Proceedings World Geothermal Congress 2010
Bali, Indonesia, 25-29 April 2010

Mineral Water Contamination Assessment in the Territory of the North Caucasus Health Resort

Irina V. Galitskaya

Institute of Environmental Geosciences Russian Academy of Sciences, Russia, Moscow, Ulanskii per. 13/2

galgeoenv@mail.ru

Keywords: mineral waters, contamination, hydrogeochemistry, narzan.

ABSTRACT

This paper considers results of mineral water contamination investigations at a North Caucasus health resort. The main research tasks were: active and potential contamination source identification, assessment of type and intensity of surface and groundwater contamination, mineral and surface water contamination interconnection estimation, division of territory into districts with different degrees of the water system contamination, and make recommendations on contamination risk minimization. Contaminant sources were identified based on industrial and agricultural sewage water composition research. Characteristic contamination changes in the springs, wells and rivers were investigated from recharge areas and discharge areas. The most intensive contamination sites of surface and mineral water were located at town boundaries, particularly in unsewered parts, and in stock-farm areas. The recommendations on liquidation of the contamination sources in the main mineral water source location particularly in the zone of depression cone were developed.

1. INTRODUCTION

Intensive withdrawal of mineral water often brings about significant changes in hydrodynamic and hydrogeochemical conditions. The anthropogenic role of in groundwater resource and quality dramatically increases. The most important criterion of rational withdrawal is the maintenance of mineral water quality. The results of mineral water contamination investigations in Kislovodsk - one of the North Caucasus health resort are considered. The name of the town is derived from natural springs of "sour water" (i.e. carbonated).

Necessity of hydrogeochemical research in the large carbonaceous mineral water field (t. Kislovodsk) was caused by unsatisfactory sanitary-bacteriological state and raised contents of nitrogen compounds in the main mineral water source and in some production wells.

The basic research goals were: 1) identification of active and potential contamination sources, 2) assessment of type and intensity of surface and groundwater contamination, 3) assessment of interconnection of mineral and surface water contamination, 4) divide territory into zones with different degrees of the water contamination, 5) recommendations for water systems protection.

To meet these goals the following research tasks were carried out: 1) gather, analyze and generalize the environmental conditions and economic activities data in the territory under consideration, 2) sample groundwater and a surface water, 3) analyze water systems' chemical compound and a sanitary-bacteriological condition.

2. ENVIRONMENTAL CONDITIONS AND ECONOMIC ACTIVITIES

The territory under investigation is located in the area of the Podkumok river and limited by the watersheds of its inflows – Alikonovka, Beryozovaya and Olhovka rivers (Fig. 1). Structurally it is located in the North Caucasian monocline. The structures of a northeast direction are important in carbonaceous mineral water formation. Disturbance zones are traced in Jurassic and Cretaceous rocks. In the hydrogeological relation North Caucasian monocline represents a typical artesian slope. The main productive carbonaceous mineral water aquifers are Tithon aquifer in Upper Jurassic rocks and Valangin aquifer in Lower Cretaceous rocks. The upper aquifers are in Lower Cretaceous rocks (Hauterive, Barrem, Apt stages) and Quaternary deposits. We will consider conditions of productive aquifers formation in more details.

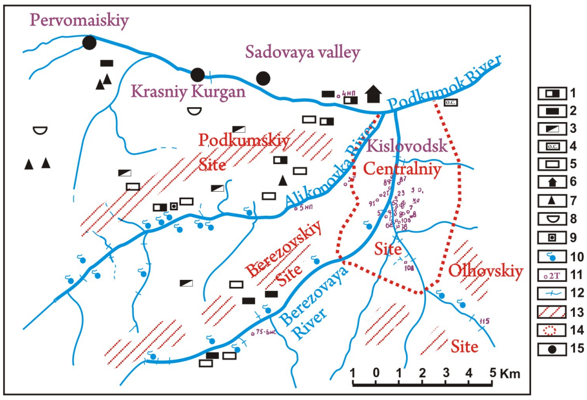

Figure 1. Scheme of the territory under investigation. Legend symbols represent: 1-garage, 2-storehouse of combustive-lubricating materials, 3-stud farm, 4-treatment facilities, 5-dairy farm, 6-poultry factory , 7-sheep farm, 8 - land fill, 9 - weed and pest-killer chemicals storehouse, 10 spring, 11-well, 12 -surface water sampling site, 13-agricultural lands, 14-urbanised territory, 15-settlement.

