole profiles indicated the presence of groundwater generally from degraded andesite, found near the surface, and noteworthy chemical elements found in the groundwater included fluoride, arsenic and calcium. The concentrations of other heavy metals were extremely low. This is most likely a result if the insufficient capacity of the groundwater to dissolve these substances (pH up to 9.1), as well as adsorption to clay and degraded andesite particles. The groundwater samples were extremely turbid, while the presence of pesticides, PCBs, PAHs, PHCs or VOCs was not detected.

Conclusions

Geoenvironmental investigations were conducted at 34 boreholes at the site of a smelter of the Copper Mining and Smelting Complex Bor, in eastern Serbia. The test results allowed for very useful conclusions to be drawn about the quality of the soil which will hold the new sulfuric acid plant. They unequivocally pointed to the degree of contamination, as a result of prior metallurgical activity. TCLP analyses imparted confidence with regard to any leaching of heavy metals from the soil, through the action of atmospheric precipitation (whose pH levels may be low) or groundwater. Based on the ecogeochemical test results, Study Area 3 is the primary area characteristic of the presence of Pb, Hg, As and PCBs. The results indicated that the technogenic deposits (smelter slag and debris) were the main source of the identified highly-toxic elements, and that the presence of PCBs was a result of operation of transformer stations, which were previously located in this part of the terrain.

The main tasks placed before the ecogeological test program were to detect any presence of hazardous waste and determine any soil pollution. The main conclusions suggest that hazardous waste is present. However, judging by the TCLP tests of heavy metals, only cadmium exceeds the quality criterion, in three dust samples. Regardless, there is the potential for an adverse impact on the workers who will participate in the reconstruction of the smelter and the building of the new plant. The soil is polluted, given that the presence of Pb, Hg, As and PCBs in excess of action (removal) concentrations, based on the Dutchlist, was detected in many soil samples collected from the boreholes in Study Area 3.

Based on geomechanical and geochemical tests, the recommendation is to consider another site for the wastewater treatment plant (Study Area 2 instead of Study Area 3).

References

Papić, P., Stojković, J. and Todorović, M. (2011): Report of geoenvironmental investigations on the locality for reconstructed smelter and sulfuric acid new plant (in Serbian), University of Belgrade, Faculty of Mining and Geology, Belgrade

Intervention values and target values – soil quality standards (The New Dutchlist), The Ministry of Housing, Spatial Planning and Environment, The Netherlands

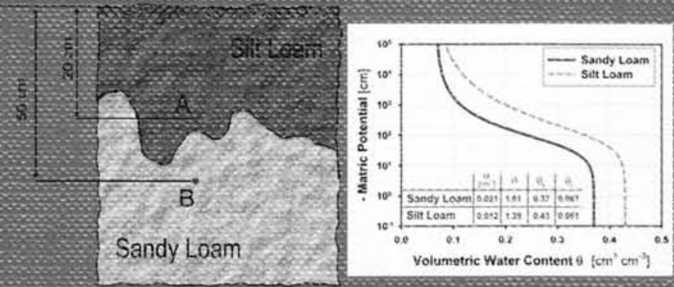
http://www.EHSO.com (The EPA TCLP: Toxicity Characteristic Leaching Procedure and Characteristic Hazardous Wastes)

Addresses of authors:
Petar Papić
Jana Stojković
Jovana Milosavljević
Maja Todorović
Marina Ćuk
University of Belgrade, Faculty of Mining and Geology
Djusina 7
11000 Belgrade, Serbia
ppapic@rgf.bg.ac.rs
jana.stojkovic@rgf.bg.ac.rs
jovana.d.milosavljevic@gmail.com
maja.todorovic87@gmail.com
marinacuk.rgf@gmail.com
Zvonimir Milijić
RTB Bor Group
Djordja Vajferta 29
19210 Bor, Serbia
zvonimir.milijic@gmail.com
Željko Kamberović
University of Belgrade, Faculty of Technology and Metallurgy
Karnegijeva 4
11000 Belgrade, Serbia
kamber@tmf.bg.ac.rs

GeoEcology textbook

Naftali Lazarovitch & Arthur W. Warrick (Editors)

Exercises in Soil Physics



352 pages, numerous mathematical equations, figures, tables. Appendix on CD
ISBN 978-3-923381-60-9 US ISBN 1-59326-264-7, € 55.00

This book is designed to complement available soil physics and vadose zone hydrology texts by providing additional practice exercises. Material is included for beginning to graduate level students and may be studied either independently or in conjunction with formal classes. More than 200 problems are presented with detailed answers. *(from Preface)*

CATENA VERLAG GMBH *GeoScience Publisher*
Ärmelgasse 11, 35447 Reiskirchen, Germany
Phone + fax (+49)6408-64978
catenaverl@aol.com, www.catena-verlag.de