

Dynamics and evolution of water and soil pollution with heavy metals in the vicinity of the KCM smelter, Plovdiv area, Bulgaria

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The study presents the results of a decade-long investigation of the environmental status in the area of the KCM smelter (Plovdiv, Bulgaria). All pollution sources, pathways and targets in the area are recognized and their roles in the overall environmental status are evaluated. The range and direction of seasonal dynamics of all analyzed factors is determined on a 10 years long base. Long-term evolutionary trends for all analyzed factors are identified and evaluated too. Current environmental situation is found to be far from alerting, but certain recommendations for further avoidance of pollution spread, as well as proper use of certain water and land resources are made.

Keywords: ground and surface water, monitoring, non-ferrous metal smelter, efflorescent and sulfate minerals, Thracian depression, Bulgaria.

INTRODUCTION

In the period 2001-2004 a large team of Bulgarian, French and Belgian researchers launched an extended, NATO SFP funded project for characterization and process modelling of environmental pollution with heavy metals and metalloids in the vicinity of the KCM smelter, Plovdiv area, Bulgaria. The results from this study are published in numerous papers and presented at numerous local and international scientific forums [1-14]. In 2009, five years after the end of the project and the implementation of the recommendations, which came out from the study results, a new state of the art evaluation has been launched, in order to check the effectiveness of the implemented measures. It was based on both a new sampling campaign in the most sensitive key-points of the area (determined during the initial study) and the results from the regular monitoring, meanwhile performed by the MOEW (Ministry Of Environment and Waters). Current paper presents the results of this study.

GEOLOGICAL SETTING AND HYDROGEOLOGICAL CONDITIONS

The non-ferrous metal smelter KCM is situated in southern Bulgaria (Fig. 1) in the tectonically predetermined Upper Thracian depression [15], surrounded by the Rhodopean and Sredna Gora

mountain massifs. The studied area (more than 200 km²) is located south of the Maritza river and lays on the left-bank terrace of Chepelarska (Chaya) river, up to the town of Asenovgrad. Its northern part is filled with Pliocene sedimentary rocks while Quaternary alluvial deposits and drift material build up its southern part [16, 17]. Quaternary and Pliocene sediments (10-300 m) are lithologically monotonous in the studied area. The basement and collars of this tectonic structure are built up by various rock types, mainly magmatic and metamorphic, containing crack hosted ground waters. Two porous aquifers are to be taken in consideration: the Quaternary sediments and the Pliocene sands. The deeper Neogene clay-sandy deposit plays the role of a lower aquiclude. The main pollution target in the area is the shallower Quaternary aquifer. However, it was found out that both aquifers are hydraulically connected in some locations [18, 19]. The aquifers are unconfined or confined with variable heads. The filtration properties of the Quaternary alluvial deposits (up to 30 m effective thickness) are relatively high, due to the high effective porosity and purity of the sandy-gravel layers. Its hydraulic conductivity is 50 to 300 m/day. Main local hydrogeological features of the Quaternary aquifer were determined by newer studies [5, 11, 20]: general flow direction of the ground waters is south to north, towards the Maritza river, which is also the main discharge acceptor (Fig. 1); recharge is provided by direct filtration of precipitations and surface waters, streaming down the northern Rhodopean slopes. Intensive watering of the agricultural lands in the area also plays a

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certain recharging role; the depth of the aquifer, below the surface depends on local topography and varies from 2.2-2.5 m (near Maritsa river) down to 25-26 m in the southernmost part of the area [11].

More specific recharge-discharge role plays the Chepelarska river [20]. Its river bed is canalized from its entrance in the area (south from the town of Assenovgrad) down to the area affected by the KCM activity. Hence, no hydraulic connection with the aquifer exists thus far. However, at the end of the river, bed correction between 0.158 and 0.386 m³/s sink in the gravel, causes a considerable point recharge [20]. From this point, down to the village of Katunitsa, Chepelarska river recharges the aquifer, while downstream, until its run into Maritsa River, it discharges it.

The Quaternary aquifer is the main water supply in the region. Numerous water wells have been drilled in this aquifer and supply public areas in the region. The total amount of used groundwater is up to 1 m³/s and the biggest pumping station is at KCM, where 10 wells with mean flow-rate 350-400 l/s have been drilled.

Hydrogeological conditions in the area are the key in prediction of the pollutant migration towards and along with the ground waters.

THE KCM SMELTER AND TYPES OF POLLUTION RELATED TO ITS ACTIVITY

The smelter was established in 1961 for processing of the Madan area lead-zinc ores. During its early history till mid 90-ies, its operation caused considerable environmental problems in the region, which is one of the most fertile ones in Bulgaria [21-24]. Starting with a big targeted loan from the Japan Bank for International Cooperation (JBIC) in 1995, KCM authorities demonstrate a strong will to re-direct the environmental policy of the company towards a respectably responsible behavior. In 1999 the first *Report for environmental damages caused by KCM Ltd., Plovdiv*. (N. Liakov, University of Chemical Technology and Metallurgy, Sofia, Bulgaria) is issued. Ever since then, the area affected by KCM activities is a subject of own monitoring by the company. Respectful amounts of funds are also invested in measures for diminishing all kinds of polluting emissions.

Our previous study in the area [25] identified the main sources of the pollution there (Fig. 1). Their contemporary status is summarized briefly below:

- Direct pollution of soil and ground waters within the factory ground is caused by ore concentrates, reagents and stock deposited, transported and processed there. This was one of

the most severe polluting mechanisms in the past. Nowadays both material storage and transportation are made in a way, avoiding spilling or infiltration in the ground. Dust spreading outside the processing plants is strongly reduced too.

- Indirect (airborne) pollution of wider land area is caused by factory chimneys, through which both dust and gaseous pollutants can be transported by wind, to reach distant land areas. This pollution mechanism was one of the first, targeted by company's environmental strategy: Installing proper chimney filters still in middle 90-ies, reduced airborne pollution by near 90%.

- Waste waters, generated in amounts exceeding 300 l/s by technological processes, used to be the main source of ground and surface water pollution in the past. After the settlement of a purification station in 2005, however, this source of pollution was practically discontinued.

- The two dumps are the main pollution sources outside the factory ground.

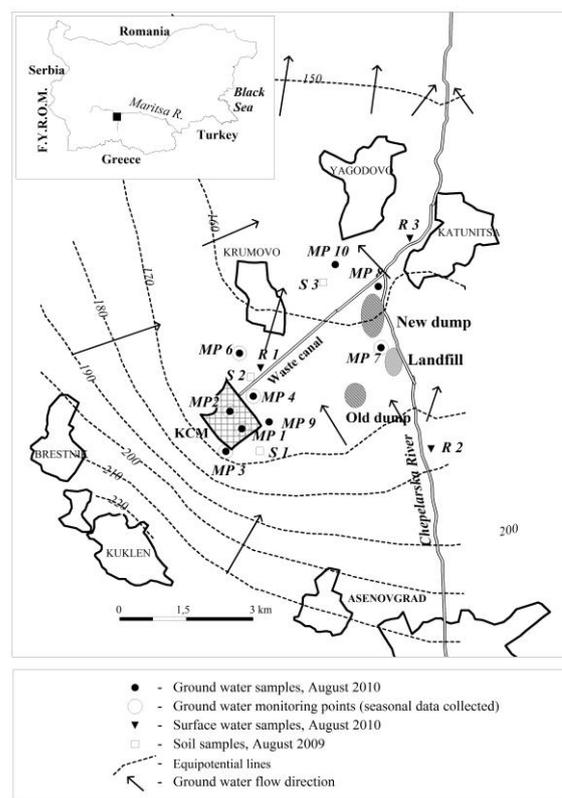


Fig. 1. Situation plan of the studied area.

