NUKLEONIKA 2004;49(Supplement 1):S17–S20

Treatment of acid drainage in a uranium deposit by means of a natural wetland

Veneta I. Groudeva,
Stoyan N. Groudev,
Anna D. Stoyanova

Abstract Acid drainage waters generated in the uranium deposit G-1, Western Bulgaria, were treated by means of a natural wetland located in the deposit. The waters had a pH in the range of about 2.4–3.9 and contained uranium and radium radionuclides, heavy metals (copper, zinc, cadmium, iron, manganese), arsenic and sulphates in concentrations usually much higher than the relevant permissible levels for waters intended for use in the agriculture and/or industry. The wetland was characterized by abundant and emergent vegetation and a diverse microflora. *Typha latifolia*, *Typha angustifolia* and *Phragmites australis* were the main plant species in the wetland but representatives of the genera *Scirpus, Juncus, Eleocharis, Potamogeton, Carex* and *Poa* as well as different algae were also present. The water flow through the wetland varied in the range at about 0.2–1.2 l/s reflecting water residence times in the wetland of about 10–50 hours. An efficient water cleanup took place in the wetland, even during the cold winter months at ambient temperatures close to 0°C. The removal of pollutants was due to different processes but the microbial dissimilatory sulphate reduction and the sorption of pollutants on organic matter (living and dead plant and microbial biomass) and clays present in the wetland played the main role.

Key words acid mine drainage • bioremediation • natural wetland • uranium • water cleanup

V. I. Groudeva, A. D. Stoyanova
Faculty of Biology,
University of Sofia,
8 Dragan Tzankov Boul, 1421, Sofia, Bulgaria

S. N. Groudev✉
Department of Engineering Geoecology,
University of Mining and Geology,
Studentski grad-Durvenitza, Sofia 1700, Bulgaria,
Tel./Fax: +359-2-687396,
e-mail: groudev@mgu.bg

Received: 16 July 2004

Introduction

The uranium deposit G-1, located in Western Bulgaria, for a long period of time was a site of intensive mining activities. These activivies were ended in 1990 but since that time the deposit is, especially after rainfall, a large source of acid drainage waters. These waters have pH usually in the range of about 2.5–4.0 and contain uranium and radium radionuclides, heavy metals (copper, zinc, cadmium, iron, manganese), arsenic and sulphates in concentrations usually much higher than the relevant permissible levels for waters intended for use in the agriculture and/or industry.

It is known that waters with similar composition have been efficient treated by means of different "passive" systems. These systems have been developed on the basis of naturally occuring biological and geochemical processes and are characterized by minimal operation and maintenance costs [1, 7]. The natural and constructed wetlands are the most typical representatives of such systems.

This paper contains data about the treatment of a portion of the acid drainage generated in the deposit G-1 by means of a natural wetland located in this deposit.

Materials and methods

The natural wetland covered an area of about 450 m^2 (approximately 70 m long and 6–7 m wide). The bottom of

Table 1. Microflora of the drainage waters and the natural wetland.

Microorganisms	Samples		
	drainage waters before treatment	waters from the wetland	sediments from the wetland
	Cells/ml (g)		
Aerobic heterotrophic bacteria	10^1–10^4	10^5–10^8	10^2–10^6
Cellulose-degrading microorganisms	0–10^2	10^2–10^6	10^1–10^4
Fungi	0–10^2	10^1–10^4	10^1–10^3
Fe^{2+}-oxidizing chemolithotrophs (at pH 2)	10^4–10^8	0–10^3	0–10^1
$S_2O_3^{2-}$-oxidizing chemolithotrophs (at pH 7)	0–10^4	10^1–10^5	10^1–10^3
Anaerobic heterotrophic bacteria	0–10^3	10^2–10^5	10^3–10^7
Sulphate-reducing bacteria	0–10^2	10^2–10^5	10^3–10^7
Denitrifying bacteria	0–10^1	10^1–10^5	10^3–10^6
Methanogenic bacteria	0	0–10^2	10^1–10^4

the wetland was located on impermeable intrusive rocks with very low hydraulic conductivity and was covered by a 20–40 cm layer consisting of soil and different sediments.

The wetland was characterized by an abundant water and emergent vegetation and a diverse microflora. *Typha latifolia, Typha angustifolia* and *Phragmites australis* were the main plant species in the wetland but representatives of the genera *Scirpus, Juncus, Eleocharis, Potamageton, Carex* and *Poa* as well as different algae were also present. Data about the microflora of the wetland are shown in Table 1.

The quality of the water was monitored at least once per week in the period October 2000 – November 2003 at different sampling points located in the wetland. The parameters measured *in situ* included: pH, Eh, dissolved oxygen, total dissolved solids and temperature. Elemental analysis was done by AAS (atomic absorption spectrometry) and ICP-MS (induced coupled plasma mass spectrometry) in the laboratory. The radioactivity of the samples was measured, using the solid residues remaining after their evaporation, by means of a low background gamma spectrometer ORTEC (HPGe-detector with a high distinguishing ability). The concentration of ^{226}Ra was measured using a 10 l ionization chamber. The total β-activity was measured by a low background instrument UMF-1500M. Mineralogical analysis was carried out by X-ray diffraction techniques. The mobility of the precipitated pollutants was determined by the sequential extraction procedure [4].

