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Increasing Concentration of Some Elements in Groundwater Due to Lack Vadose Zone in Aquifer

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Abstract : The authors in their professional praxis have seen that the presence and absence of vadose zone in the upper part of aquifer, with intergranulary porosity type, is a prerequisite for enhanced concentrations of iron and manganese in groundwater. The natural aeration zone in vadose zone of the upper part of aquifer enables additional enrichment of groundwater with oxygen, which is spent on the account of biochemical processes in the direction of their flow. The absence of this zone in aquifer directly influences higher iron and manganese content in groundwater, often above the permissible concentration in drinking water. In order to eliminate this problem, in this paper proposals of future works were made, different of the usual procedure of hydro geological research. It will bi possible to examine the effect of aeration of groundwater in the aquifer, during the performing of the wells.
Kew words: vadose zone, iron, manganese, hydrochemistry, groundwater

1.0 Introduction

Vadose zone is zone above water table, through which water is infiltrated, and in which the pores and cracks in the soil, and rocks are filled with air and partially with capillary water (Figure 1). This work processes the influence of part of the vadose zone which is situated (or is sometimes completely missing) in the aquifer with marked intergranulary type of porosity, i.e. in its upper or higher part on the content of iron and manganese. Namely, in this aquifer zone, natural aeration of the groundwater is made which has a positive influence on its chemical composition. Role of vadose-zone flow process is explained by [1-4]. One major cause of manganese mobilization in aquifers is reductive decomposition and dissolution of compounds such as Mn-OOH and MnO2. In the normal pH range of groundwater (pH 5 – 8), dissolved iron is present as Fe^{2+}. The main sources of Fe^{2+} include [5-9]:

• the dissolution of iron (II) bearing minerals;
• the reduction of iron oxyhydroxides (Fe-OOH) present in the sediments e.g. magnetite, ilmenite, pyrite, siderite, iron (II) bearing silicates and clay minerals such as smectites;
• the oxidation of arsenopyrites.

If the saturation zone in direct contact with aquitard in overlie of the aquifer, with marked intergranular type of porosity, i.e. if the aquifer is subartesian or artesian (Figure 2), due to biochemical processes, anaerobic conditions are created which generates an increased content of iron and manganese in groundwater.

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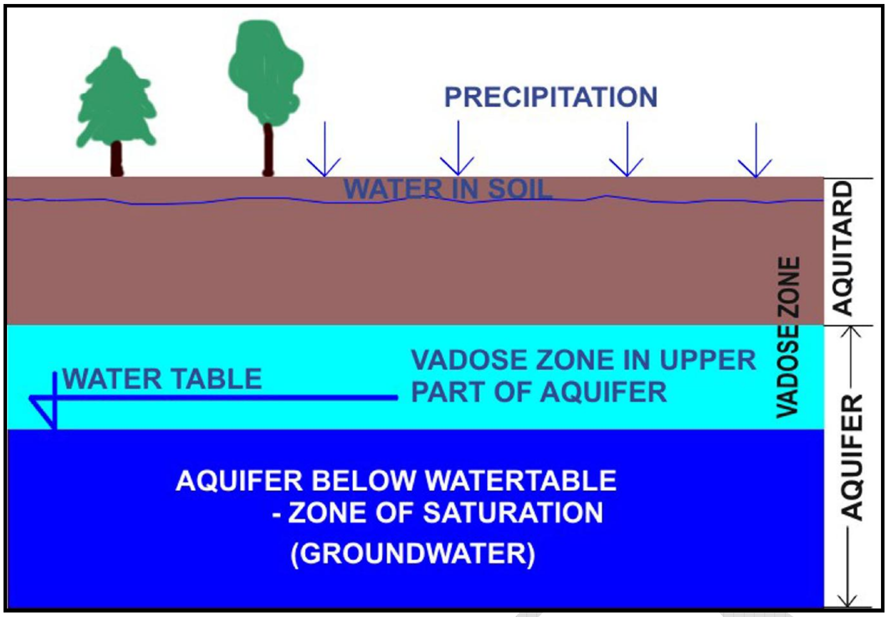

Figure 1: The scheme of the aquifer with present vodose zone in the aquifer itself

A good understanding of this influence can help the researchers with planning the research works, the choice of well location and projecting the well for abstraction of groundwater.