The *older one* is not in operation long ago, but is still generating both dust pollution of the surrounding land area and chemical pollution of the ground waters beneath. Although more or less stable, this dump keeps slowly cracking and demolishing, which constantly uncovers fresh material to react with rainfall water.

The *new dump* used to be a very serious pollutant in the area until 2008, when a significant part of it was removed and the rest was re-deposited in a new, properly equipped dump site, adequately isolated and supplied with draining and purification system for the infiltrating rainfall waters.

- Sources not connected to KCM: Populated places, old landfill, fertilized agricultural lands. Although not as important, the net influence of these sources should also be taken in consideration.

METHODS

In both 2001-2004 and 2009-2010 campaigns same sampling and analytical procedures have been followed in order to make sure that comparable results will be obtained. Since during the first period some of the required ISO standards had still not been established, their respective drafts, available by that time from the ISO site, have been used.

Water samples were collected from river streams, canals and wells (hydrogeological monitoring points - MP), using bailer and following the standard procedure ISO 5667-1, 2, 3, 6, 10, 11, 14. Samples were filtered through 0.45 µm sieves and conserved with concentrated HNO₃ until pH of <2 was reached. Total mineralization was measured with electronic conductometer Seibold in the bailer, before filtering and conservation.

Soil samples were collected using stainless steel hand drill and/or shovel, following the standard procedure ISO 5667-12:2002 for the canal sediments and ISO 10381-1:2005 and 10381-2:2005 for soils on farming lands.

In order to determine the mobile forms of chemical species in soils, during the 2001-2004 campaign, soil samples were subjected to sequential chemical extraction (SCE) [26-28]. Since batch leaching test, as part of the SCE, showed most informative results, only this test was applied during the next campaign (2009-2010). The standard procedure used was draft: ISO 18749:

Laboratory analyses of chemical elements in waters, soils (completely dissolved in 3 acids) and mobile chemical species (batch solutions from leaching tests) were performed using ICP-AES (Jobin Yvon, Ultima 2), in the Geological Institute, BAS, using the standard procedure ISO 11885:2001.

Saturation indices and speciations of the waters are calculated using the Visual MINTEQ 3.0 software and databases (<http://www2.lwr.kth.se/English/Oursoftware/vminteq/index.html>).

RESULTS

Waters: seasonal dynamics 2009-2010

Total Dissolved Solids. The following Fig. 2 represents the seasonal variation of Total Dissolved Solids (TDS) in 6 ground water drill wells in the area, measured quarterly during the year 2009. While the mineralization in the wells from the relatively non-polluted area, providing technical water for the KCM (MP 6), remains rather uniform (variation below 80 mg/l), the wells within the factory quarters (MP1, 2 and 3) show variations as big as 300-400 mg/l. Along with the human activity, this behavior is due to the fact that this aquifer is far from the river, hence hydraulic connection with it almost does not exist, thus its abundance is in pronounced dependence on the level of precipitation. During dry periods water level in these wells can drop down to below 1 m (as registered for drill well 3) and turns dead, causing overconcentration of dissolved phases. Pumping can change this situation. Although drill well 6 is not much closer to the river, such phenomenon is not observed there, because the instant consumption of its water reserves results in instant dilution by the attracted fresh water from the surrounding aquifer.

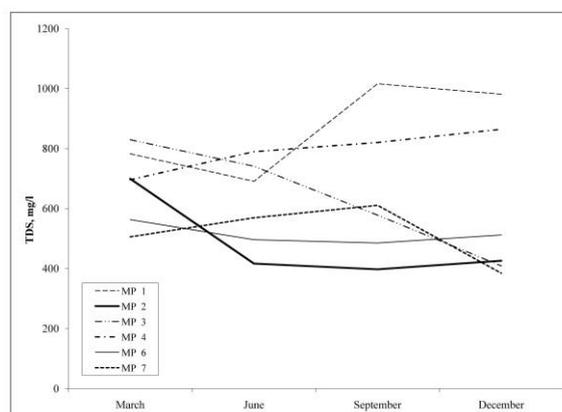


Fig. 2. Variations of TDS in the monitoring stations during 2009.

Macro composition. As seen on Fig. 3 dominant waters have hydrocarbonate Ca character, with insignificant seasonal variations.

Sulfate and heavy metals. As seen on Fig. 4, in MP1 and rarer 2 and 3 (inside or close to the factory ground) sulfate concentrations often show peaks, even above the Upper Regulation Limits (URL, as postulated in State Gazette 87/30.10.2007 and addenda 2/08.01.2010 and 15/21.02.2012) No off-limit values are registered for Cd and Zn, but Pb keeps 2-7 times above the regulation in most stations.

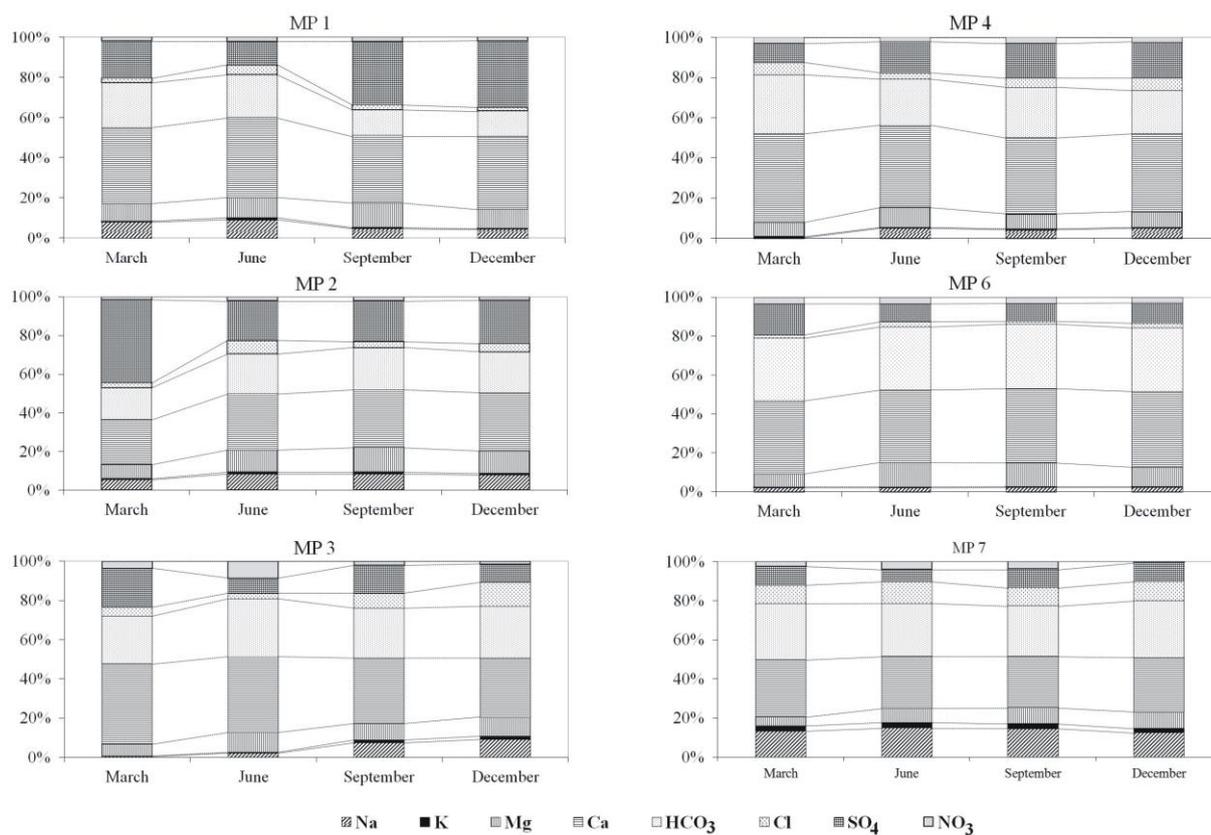


Fig. 3. Characteristics of the macro-composition of waters in the monitoring stations, 2009.