The *Tithon aquifer* receives the basic recharge at the expense of atmospheric waters infiltration on the southern slope of Skalistii ridge and also in valleys of the rivers Alikanovka and Beryozovaya where water bearing rocks occur on the surface. Water bearing rocks are presented by anhydrites (Olhoskii site), sandstones and gravelites (Centralny and Podkumskiy sites); and granite slack (Beryozovskiy site) of Jurassic age. Tithon aquifer discharges into the central part of the Kislovodskii swell and in a valley of the river Beryozovaya. Carbonaceous mineral springs from tithon rock are known only in the valley of river Beryozovaya in the tectonic infringements zones. Carbonaceous mineral waters in Tithon aquifer are extended locally within separate zones with special geostructural conditions.

Valangin aquifer is absent only in the southwest in the valleys of Alikonovka and Beryozovaya rivers. Water bearing rocks are presented by dolomitic limestones of the Cretaceous age. The aquifer recharge area is where infiltration of atmospheric precipitation occurs into water-bearing rock outputs. The regional recharge area is located in the south, where there is the strong karstification of limestones. In addition essential importance has a local recharge both Valangin and Tithon aquifers. Flood plains are believed to be local recharge areas of groundwater. In flood plains of the rivers Beryozovaya and Olhovka Tithon and Valangin rocks are on the surface or lie down on insignificant depth under Quaternary deposits. In this sites groundwater are directly connected with river water and water of the alluvial deposits, so the latter contamination creates the real threat of mineral water contamination.

Discharge of the aquifer occurs through the largest mineral water spring Narzan and the high-flow-rate fresh water springs (Finkgejzer, Chaveli, etc.). As a result of long-term natural discharge and particularly mineral water withdrawal from the wells the cone of depression was generated in the central part of a mineral field. The consequence of natural regime disturbance and significant water level reduction was fresh and mineral groundwater contamination as a result of activation of contaminated water entering from upper Quaternary aquifer and rivers.

It is important to emphasize that fresh waters of Valangin aquifer extend through most of the territory, and carbonaceous mineral waters are developed only in the parts where confined water of Tithon aquifer discharges into the Valangin aquifer. Since productive Tithon and Valangin aquifers are closely hydraulically connected, they are often considered as united Tithon - Valangin aquifer.

Thus hydrogeochemical situation in the territory under consideration is characterized by significant variability. This is caused mainly by heterogeneous lithofacies, rock jointing and karst conditions of aquifers recharge and disharge. Fresh groundwaters are wide-spread at the most territory. Carbonaceous mineral waters are spread only in the fault zones where carbonic fluid rises from the crystal basement. Chemical composition formation of groundwater is substantially caused by rock leaching which becomes most significant when the water contains dissolved carbonic gas at the tectonic infringement sites. The hydrogeological peculiarity of this region is a hydraulic connection between groundwater of the adjacent aquifers, and that is very important - between groundwater and surface water. Broad development of karst, intensive jointing of rocks, partitioned relief promote the hydraulic connection groundwater and surface water that result in anthropogenic contamination of main productive mineral water aquifer.

Sources of water pollution are caused by communal services of town–resort and agricultural territory in its vicinity. Many town enterprises haven`t treatment facilities and throw the crude waste water in surface streams. There were no sewage-purification facilities at the most part of town territory and territories of the other human settlements near the main town. The essential sources of contamination are livestock wastes of stock-farms, fowl-farms, surface runoff from agricultural lands, where mineral fertilizers and pesticides were used, as well as from pastures.