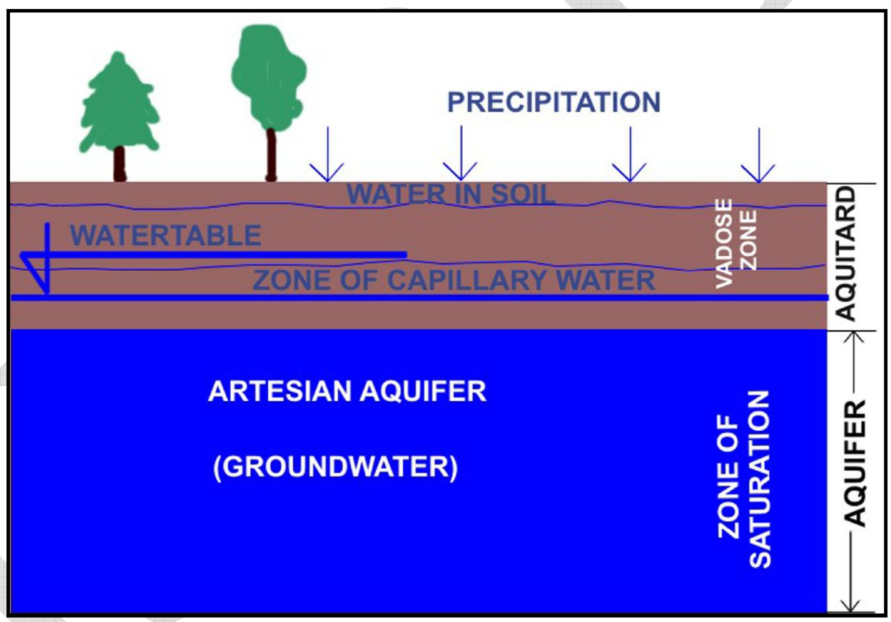

Figure 2. The scheme of vadose zone and saturation zone in aquifer with the level of water under pressure

The authors of this paper have noticed in their professional practice on many terrains in Republic of Srpska that the presence or absence of vadose zone in aquifer (zone of natural aeration), just above the water table, influences the content of iron and manganese in aquifers with strong intergranular porosity type. It is often the case that this water cannot be used for water supply. In aquifers with fractured porosity type, this influence is not present because of the great speed of the groundwater flow, and the short time of retaining water in underground, and little total intensity of biochemical and chemical processes in goundwater.

Many cases with higher presence of iron and manganese and groundwater along with the absence of vadose zone in the aquifer itself, which proves spatial this dependence.

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2.0 Presence and origin of iron and manganese in the groundwater

Higher level of iron and manganese in water changes organoleptic properties because of sediment, which stands out (orange and brown colour), it has an unpleasant smell and the taste of water associates with metal. Iron and manganese react with dissolved oxygen to form insoluble compounds. Therefore, they are usually not found in waters that contain high amounts of dissolved oxygen [5,10,11].

Interpretation of origin of these components in certain aquifer is different. The reasons are first to be searched in the existence of local pollutants in the zone of sanitary protection of water source. In certain cases the reasons are searched in mineralogical-petrographic, i.e. lithological characteristics of terrain, because at first glance it is thought that the rocks, through which water passes, are the cause of such an unpleasant the chemical content. However, the most common cases are those with higher presence of iron and manganese in groundwater, where there are no mineral deposits, rich with iron (alluvial, pliocene and pleistocene gravely-sadly aquifers). In sand and gravel, there are different minerals in the structure of grains made from dissolution of primary rocks, their transport and sedimentation in river valley and neogene basin. From the iron minerals, in sand the following can be found: magnetite (Fe_3O_4), siderite ($FeCO_3$), hercinite ($FeAl_2O_4$), jacobsite ($MnFe_2O_4$), franclinite ($ZnFe_2O_4$), chromite ($FeCr_2O_4$), etc. Frequently minerals of menganese are galaxy ($MnAl_2O_4$) and hrodochrosite ($MnCO_3$).