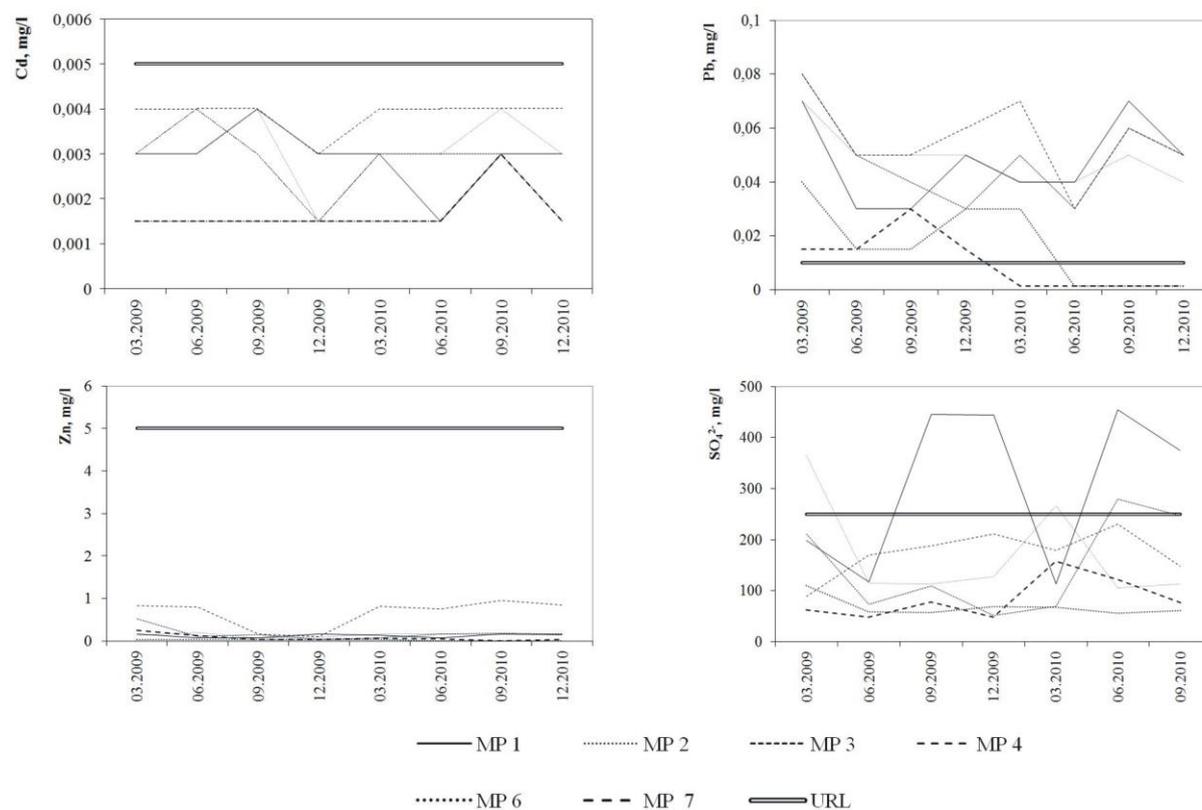


Fig. 4. Variation in levels of SO₄, Zn, Cd, Pb in all monitoring stations, 2009-2010.

Only after the spring of 2010 the drill wells situated farther from the factory (6 and 7) show Pb values below URL.

Nitrates. Nitrates also show random over-regulation bursts, which are most probably due to treatment of the agricultural lands with fertilizers and have no connection with the KCM activity.

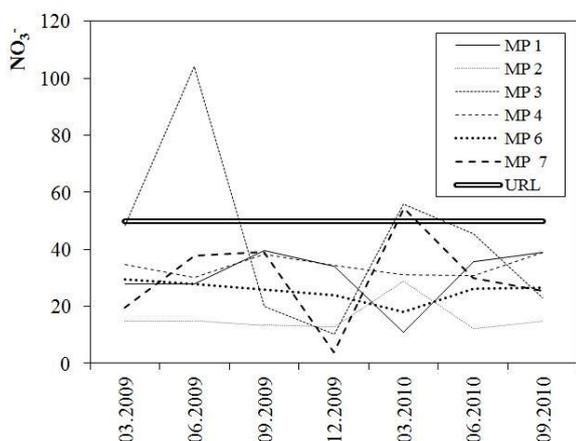


Fig. 5. Nitrate concentrations in all monitoring stations, 2009.

Waters: long-term evolution trends

Data collected lately (2009-2010) were compared to the data from the previous study period (2001-2004) and interim monitoring data. Figures 6-9 represent the concentration trends of the most important pollutants in the 4 monitoring wells situated inside or close to the factory.

Along with the general diminishing trend for all pollutants in all wells, a severe one-time polluting event is registered in 2001. It is recorded on all diagrams, but shows different extent in the different wells. MP4 is the one mostly affected. In order to make it possible to represent this event in MP4, the vertical scale of the diagrams for this well is significantly smaller. The frames of the spaces, comparable with other 3 diagrams, are shown there with dashed contour.

Zn concentrations in all monitored wells are around 0.2 mg/l, with negligible variations and remain much below the regulation limit (5 mg/l) during the whole monitoring period. Even during the one-time event in 2001, when the concentrations of all monitored pollutants dramatically rise, Zn remains below the regulation limit in 3 of the 4 monitored wells. Only in MP4 Zn concentration reaches 2 times above the regulation limit, remaining off-limit until the end of 2002 and stabilizes at around 0.5 mg/l afterwards.

Cd concentrations in the beginning of the monitoring period are of the order 0.025 mg/l (5-7 times above the regulation limit 0.005 mg/l), slowly

decreasing until 2006, when they instantly stabilize under the URL. The one exception from this trend is the pollution event in 2001, when URL is overridden from 15 times in MP1 to 150 times in MP4. MP4 is again the mostly affected well, and Cd concentration there drops below URL only after 2006.

Pb concentrations in all monitored wells show insignificant dynamics and levels of the order 0.1 mg/l (10 times above the URL of 0.01 mg/l), demonstrating slow diminishing trend, but remaining above URL until current. Contrary to Zn and Cd, the polluting event from 2001 is recorded only in MP3. A common behavior, linking all 3 considered pollutants is that the 2001 event is markedly better expressed in wells outside the factory, while wells inside are less or not at all affected. This fact gives some grounds to think that in 2001 some primary source of pollution existed outside the factory.

Sulfate concentrations keep under the regulation limit in all monitored wells in the beginning of the monitoring period and even show some diminishing trend until 2006. However, a slow but stable increasing trend is recorded afterwards. Currently, wells inside the factory show levels of the order 2 times above URL, while these outside approach this limit. Level dynamics is increasing too.

Waters: speciation modelling

Chemical composition alone is not enough for understanding the processes of water pollution and purification. Especially when passive remediation strategy is chosen, like that in the KCM area, limiting undertaken measures to just reducing the pollution sources, it is very important to know the chemical speciation, because it is the key to understanding the natural, self-purification mechanisms.