3. RESEARCH TECHNIQUE

Sampling fresh and mineral groundwater of Tithon-Valangin water complex and surface water was organized to research the type and intensity of water and identify potential sources. We sampled groundwater from shallow wells, and production wells with and without draw-down. The main rivers Alikonovka, Beryozovaya and Olhovka have been sampled taking into account the placement of contamination sources. Most dumping of sewage was carried out in brooks and inflows of main rivers, so sampling was carried out upstream and downstream from the contamination source. Also rivers were sampled upstream and downstream from inflow of the brook. Surface water samples were filtered through membrane filters with pore diameter 0.45 mm. Surface water samples were filtered for division of solid and liquid phases. In a liquid phase all components (see below) were analyzed, the solid phase of samples were measured for heavy metals and manganese. In this paper we consider the results only of the dissolved element forms.

The list of analyzed indicators and components included: pH, ammonium, nitrite, nitrate, chloride, phosphate, sulphate, potassium, pesticides, oil products, phenol, heavy metals, surfactant species, and e coli. The list has been chosen on the basis of the industrial, domestic and agricultural waste waters sources.

Concentration coefficients (ratio of actual concentrations in water to their background concentrations) were calculated to evaluate the intensity of anthropogenic impact. Sampling of background concentrations were formed on the basis of water sampling results at the territories, located outside of direct anthropogenic influence zones. The background concentrations in groundwater were characterized by practically the same values and differed from regional and global concentration insignificantly.

4. RESULTS AND DISCUSSION

Analysis of the results has allowed us to establish the following.

1. At the territory of mineral water field there were observed the chemical contamination of surface water (rivers, brooks) and groundwater (fresh and mineral groundwater). Contamination was fixed both within town and agricultural territories. Main contaminants were nitrite and ammonium, reaching very high concentrations at separate sites, as well as intestinal bacteria. Water contamination levels of phosphate, nitrate, chlorine-containing pesticides were much lower and more local. Raised concentrations of potassium, chloride, sulphate, manganese and heavy metal in water probably depended to a large extent on natural factors. At present, it was impossible to uniquely define their anthropogenic contribution to chemical composition of water system. In addition to that at the separate areas, in surface streams particularly, raised concentrations of some metals (cadmium, copper, nickel, zinc), potassium and chloride were fixed, as well as sulphate and manganese, certainly connected with anthropogenic factor impact. That is why when monitoring of water system in given region it is reasonable to introduce these contaminants in the list of controlled ingredients.

2. Groundwater contaminants in the zone of most typical anthropogenic sources influence in the region under investigation were characterized, first of all, the different nitrogen forms in that or other correlation. Urban territory particularity had increased concentrations of phosphate,

entering with the town sewages, but in the zone of the agricultural influence raised potassium and zinc concentrations (in result of potassium and calcareous fertilizers and pesticides usage). Generalised associations of water contaminants in zones of the different contamination sources influence it is possible to present in following type (elements in the associations are located in order of the concentration coefficient values decrease, in brackets components are presented, comprised in associations conventionally):

Zones of the town *influence*: for surface water - NO_2 NH_4 NO_3 PO_4 (Zn K Cu Ni), for groundwater - NH_4 NO_2 NO_3 PO_4 (K Zn Cu Ni),

Zones of the stock-raising farms influence in river valley: for brooks, drain the territory of stock-raising farms - NO_2 NH_4 NO_3 PO_4 (K Zn), for sources of fresh groundwater - NO_3 NO_2.

Zone of the agricultural lands influence (fertilized fields, pastures and others) and summer temporary stock-raising farms:

for mineral water - NH_4 Zn Ni,

for fresh groundwater –K Zn NO_2 NO_3 (Ni Cu),

for surface water – K Zn NO_2 NO_3.

Compositions of contaminant associations for groundwater and surface water were practically identical. It indicate that contamination of groundwater is conditioned by change of surface water quality to a considerable degree.

On the basis of geochemical estimation result of the water system state within explored region zones, differing on degree and nature of the contamination were chosen (Table 1).