Apart from these, the presence of the following iron-manganese minerals is also possible: axinite, pyralspite, almadine, spessartine, turmaline, etc. Excerpts of dolomite and limestone, and deposited conglomerates, gravel and sand made from transport of these parts, usually contain chemical impurities of iron and manganese.

So, iron and manganese are practically present in all geo-environments, but in groundwater of all these environments, they are not present in higher percentage.

In the area of fractured limestone and dolomite terrains of Herzegovina and Romanija, and the basin of the upper flow of the river Drina, Bosna, Vrbas, where the groundwater flow is fast, and where the upper part of aquifer has present vadose zone, i.e. the aquifer is not artesian, groundwaters do not have a higher content of iron and manganese. However, groundwaters of the Panonian basin rim (in the immediate catchment of the river basin in the territory of Republic of Srpska) and some aquifers in northern part of Republic of Srpska and Brcko district have higher content of these elements in wider area, in what the authors of this work convinced through their own hydro geologic and hydro chemical research, i.e. based on the results of physical-chemical water analysis results, whose statement is given in this paper.

3.0 Correlation of vadose zone existence in aquifers with intergranular porosity type and iron and manganese content in groundwater

In the following text, the examples of presence or absence of close zone of natural aeration in vadose zone of the aquifer itself are presented, with present air above the level of groundwater, and along with that, the presence of iron and manganese in those aquifers. This type of correlation of two characteristics of aquifer can give contribution to the understanding of existence and intensity of this dependence, i.e. influence.

In the far northeast of Republic of Srpska, in peripheral part of Panonian basin (Semberija and Posavina), with many years of research and following, we established that groundwater in pliocene gravel and sand sediments from the recharge zone (I) and closer zone (II) in mountainous part of Majevica mountain, have good quality. But, in further zones of groundflow (IV), groundwater have increased content of iron and manganese sometime in some of boreholes in artesian aquifer near river Sava. In Figure 3 a conceptual hydrogeological model of peripheral part of Panonian neogene basin, which in the zone far from the recharge zone, does not have vadose zone in the aquifer itself, i.e. there is no natural aeration, so it has anaerobe conditions and by that the conditions for generating higher content of iron and manganese. Figure 3 shows simplified schematic display of the zone of higher iron content in artesian groundwater on the peripheral part of Panonian basin in the function of nonexistence of vadose zone in aquifer itself, and on the account of consumption oxygen during transport of groundwater.

The so-called consumption oxygen in groundwater flow happens because of present microorganisms in water, on the account of biodegradation of organic matters in groundwater and geo-environment, and on the account of chemical processes of oxidation in geo-environment. A rainwater contents average 63,2% nitrogen, 35,0% oxigen and 1,8 % CO_2 [1,6]. That implies high content of dissolved oxygen in groundwater, because in hilly terrains, where pliocene layers have contact with surface, recharge of aquifer is done mainly from rainfall with dissolved oxygen.

In transitional zone (III), i.e. in the first part of groundwater flow, although there is no present vadose zone of natural aeration in the aquifer itself, oxygen dissolved in water is “wasted”, so water in that part of aquifer in its physical-chemical characteristics corresponds drinking water.

Spatial distribution of water with different quality is interesting in the same aquifer, from the aspect of drinking water norms.

In the zone closer to the recharge zone of this part of goundwater flow, water in its physical-chemical structure, often matches the norms of drinking water, but is microbiologically faulty. In transitional zone it is both physically-chemically and bacteriologically valid. However, om the zone further from the recharge zone, i.e. in the zone where the whole aquifer is in saturation zone, where vadose zone in aquifer is completely missing, water becomes faulty to drink due to higher content of iron, and sometimes manganese, although it is still bacteriologically correct (example of Posavina). Higher content of iron in aquifers is contributed by little speed of underground flow, present marly sediments and peat, as well as low pH [11,12].