In order to do so, we used the modelling software Visual MINTEQ, allowing the determination of migration forms of the elements and the direction of the dissolution - precipitation processes for the existing mineral phases. Following figures show the modelled speciation of the most important heavy metal pollutants in the area: Cd, Pb and Zn, as follows:

Cd is represented mainly by Cd⁺² ions - 52-84%. Most of the other Cd forms are less than 1%. More significant amounts show:

- MP4 - Cd⁺² > CdCl⁺ > CdHCO₃⁺ > CdSO₄(aq) > CdCO₃(aq);
- MP7 - Cd⁺² > CdCl⁺ > CdHCO₃⁺;

- MP9 - $\text{Cd}^{+2} > \text{CdHCO}_3^+ > \text{CdSO}_4(\text{aq}) > \text{CdCO}_3(\text{aq}) > \text{CdCl}^+$;
- R1 - $\text{Cd}^{+2} > \text{CdCO}_3(\text{aq}) > \text{CdSO}_4(\text{aq}) > \text{CdCl}^+ > \text{Cd}(\text{CO}_3)_2^{-2} > \text{CdHCO}_3^+$;
- R3 - $\text{Cd}^{+2} > \text{CdSO}_4(\text{aq}) > \text{CdCO}_3 > \text{CdCl}^+ > \text{CdHCO}_3^+(\text{aq})$.
- MP1 - $\text{Zn}^{+2} > \text{ZnCO}_3(\text{aq}) > \text{ZnHCO}_3^+ > \text{Zn}(\text{OH})_2(\text{aq}) > \text{ZnSO}_4(\text{aq}) > \text{ZnOH}^+$;
- MP4 - $\text{Zn}^{+2} > \text{ZnHCO}_3^+ > \text{ZnCO}_3(\text{aq}) > \text{ZnSO}_4(\text{aq})$;
- MP6 - $\text{Zn}^{+2} > \text{ZnCO}_3(\text{aq}) > \text{ZnHCO}_3^+ > \text{ZnSO}_4(\text{aq})$;
- R1 - $\text{Zn}(\text{OH})_2(\text{aq}) > \text{ZnCO}_3(\text{aq}) > \text{Zn}^{+2} > \text{ZnOH}^+ > \text{ZnSO}_4(\text{aq})$;
- R3 - $\text{Zn}^{+2} > \text{ZnCO}_3(\text{aq}) > \text{ZnSO}_4(\text{aq}) > \text{ZnHCO}_3^+ > \text{ZnOH}^+ > \text{Zn}(\text{OH})_2(\text{aq})$.

Pb is represented mainly by PbCO_3 - 58-67%. The following components are found in concentrations above 1%:

- MP4 - $\text{PbCO}_3(\text{aq}) > \text{PbHCO}_3^+ > \text{Pb}^{+2} > \text{PbOH}^+ > \text{PbSO}_4(\text{aq})$
- R1 - $\text{PbCO}_3(\text{aq}) > \text{Pb}(\text{CO}_3)_2^{-2} > \text{PbOH}^+ > \text{Pb}(\text{OH})_2$;
- R3 - $\text{PbCO}_3(\text{aq}) > \text{PbHCO}_3^+ > \text{Pb}^{+2} > \text{PbOH}^+ > \text{PbSO}_4(\text{aq}) > \text{Pb}(\text{CO}_3)_2^{-2}$.

Zn is represented mainly by Zn^{+2} ions (56-82%), with the exception of the waste water canal (R1), where the dominant form is Zn hydroxide 59%. Following phases are represented above 1%:

Same software Visual Minteq was used to determine the saturation indices for different minerals. This parameter can serve in forecasting the probability for dissolution (negative index values) or precipitation (positive values) for the respective mineral (Table 2). In order to make the results clearer, we only show mineral species with positive (normal font) and close to zero (italics) index values. In this way it becomes clearly visible that the only mineral phases tending to precipitate are Fe, Mg and Mn oxides and hydroxides, while Ca and Mg carbonates can only temporarily form solid phases, which will easily dissolve back at any minor change in water composition.

Table 1. Descriptions of sampling and monitoring points involved in this study. Locations are given on Fig. 1

Point symbol, as labeled on Fig. 1	Type	Description
MP 1	Groundwater	Monitoring well on factory ground, close to Zn production shed
MP 2	Groundwater	Monitoring well on factory ground, close to Pb production shed
MP 3	Groundwater	Monitoring well outside the factory ground, close to its SW corner
MP 4	Groundwater	Monitoring well south from the waste water canal, close to its beginning
MP 6	Groundwater	Well from the factory water supply system
MP 7	Groundwater	Monitoring well between the new clinker dump and the old domestic waste landfill of Assenovgrad
MP 8	Groundwater	Monitoring well between the new clinker dump and the waste water canal
MP 9	Groundwater	Well used for water supply of the Litex gas station, close to the NE corner of the factory ground.
MP 10	Groundwater	Monitoring well, NW from the end of the waste water canal
R 1	Waste water	Surface water sample: beginning of the waste water canal
R 2	River	Surface water sample: Chepelarska river, before entering the territory affected by KCM activity.
R 3	River	Surface water sample: Chepelarska river, after the inflow of the waste water canal.
S 1	Soil	Agricultural land, southern (lee) from the factory ground, strongly affected by airborne pollution.
S 2	Soil	Agricultural land, close to the beginning of the waste water canal
S 3	Soil	Agricultural land, close to the end of the waste water canal and the new clinker dump

Table 2. Saturation indices for different minerals (undersaturated phases are shown in italics)

Mineral	MP1	MP2	MP3	MP4	MP6	MP7	MP8	MP9	MP10	R1	R2	R3
bixbyite (Mn,Fe) ₂ O ₃	35.1	29.2	29.4	28.7	12.2	31.1	31.8	28.7	35.7	40.7	35.0	39.3
hematite Fe ₂ O ₃	14.0	13.9	14.0	13.7	14.6	14.0	13.4	13.8	16.3	16.8	15.4	16.8
magnesioferite MgFe ₂ O ₄	7.5	6.1	6.1	5.4	7.2	5.3	4.6	5.9	9.4	11.9	8.7	12.0
maghemite γ-Fe ₂ O ₃	6.8	6.4	6.8	6.5	7.5	6.9	6.3	6.4	8.6	9.8	7.9	9.1
goethite FeO(OH)	5.8	5.7	5.8	5.7	6.1	5.8	5.5	5.7	7.0	7.2	6.5	7.2
lepidocrocite γ-FeO(OH)	5.2	5.0	5.2	5.1	5.6	5.3	5.0	5.0	6.1	6.7	5.8	6.4
ferrihydrate Fe ₂ O ₃ *½H ₂ O	2.9	2.9	2.9	2.8	3.2	2.9	2.6	2.9	4.2	4.3	3.7	4.5
dolomite CaMg(CO ₃) ₂	0.6	-0.4	-0.3	-0.5	0.0	-1.3	-1.8	-0.3	-1.9	2.0	0.1	1.6
calcite CaCO ₃	0.4	0.0	0.1	0.2	0.2	-0.4	-0.6	0.1	-0.7	1.4	0.3	1.1

Table 3. Comparison of recent leaching test results (2010) with data from the 2001-2004 campaign. Values exceeding action limit are shown in bold, those between target and action – in italics. Values below detection limit are pointed by “nd”