Zone of the summer temporary stock-raising farms and pastures influence were characterized by the least and at the same time by specific contamination. In surface water the most high concentrations were typical for nitrite (concentration coefficient value Kc to 9), nitrate (Kc to 4), ammonium (Kc to 6), in fresh groundwater - for nitrite (Kc to 7), nitrate (Kc to 6), in mineral water - for ammonium (Kc to 24), But the most characteristic feature of given zones was comparatively high contents of potassium and zinc, concentration coefficient values for which reached: for surface water - 36 and 20, for fresh groundwater - 42 and 20, for mineral water - 20 and 7. Raised concentration of nickel and copper were also fixed, in groundwater in the zone of the summer temporary stock-raising farms influence. It is necessary to note that according to the data presented in [Leor (1979)] sewers and waste stock-breedings are characterized by high contents of the zinc and copper.

Zone of stock-raising farms and intensive utilized pastures influence is characterized by more high contamination level in contrast with previous zone. It mainly became apparent at considerable increase of ammonium, nitrite and nitrate concentrations. Concentration coefficient values were: *in surface water* for ammonium - to 38, for nitrite- to 80, for nitrate -to 24, for potassium -to 2, for zinc -to 3, *in fresh groundwater* -for nitrate- before 18, for nitrite -before 2. Thereby, stock-raising farms influence was revealed, first of all, in increased nitrogen compounds supply of natural water. Spatial distribution of contaminant in surface water is characterized by gradual increase of their concentration to maximum values in sources, usually located on the river valley slopes or watersheds and gradual reduction to background concentration downstream. The influence of stock-raising farm standing by itself on surface water composition is fixed on the distance approximately in 1 km.

Table 1: Characteristic of groundwater and surface water contamination at the mineral water field.

Zone of influence	Natural water	Typical complex of contaminants and concentration coefficients
Agricultural lands	Streams	$K_{20\text{-}36}$ $Zn_{5\text{-}9}(NO_2)_{5\text{-}9}$ $(NO_3)_{2\text{-}4}$
	River water	Zn_{25} K_{40} $(NO_2)_5$ $(NH_4)_3$ $(NO_3)_3$
	Fresh groundwater	$K_{8\text{-}30}$ $Zn_{10\text{-}20}$ $(NO_2)_{1\text{-}5}$ $(NO_3)_{3\text{-}4}$
	Mineral water	$(NH_4)_{24}$ K_{20} Zn_6 Ni_4 Cu_2
Stock-raising farms	Streams	$(N0_2)_{5\text{-}8}$ $(NH_4)_{2\text{-}38}$ $(NO_3)_{1\text{-}24}$ $Zn_{1\text{-}3}$ K_2
	River water	$(NH_4)_{26\text{-}34}$ $(NO_3)_{4\text{-}14}$ $(NO_2)_{6\text{-}7}$
	Fresh groundwater	$(NO_3)_{5\text{-}18}$ $(NO_2)_{1\text{-}2}$
Town	River water above the town	$(NO_3)_5$ K_3
	River water in the center of the town	$(NO_2)_{26}$ $(NH_4)_{13}$ $(NO_3)_{11}$ $Zn_{11}(PO_4)_4$
	River water below the town	$(NO_2)_{50\text{-}160}$ $(NH_4)_{14\text{-}17}$ $(NO_3)_{7\text{-}11}$ Zn_5 $(PO_4)_2$
	Fresh groundwater in the center of the town	$K_{54\text{-}120}$ $(NO_3)_{48\text{-}66}$ $(NO_2)_{1\text{-}10}$ $Zn_{1\text{-}5}$ $Ni_{1\text{-}2}$
	Fresh groundwater above the town	$(NO_3)_3$
	Mineral water of the main source	$(NO_3)_{25}$ K_{20} $(NH_4)_5$ $(NO_3)_{22}$ K_{20} $(NH_4)_3$ $(NH_4)_{29}$ $(NO_3)_{11}$ K_8 $(PO_4)_3$ Zn_2

Zone of town influence is characterized by the most intensive contamination. Presence of the different contamination sources with overlaying areas of influence, as well as changeable servicing mode of the mineral field has conditioned the significant changeability of the groundwater composition within the town limits. Very high concentrations of nitrogen compounds are found in the surface water (concentration coefficients are to ten times above background level). It is significant that phosphate concentration exceeds background level to 5 times, zinc concentration - to 11 times, copper and nickel concentrations – to 3 times. Significant concentrations of cadmium, lead, manganese are fixed in surface water within the town limits exactly. Maximum concentration of nitrogen compounds, potassium, phosphate, manganese and heavy metal are typical main for the main river below town treatment facilities. The sewages influence in this river tells is observed at several kilometres' distance from the town.