The water flow during the period of study varied in the range at about 0.2–1.2 l/s reflecting water residence times in the wetland of about 10–50 hours.

The isolation, identification and enumeration of microorganisms were carried out by metals described elsewhere [2, 3, 5, 6].

Results and discussion

The regular monitoring of the water revealed that the concentrations of pollutants steadily decreased during the water flow through the natural wetland and the wetland effluents were characterized by pollutants concentrations lower than the relevant permissible levels for waters intended for use in the agriculture and/or industry (Table 2). The removal of pollutants markedly depended on the ambient temperature (Table 3). However, good results were achieved even during the cold winter months (December–February) at temperatures close to 0°C, although at longer residence times. The removal of pollutants was due to different processes but microbial dissimilatory sulphate reduction and the sorption of pollutants on organic matter (living and dead plant and microbial biomass) and clays minerals present in the wetland played the main role. The anaerobic sulphate-reducing bacteria were a quite numerous and diverse population in the wetland (Table 4). These bacteria were well adapted to the high concentrations of heavy metals in the drainage waters. The alkalinity produced during the microbial sulphate reduction in the form of hydrocarbonate ions as well as the alkalinity produced by the solubilization of some acid consuming minerals (mainly carbonates) present in the wetland gradually increased the pH and stabilized it around the neutral point. The non-ferrous metals (copper, zinc, cadmium) were precipitated mainly as the relevant insoluble sulphides by the hydrogen sulphide produced by the sulphate-reducing bacteria. Portions of the iron and arsenic were precipitated also as sulphides. Uranium was removed mainly as uraninite (UO_2) as a result of the prior reduction of the hexavalent uranium U(VI) to the tetravalent state U(IV).

The removal of manganese was connected mainly with the microbial oxidation of the bivalent manganese to the tetravalent state. The Mn^{4+} was then precipitated as dioxide manganese MnO_2. A portion of the iron was also removed as a result of its prior oxidation (mainly biological) to the ferric state, followed by hydrolysis to ferric hydroxide. Most of the bacteria able to oxidize Fe^{2+} and Mn^{2+} were related to the genera *Metallogenium*, *Sphaerotilus, Crenothrix, Leptothrix* and *Siderocapsa*. Some arsenic was removed as a result of its adsorbtion on the iron hydroxides formed in the wetland. Heteritrophic bacteria (related to the genus *Pseudomonas*) able to oxidize As^{3+} to As^{5+} at slightly acidic and neutral pH were isolated from the wetland. This oxidation process explained the presence of some As^{5+} ions adsorbed on these hydroxides.

Table 2. Date about the drainage waters before and after their treatment by the natural wetland.

Parameters	Before treatment	After treatment	Permissible levels for waters intended for use in agriculture and industry
Temperature, °C	(+0.1)–(+24.4)	(+0.1)–(+25.1)	–
pH	2.40–3.92	6.8–7.7	6–9
Eh, mV	(+325)–(+521)	(+230)–(+390)	–
Dissolved oxygen, ml/l	1.4–4.6	2.3–5.5	2
Total dissolved solids, mg/l	590–2354	323–1071	1500
Solids, mg/l	25–91	21–71	100
Dissolved organic carbon, mg/l	0.5–3.2	14–44	20
Sulphates, mg/l	325–1351	170–590	400
Uranium, mg/l	0.37–4.10	<0.1	0.6
Radium, ^{226}Ra, Bq/l	0.05–0.35	<0.05	0.15
Total β-activity, Bq/l	0.35–1.70	<0.5	0.75
Copper, mg/l	0.68–8.42	<0.5	0.5
Zinc, mg/l	1.45–19.23	<1.0	10
Cadmium, mg/l	0.02–0.12	<0.01	0.02
Arsenic, mg/l	0.21–0.59	<0.1	0.2
Iron, mg/l	114–905	<1.0	5
Manganese, mg/l	1.4–28	<0.7	0.8

Portions of the uranium and of the heavy metals and arsenic as well as of the radium were removed by their accumulation and sorption by the plant and microbial biomass and by their sorption on the clay minerals in the wetland. The contents of pollutants in the main plant species present in the wetland were much higher than those in the relevant species grown in wetland non-polluted with the above-mentioned pollutants (Table 5). It must be noted, however, that different specimens of one and the same species differed considerably from each often with respect to their content of pollutants, regardless of the fact that had been grown under similar conditions. In most cases, the amount of pollutants adsorbed on surface of the plant biomass was considerably higher than the amount accumulated inside the biomass. The higher concentrations of pollutants were detected in the root system of the plants, and the concentrations in the leaves and stems were much lower. Some algae (mainly such related to the genera *Pediastrum, Eudorina, Volvox, Melosira* and *Scenedesmus*) and microorganisms (mainly such related to the genera *Aspergillus, Penicillium, Pseudomonas* and *Bacillus)* also adsorbed pollutants. The total content of heavy metals in some algae exceeded 10 g/kg biomass, and that of radium

Table 3. Removal of pollutants from the drainage waters during the different climatic seasons.