Sample	Concentration (µg/l), 2001						Concentration (µg/l), 2010						
	Cd	Zn	Pb	Cu	Cr	Co	Cd	Zn	Pb	Cu	Cr	Co	
S1	76	1371	641	136	4	3	13	221	nd	31	nd	nd	
S2	5	32	17	36	2	1	nd	nd	nd	nd	nd	nd	
S3	7	48	20	68	3	1	nd	15	nd	110	nd	nd	
Boundary levels according to the New Dutch list						Sample	Decrease (times)						
Action	6	800	75	75	30	100	S1	5.8	6.2	many	4.4	many	many
Target	0.4	65	15	15	1	20	S2	many	many	many	2.6	many	many
							S3	many	3.2	many	0.6	many	many

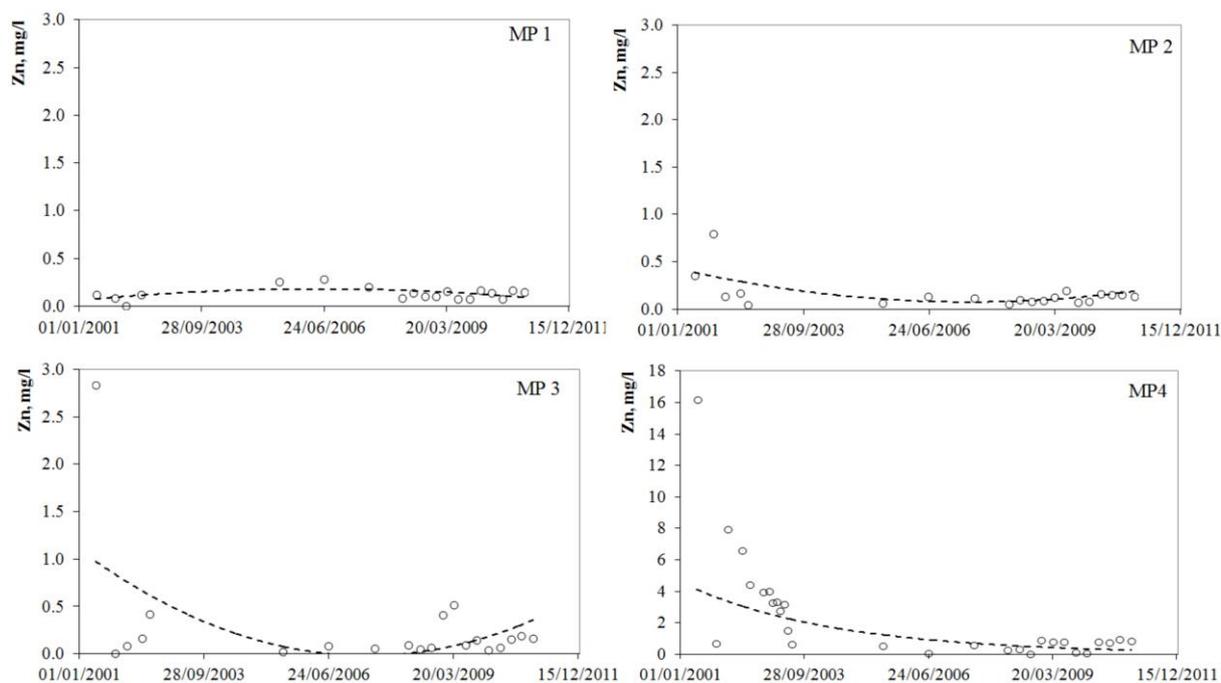


Fig. 6. Zn concentration trend in monitoring stations MP1 - MP4.

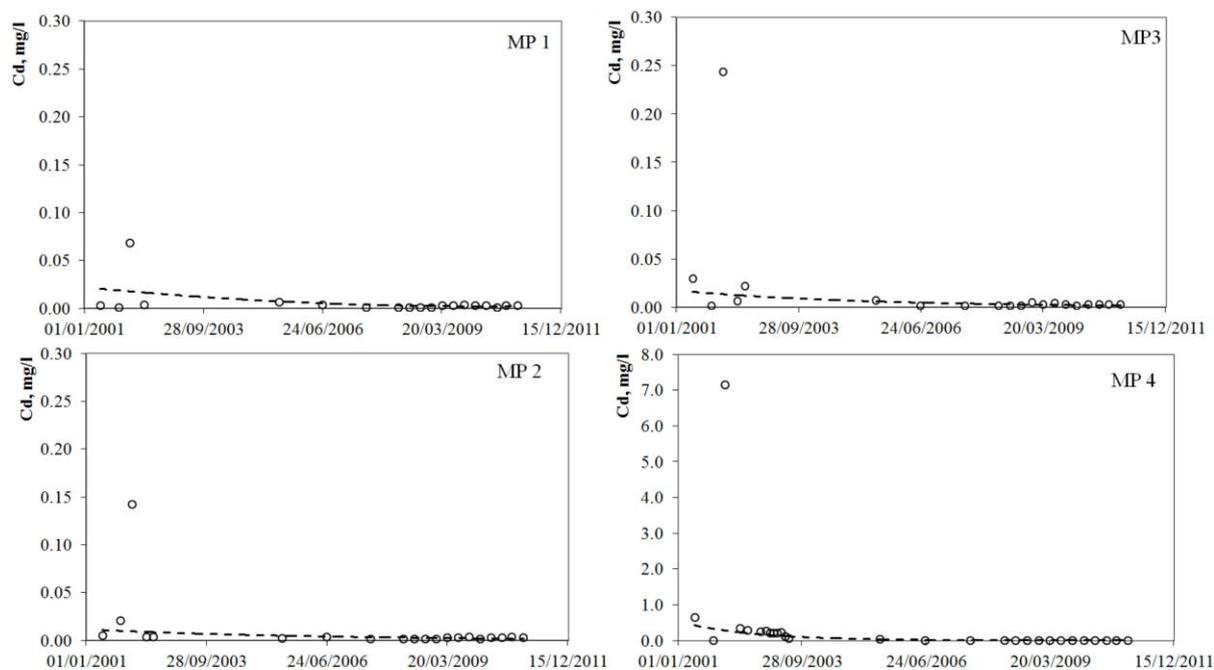


Fig. 7. Cd concentration trend in monitoring stations MP1 - MP4.

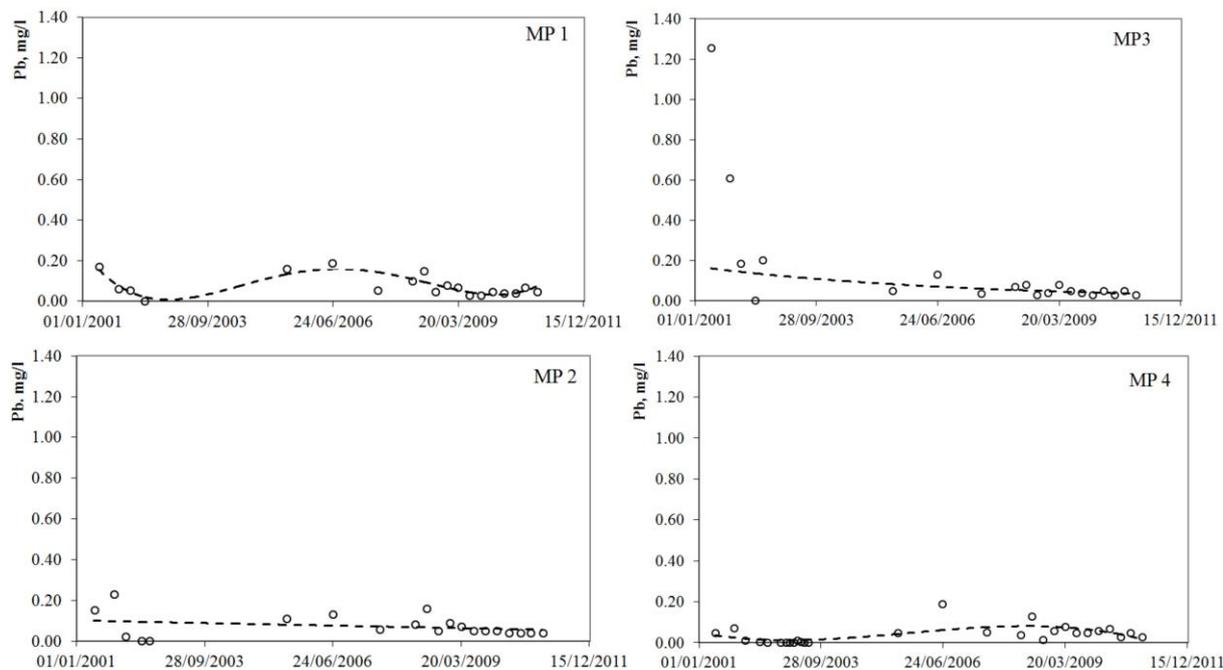


Fig. 8. Pb concentration trend in monitoring stations MP1 - MP4.