High raised concentration of potassium and nitrite are found in fresh high-flow-rate sources. Mineral water quality in the discharge area depends to a large extent on intensive contamination of fresh water in the higher part of the aquifer. High concentrations of ammonium (Kc to 60) and potassium (Kc to 40) are revealed in majority wells of mineral water, but in water with unfavourable sanitary-bacteriological state, raised nitrate concentrations (Kc to 25) is found out. Raised phosphate concentrations (Kc to 3) are revealed in mineral water everywhere. There is no doubt that contamination of mineral water in the main source (used for balneological treatment) is basically conditioned by influence of the town sewages and surface runoff from town territory. The latter is particularly characteristic for unsewered urban districts. It led to surface streams and groundwater contamination, as well as main aquifer fresh groundwater, which is one of mineral water components of the source. In condition of the intensive mineral water usage the increase of polluted surface and groundwater overflowing and contaminated fresh groundwater arrival are conditioned the contamination of mineral water.

4. RECOMMENDATIONS

Recommendations for the organization of the actions directed to quality of mineral water maintenance have been developed by the account of the results of research, the analysis of a information lack, the territory zoning on sites with different degree of groundwater and surface water contamination.

1. First of all it is necessary to carry out the detailed researches of a hydrogeological situation in considered territory, including aquifer levels and their ratios changes; clarification of the depression cone sizes; revealing of local recharge sites because the placement of pollution sources here poses considerable threat to mineral water quality.

2. In the Centralniy site, located in the zone of the urban territory influence and characterized by the most intensive contamination of mineral water, and also surface water currents, acceptance of urgent measures for contamination sources liquidation in the area of the Tithon - Valangin aquifer cone of depression impact is recommended. The special attention should be turned on the liquidation of fresh groundwater contamination sources on southern uptown, because the polluted fresh groundwater pulling up from the south affects adversely to mineral spring Narzan.

3. In a zone of cattle-breeding farms influence in the Alikonovka river valley it is recommended to take of measures for prevention of waste water river outlet from the farms located on river valley slopes and pollute the fresh groundwater sources and river water also.

4. For the control over groundwater (mineral and fresh) and surface water changes it is necessary to create the monitoring system. First for the groundwater control the construction of a special network of wells from regional recharge area to the discharge area in the center of mineral water field is reasonable. Secondly, for the surface water control the organization of special hydrometric posts on the main rivers is recommended.

5. CONCLUSION

Results of groundwater and surface water contamination research in the territory of large carbonaceous mineral water field allowed us to establish the following: 1) chemical and bacteriological contamination of surface water (rivers, brooks) and groundwater (fresh and mineral) is widespread; 2) main contaminants were nitrite and ammonium, reaching very high concentrations at separate sites, as well as intestinal bacteria; 3) occurrence of the same contaminants associations in groundwater and surface water allowed us to assume their close interrelation and, as consequence vulnerability of mineral waters to pollution; 4) the greatest degree of contamination was in water systems in city boundaries that defines the necessity of urgent measures for pollution source liquidation in a capture zone of cone of depression; 5) mineral water spring contamination was substantially caused by the cone of depression formation in Tithon - Valangin aquifer as a result of long-term natural discharge and particularly mineral water withdrawal from the wells.

Thereby in connection with constantly increasing degree of the water systems contamination it is necessary to carry out water-protective measures, directed on conservation the necessary quality of mineral water and including both liquidation of the revealed sources of contamination, prevention of waste water river outlet and organization of monitoring of water systems.

REFERENCES

Leor R. Pererabotka i ispolsovanie selskohozjastvennih othodov. Mockva, 1979, P. 415.