Pollutants	Pollutant removal, g/24 h	
	during the warmer months	during the cold winter months (at 0–5°C)
Uranium	60–235	21–88
Copper	86–440	30–132
Zinc	170–923	44–316
Cadmium	1.4–6.4	0.5–1.9
Arsenic	28–82	12–37
Manganese	114–846	51–260
Iron	10,540–48,114	3761–12,035

Table 4. Sulphate-reducing bacteria in the sediments from the natural wetland.

Sulphate-reducing bacteria	Cells/g dry sediments
Desulfovibrio (*D. vulgaris*, *D. desulfuricans*, *D. saprovorans*)	10^2–10^7
Desulfobulbus (*D. elongatus*, *D. propionicus*)	10^2–10^6
Desulfococcus (*D. postgatei*)	10^1–10^4
Desulfobacter (*D. multivorans*)	10^2–10^5
Desulfobacterium (*D. autotrophicum*, *D. vacuolatum*)	10^1–10^3
Desulfotomaculum (*D. nigrificans*, *D. orientis*)	10^1–10^2
Desulfosarcina (*D. variabilis*)	10^2–10^4

Table 5. Content of pollutants in different plant species from the natural wetland.

Pollutants	*Typha latifolia*		*Typha angustifolia*		*Phragmites australis*	
	I	II	I	II	I	II
U, mg/kg	35–170	ND	23–141	ND	21–123	ND
^{226}Ra, Bq/kg	25–125	ND	15–105	ND	17–115	ND
Cu, mg/kg	71–280	7	41–215	6	32–170	5
Zn, mg/kg	46–315	5	44–264	7	37–212	7
Cd, mg/kg	8–51	ND	5–32	ND	9–37	ND
As, mg/kg	32–95	3	73–71	5	19–104	3
Mn, mg/kg	82–370	10	73–392	8	55–305	8

Notes: I – data about plant specimen grown in the wetland; II – data about plant specimens grown in a wetland non-polluted by radionuclides and heavy metals.
ND – not detected.
All contents are expressed per kg dry biomass.

exceeded 500 Bq/kg. Negative effects of the pollutants on the growth and activity of the indigenous plant and microbial communities were not absened.

During the cold winter months, when the plant and microbial growth and activity were markedly or even complitely inhibited, the role played by sorbents such as dead plant biomass and clays in the water cleanup was essential. In the sediments precipitated during this time of the year the pollutants were presents mainly as the easily soluble exchangeable and carbonate fractions and the contents of sulphides and uraninite were much lower than the relevant contents in the sediments precipitated during the warmer months. The contents of pollutants in the dead plant biomass steadily increased during the winter months and usually reached values much higher than those in the living plants during the wormer months. The contents of pollutants in the clays present in the wetland steadily increased during the winter months. The total content of non-ferrons metals in some clay specimens exceeded 10 g per kg dry clay, and the contents of uranium and radium 1 g and 1000 Bq/kg, respectively.

The data from this study revealed that treatment of waters polluted with radionuclides, heavy metals and arsenic can be efficiently carried out by natural wetlands with a proper size and located in regions with suitable geological, hydrogeological and climatic conditions. Such water cleanup can be regarded as one of the most typical examples of sustainable development of natural ecosystems.

Acknowledgments The European Commission under the project No. QLRT-2001-02916 "Multifunctional permeable barriers carrying well performing microbial biofilms for treatment of mixed polluted plumes" as well as the Bulgarian Science Foundation project B1206/02 financially supported a part of this work.

References

1. Groudeva VI, Groudev SN (1998) Cleaning of acid mine drainage from uranium mine by means of a passive treatment system. Miner Process Extr Metall Rev 19:89–95
2. Groudeva VI, Ivanova IA, Groudev SN, Uzunov GC (1993) Enhance oil recovery by stimulating the activity of the indigenous microflora of oil reservoir. In: Hydrometallurgical technologies. TMS, The Minerals, Metals & Material Society, Warrendale, PA. Vol II, pp 349–356
3. Karavaiko GI, Rossi G, Agate AD, Groudev SN, Avakyan ZA (1988) Biogeotechnology of metals. Manual. GKNT International Projects, Moscow
4. Tessier A, Campbell PGC, Bisson M (1979). Sequential extraction procedure for speciation of particulate trace metals. Anal Chem 51;7:844–851
5. Widdel F, Bak F (1991) Gram-negative mesophillic sulphate-reducing bacteria. In: The prokaryotes, 2nd ed. Springer, New York. Vol IV, pp 3352–3378
6. Widdel F, Hansen TA (1991) The dissimilatory sulphate and sulphur-reducing bacteria. In: The prokaryotes, 2nd ed. Springer, New York. Vol IV, pp 583–624
7. Younger PL (ed) (1997) Mine water treatment using wetlands. University of Newcastle, Newcastle, UK