Waters: hydrodynamic modelling

Last, but not least, the hydrodynamics of the aquifer is an important key to understanding the hydro-chemical dynamics, since dilution of the ground water is a factor that can dramatically change its chemical equilibrium and it is the one that can do so faster than any other. Therefore, a thorough investigation of the Chepelarska river-bed

correction was undertaken, since it was expected to be a potential source of serious hydrodynamic disturbances [20]. The most important result of this study is that in the corrected part of the river bed, the feeding of the aquifer has a rate of 70 l/s. This causes both elevation of ground water levels close to the river bed (even partial swamping) and intensive dilution of the aquifer.

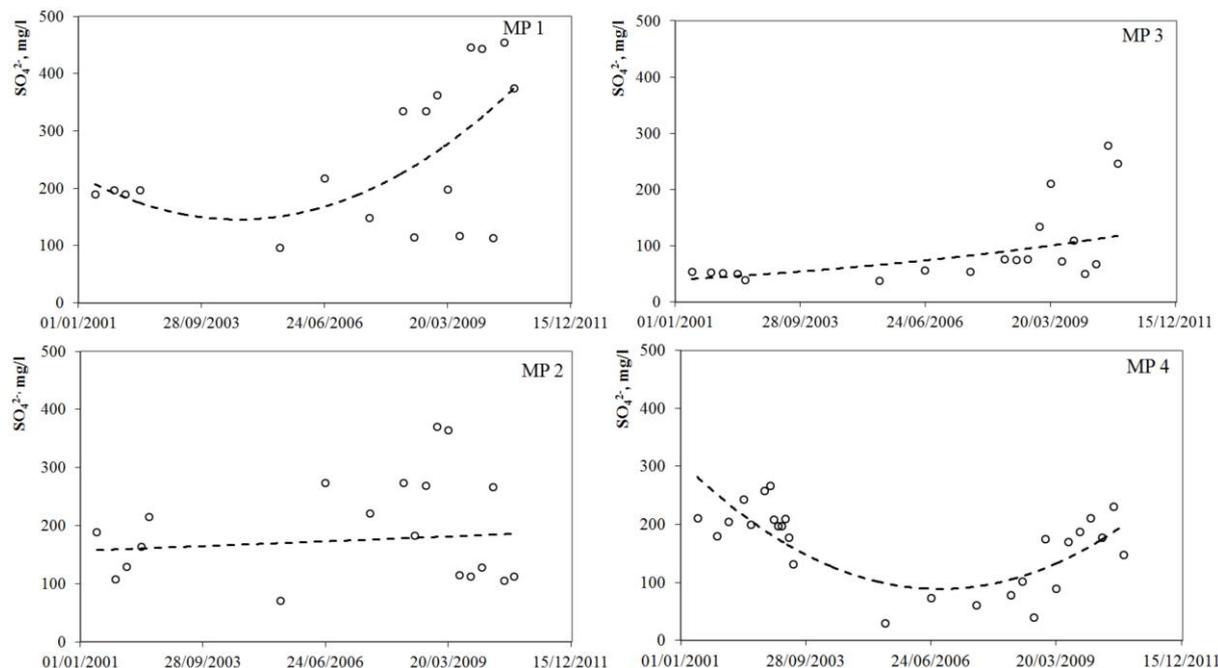


Fig. 9. Sulfate concentration trend in monitoring stations MP1 - MP4.

Soils: bulk macro and micro chemical composition

The bulk macro-chemical composition of three soil samples collected close to the waste water canal (the most important potential source of soil pollution, remaining after the remediation measures undertaken after 2004) is given on Fig. 10. Two of these samples (S2 and S3) show similar compositions, represented as oxides on the pie diagrams: SiO₂ 60-65%; CaO 15-17%; Al₂O₃ 9-10%; other alkali and transition metal oxides – below 10%. This composition well corresponds to the normally expected mineral composition of the soils in the area, dominated by feldspars, amphiboles, quartz and clay ± some carbonates. Sample S1, however, significantly differs from this pattern: SiO₂ 40%; Fe₂O₃ 36% and S 9%. This composition shows significant sulfide (sulfate) content and rusty (iron oxide) material, which can only come through direct pollution from ore concentrate.

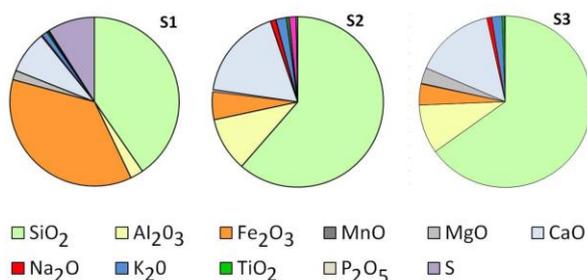


Fig. 10. Bulk macro chemical composition of soils from the banks of the waste water canal, 2010.

On the following Fig. 11 this same sample also shows the highest contents of heavy metals there and seemingly keeps acting as a long lasting secondary source of pollution.

Soils: pollution sources and pathways

The two main pathways of soil pollution are: 1) airborne pollution with industrial dust; and 2) *in situ* deposition of toxic compounds from infiltrating polluted waters. The potential sources of dust pollution in the area are also two: 1) the factory buildings and chimney; 2) the two clinker dumps. The only source of water-transported pollution is the waste water canal, and this way of pollution was believed to apply only for cases of leakage from canal damages. Our study proved yet another case of polluting from this source: deposition of canal mud on its banks during maintenance cleaning works.

Soils: mobile portion of the heavy metal contents

Even high concentrations of heavy metals in soils can be ecologically safe, if fixed in insoluble mineral compounds and *vice versa*: even low concentrations of highly soluble toxic compounds can impose high ecological threat. Therefore, determination of the mobile portion of the heavy metal content is the crucial point in risk assessment of a polluted soil area. This has been done during the 2001-2004 campaign and the results were rather distressing.

In order to evaluate the effect of the remediation and elimination of pollution sources in the area,

most important sampling points used during the 2001-2004 campaign, were re-sampled in 2010 and subjected to the same batch leaching test as the one previously performed. Both result sets were then compared as shown in Table 1, to reveal the evolution trends.

The positions of the sampling points, chosen for re-sampling in this study, were determined by the sources and pathways of pollution that they presumably reflect as follows:

S1: This point was found to represent the absolute maximum values for all heavy metals registered in the area during the 2001-2004 period. The recent pollution here is entirely airborne, mostly by direct emissions from the factory buildings and inner factory space. However, it is not impossible that during certain past period, ore concentrates have been deposited here, if not enough space was available within the factory ground. Pollution from the chimney also contributes for the situation, to a lesser extent.

S2: Soil pollution here is entirely due to infiltrated waste waters, through canal leakages. Rarer, but significant pollution is caused by maintenance (clean up) activities, done regularly, when sand and clay material from the canal bottom are extracted and deposited at its banks. As far as extracted material is mostly built of clay, which is known to show very high sorption ability towards heavy metals, this material, deposited on the canal banks represents a long acting secondary source of pollution, both for the soils and the ground waters in the area.

S3: The pollution here is from combined influence: a. direct airborne transport of dust from the dump; b. before the remediation, when the material was deposited directly on the unsecured ground, without any hydro-isolation, the precipitation, infiltrated through the waste, used to reach ground water, mobilizing there heavy metals and sulfate ions; c. as far as the area is in the close vicinity of the waste water canal, the above described influence is in effect here too.

Before being able to comment the obtained results, few words are worth on the New Dutch List values, used for reference in the above table. Since both EC and Bulgarian regulation has no explicit norms for all elements in soils, and especially no norms for leaching test values, the popular Dutch list values (lower left on Table 3) were employed. This document is used in most European studies as a comparison background, when local regulation is not enough specific. Its upper row of values (bold) are concentrations of the respective element in water (leachate), requiring immediate action. The

lower (normal) values are target values, more or less corresponding to background values in Dutch soils, far from any pollutant. Any values between these two require monitoring, but not immediate action. Similar font code we used for categorizing data in result sets above: bold – requiring action; italics – requiring monitoring; normal – below the target value.

The data in Table 1 can be summarized as follows:

1. In 2001 all the elements except Co, in all sampling points, except Zn in points 2 and 3, required action or monitoring. In 2010 most elements in most points are not just below the target values, but most of them even below detection limits. This fact proves a clear reduction of the pollution levels, demonstrated by the normal font code in lower right quarter of the table, showing levels of reduction in times.

2. The extremely polluted point *S1* still shows Cu and Zn values requiring monitoring, and Cd – requiring action, but all values are significantly lower than previously registered and the high levels of reduction convince us, that within few years this point will also reach target values, without any special measures to be undertaken. In any case, for the moment it is not recommended to use this area for agricultural activities.

3. There is one exception from the very promising trend of pollution reduction: the Cu in point 3. This is the only case, where we registered increase of the pollutant concentration (bold in lower right quarter). The registered value even changes the category of this point from “requiring monitoring” in 2001 to “requiring action” in 2010 (bold in upper right quarter). The reason for this phenomenon is, beyond any doubt, the cardinal reorganization of the clinker depot nearby, which mobilized vast amounts of soluble copper sulfates available therein. Nevertheless, since the new dump site is organized in a way dramatically restricting all possible pollution pathways, we believe that the trend in Cu levels here is already negative and will reach target levels within few more years. In any case, this point is worth monitoring meanwhile.

4. The presence of Pb, Zn, Cu and Cd in the sampled soils is technogenic and the drastic decrease of their concentrations after restricting the pollution sources, proves that KCM factory was the only source of these elements in the area and that the restricting measures undertaken were highly effective.

5. Co and Cr contents, which before the pollution restricting measures were close to or below the target values, are now under the detection

limits. Although mostly geogenic, the fact that there is some decrease, proves that at least some small part of their content used to come from the KCM factory, and now it no longer contributes to observed levels.

Chemical processes in depth of the clinker deposits

One point, which was actually clarified during the 2001-2003 campaign, but still remains important for the understanding of currently observed phenomena, is the behavior of the deposited solid waste material under atmospheric conditions. It became clear, that the glassy material, traditionally considered chemically stable (insoluble), thus ecologically safe, becomes an ecological time bomb, when deposited with the residual coke, which is part of the technology used. The sulfide component, wetted by the rainfall, starts producing sulfuric acid, acting as strong oxidizer against the coke (about 12% mean content). This causes underground burning, at the expense of the coke and consuming the oxygen from the air in the dump pores and from decomposed silicates. Along with the production of significant amounts of CO₂, the temperature rises over several hundred degrees centigrade and provokes chemical changes of sulfides into sulfates, growing in the form of efflorescent masses in gas exhalation areas. Excess sulfur is deposited there too (Fig. 12).

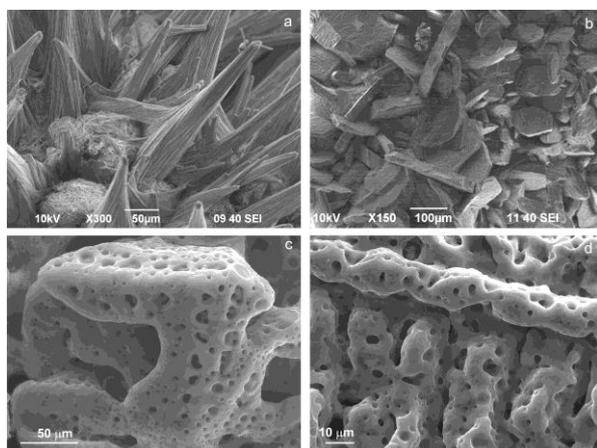


Fig. 12. SEM images of efflorescent minerals: a) ditrichite, b) chalcantite, c-d) native sulfur.

The following minerals were observed: chalcantite, antlerite, melanterite, copiapite, halotrichite, apjohnite, ditrichite, gypsum [29]. All these minerals are extremely soluble in rain water. Each rainfall dissolves significant sulfate masses, mobilizing both the acidifying sulfate anions and the heavy metal cations Cu, Fe, Zn, Ca, Al, Mn. This results in significant pollution of surface and ground waters, as well as forming of airborne

pollution in nearby soils. Although significantly reduced after the reorganization of the dump site, these phenomena are still there, since fresh efflorescent masses were observed during 2010 field works.

CONCLUSIONS

Ground waters in the area have predominantly hydro-carbonate calcic character. The levels of total dissolved solids show moderate mineralization (~500 mg/l) and insignificant seasonal variations (in the limits of 80 mg/L) for the parts of the aquifer, not too close to the factory. Within the factory ground and in its immediate vicinity, however, TDS can reach 1000 mg/L and shows significant seasonal variations. Main chemical species, responsible for the high TDS in and close to the factory, are sulfate ions and aqueous PbCO₃. Lead is the only pollutant, showing concentrations instantly above regulation limits in this part of the aquifer. Although pretty high (7-8 times above URL), these concentrations show clear diminishing trend and in ground waters farther from the factory they are already below URL, after the spring of 2010. Along with the disrupted sources of pollution, the intensive dilution of this part of the aquifer with fresh river water, caused by the river-bed correction, acts as a positive purification factor. Zn and Cd are way below URL in all tested wells.

SO₄ ion exceeds URL only in drill well 1 (within the factory ground) and only during dry seasons, when the ground water level here drops below 1 m and “turns dead”. However, contrary to all heavy metals, the long term trend of SO₄ concentration change is positive, witnessing for the formation of a steadily growing body of sulfatized water body right below the factory.

The analysis of saturation indices of all possible chemical species in the studied waters clearly shows that only Fe and less Mn and Mg oxides and hydroxides are able to precipitate from ground waters of the area. In addition, Ca and Mg carbonates can precipitate from the waste water canal. Since neither of these species is toxic and none of them is considered a pollutant, it becomes obvious, that no water-transported pollution of the soils in the area is possible. This leaves airborne pollution of soils as the only possible polluting pathway. Waters, on the contrary, can be polluted from polluted soils, acting as a secondary source of pollution, which became obvious from the effect of the canal cleaning on the close-by ground waters.

Fortunately, mobile forms of all monitored elements in the soils show levels at or below the target of the *Dutch List* (in most cases even below

detection limits). Only point S1, in the immediate lee vicinity of the factory shows Cd contents requiring action and Cu and Zn requiring monitoring. Very fast diminishing trend, observed for all the elements in all tested points, however, convinces us that even without any specific action, these values will reach the target very soon. One exception from this trend is the Cu content close to the clinker waste dump. It shows values somewhat higher from those registered in 2001. The reason for this increase is clearly the movement of the material during the reorganization of the dump. This is a one-time, short term source of pollution and its consequences are gradually fading.

Summarizing, the ecological situation in the area is far from alerting. Most soils can be used for farming and most waters can be used for melioration. There are two recommendations, which can be derived from the results of the study: 1. when cleaning the waste water canal, avoid depositing the extracted mud on its banks; 2. Identify and disrupt the source of acidifying (sulfatizing) the ground water below the factory. All other over-regulation values are going to reach target without any intervention, soon. Nevertheless, it seems reasonable to avoid using the waters from wells 1-4 and 9, for any reasons other than purely technical, meanwhile. Farming on the few hundred meters, immediately south from the factory (point S1), should also be avoided for a few more years.

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REFERENCES

1. E. Pentcheva, A. Benderev, V. Spasov, I. Petkov, N. Velitchkova, V. Hristov, *Geologica Balcanica*, **32**(2-4), 97 (2002).
2. R. Atanassova, T. Kerestedjian, in: Depo Tech–Abfallwirtschaftstagung (Publication in Konferenzbericht, Leoben, Austria; 2002), K-E. Lorber et al. (eds.); Verlag Gluekauf, Essen, 2002, p.421.
3. A. Benderev, E. Pentcheva, E. Hrischeva. Approaches to Handling Environmental Problems in the Mining and Metallurgical Regions, Kluwer Academic Publishers Netherlands, 2003.
4. T. Kerestedjian, R. Atanassova, N. Piperov, in: Mineral Exploration and Sustainable Development (Proc. 7th Biennial SGA Meeting, Athens, Greece, 2003), D. Eliopoulos et al., (eds.) Mill. Press Rotterdam, Netherlands, 2003, Vol. 1, p. 29.
5. E. Pentcheva, A. Benderev, N. Velitchkova, L. Van't dack, in: Mine Producing, Geology and Environmental Protection (3^d International Scientific Conference Albena, Bulgaria, 2003), 2003, p. 277
6. E. Pentcheva, A. Benderev, R. Atanassova, in: Mine Producing, Geology and Environmental Protection (3^d International Scientific Conference Albena, Bulgaria, 2003), 2003, p. 317.
7. P. Gerginov, I. Petkov, V. Spassov, in: Mine Producing, Geology and Environmental Protection (3^d International Scientific Conference Albena, Bulgaria, 2003), 2003, p. 287.
8. E. Pentcheva, N. Velitchkova, M. Karadjov, in: Mine Producing, Geology and Environmental Protection (3^d International Scientific Conference Albena, Bulgaria, 2003), 2003, p. 295.
9. R. Atanassova, T. Kerestedjian, G. Satchanska, in: Mine Producing, Geology and Environmental Protection (3^d International Scientific Conference Albena, Bulgaria, 2003), 2003, p. 305.
10. E. Pentcheva, N. Velitchkova, R. Atanassova, A. Benderev, M. Karadjov, in: WIR 11 (Proceedings of the 11th International Symposium on Water-Rock International, Saratoga Springs, 2004), R.B. Wanty, R.R. Seal (eds.) A. A. Balchema Publishers, New York, USA, 2004, p.1609.
11. A. Benderev, I. Petkov, B. Mihaylova, in: Mine Producing, Geology and Environmental Protection (4th International Scientific Conference Albena, Bulgaria, 2004, p. 347.
12. V. Hristov, R. Atanassova, A. Benderev, in: 5th International Symposium on Eastern Mediterranean Geology, Thessaloniki, Greece, 2004, p. 994.
13. E. Pentcheva, C. Fouillac, R. Gijbels (Project Co-Directors). Final report - NATO Sfp Project: „Dynamics, evolution and limitation of heavy metal water pollution in the Plovdiv region (Bulgaria)”, Sofia, 2004.
14. E. Pentcheva, M. Karadjov, N. Velitchkova, in: Proceedings of 14th Intern. Symposium “Ecology 2005”, Burgas, Bulgaria, Ecology Scientific Articles Vol. III, Part 3, 2005, p. 169.
15. S. Boiadjiev, I. Boianov, D. Kojuharov. Rhodopes central massif. in: Tectonic of Bulgaria. Technika, Sofia, 1971, p. 49.
16. D. Kouzhoukharov, E. Kouzhoukharova, R. Marinova. Explanation note to the geological map of Bulgaria 1:100000. Sheet Plovdiv. KGMR and PGPGK, Sofia, 1992, p. 41.
17. D. Kouzhoukharov, E. Kouzhoukharova, R. Marinova. Explanation note to the geological map of Bulgaria 1:100000. Sheet Chepelare. KGMR and Geology and Geophysics corp., Sofia, 1994, p. 82.
18. I. Petkov. PhD tesisq 2003, 36 p.
19. H. Antonov, D. Danchev. Groundwaters in NR Bulgaria. Technika, Sofia, 1980.
20. A. Benderev, B. Mihaylova, P. Gerginov, V. Hristov, V. Singh, *Engineering Geology and Hydrogeology*, **26**, 135 (2012).
21. G. Hinov, L. Fajtondjiev, *Soil Science and Agrochemistry*, **12**, 5, (1977).
22. J. Hristova, S. Kujkin, P. Kosturkova, N. Dantcheva, *Mining and Geology*, **2**, 12 (1994).

23. N. Stoyanov, *BULAQUA*, **1**, 32 (2007).
24. S. Dimovski, N. Stoyanov. *Annual of University of Mining and Geology "St. Ivan Rilski "*, **54** (part I, Geology and Geophysics), 125 (2011).
25. A. Benderev, B. Mihaylova, T. Kerestedjian, R. Atanassova, V. Singh, *Proc. GEOSCIENCES 2009*, 123 (2009).
26. A. Tessier, P. G. C. Campbell, M. Bisson, *Anal. Chem.*, **51**(7), 844 (1979).
27. J. Jones, *Environ. Geochem. Health*, **15**(2-3), 185 (1993).
28. Z. Ahnstrom, D.R. Parker, *Soil Science Society of America Journal*, **63**, 1650 (1999).
29. R. Atanassova, T. Kerestedjian, *Geochem. Mineral., Petrol.*, **47**, 51 (2009).

ДИНАМИКА И РАЗВИТИЕ НА ЗАМЪРСЯВАНЕТО НА ВОДИ И ПОЧВИ С ТЕЖКИ МЕТАЛИ В РАЙОНА НА КЦМ, ПЛОВДИВСКА ОБЛАСТ, БЪЛГАРИЯ

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(Резюме)

Настоящият материал представя резултатите от дългогодишни изследвания на състоянието на околната среда в района на КЦМ (Пловдив, България). Установени са всички източници на замърсяване в изследвания район и са оценени пътищата и обектите на замърсяване, както и тяхната роля в общото състояние на околната среда. Определени са границите и посоката на проявление на сезонната динамика по всички анализирани показатели за 10 годишен период. Проследени и оценени са също и дълговременните тенденции на техните промени. Установено е, че сегашното състояние на околната среда е далеч от алармиращо, но са направени някои препоръки за предотвратяване на по-нататъшно разпространение на замърсяването, както и за правилното използване на някои водни и почвени ресурси.