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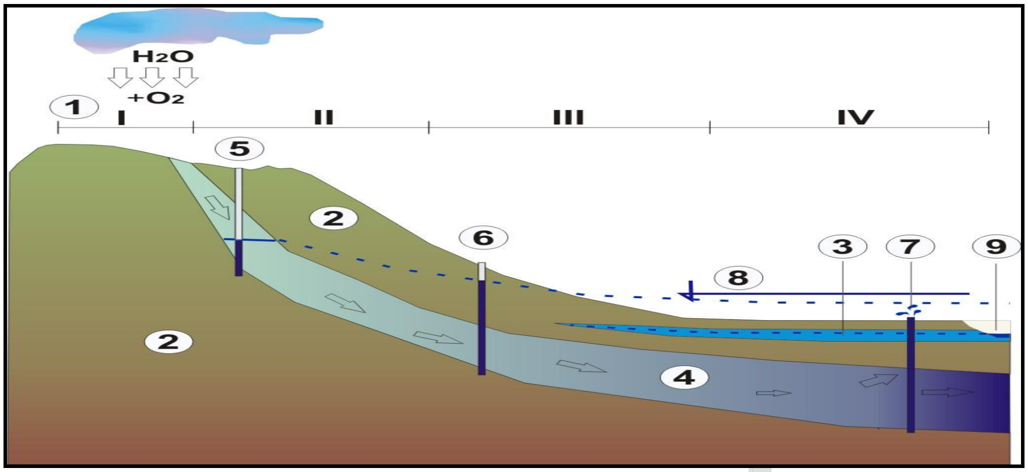

Figure 3. Simplified schematic display of the zone of higher iron content in artesian groundwater on the peripheral part of Panonian basin; Legend: I Recharge zone, II Zone of good quality of groundwater, III Transitional zone, IV Zone of groundwater with higher content of iron and sometimes manganese, 1 - Infiltration area, 2 - aquitard, 3 - Unconfined aquifer, 4 Confined aquifer, 5 Water well, 6 Nonflowing artesian well, 7 Flowing artesian well, 8 Water table, 9 River

Higher content of iron near the City of Zvornik (Figure 4) is recorded in water from piezometer BCP-4 [2,6], concentration 9,8 mg/l and manganese 4,0 mg/l, and in piezometers BCP-7, 6 and 9 in the limits of drinking water [10-13]. This can be explained by presence, i.e. absence of vadose zone and bigger speed of underground flow in the parts of alluvion which is closer to the river Drina.

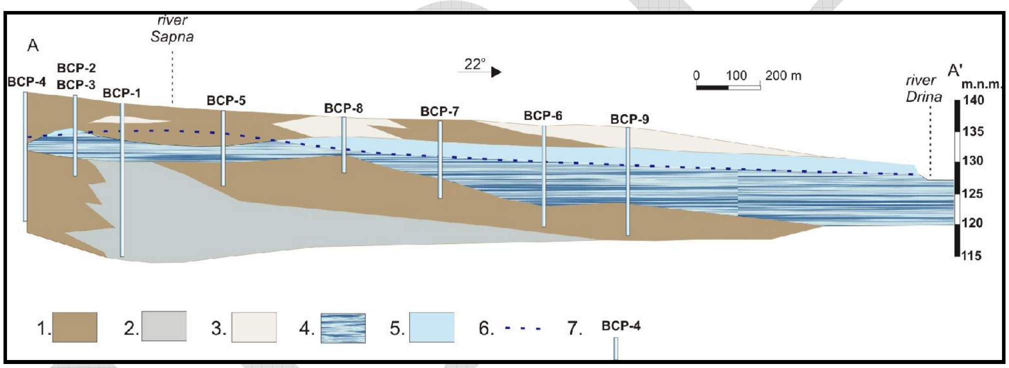

Figure 4. Hydrogeological cross section of area near Zvornik with higher content of iron in water in one part of cross hole (borehole BCP-1 where the level of the groundwater is in the zone of clay overlayer i.e. there is no vadose zone in aquifer; Legend: 1. Clay 2. Marl 3. Sand and sand with clay 4. Aquifer below the watertable 5. Vadose zone of aquifer 6. The water table 7. Borehole

Higher content of iron from 0,72 – 1,7 mg/l and manganese from 0,20 to 1,55 mg/l (Table 1), and occasionally ammoniac in groundwater near Kozarska Dubica (Figure 5) is the result of anarebic conditions in the zones where vadose zone in the aquifer itself is missing (this is determined by boreholes in areas Djolovi and Medjedja).

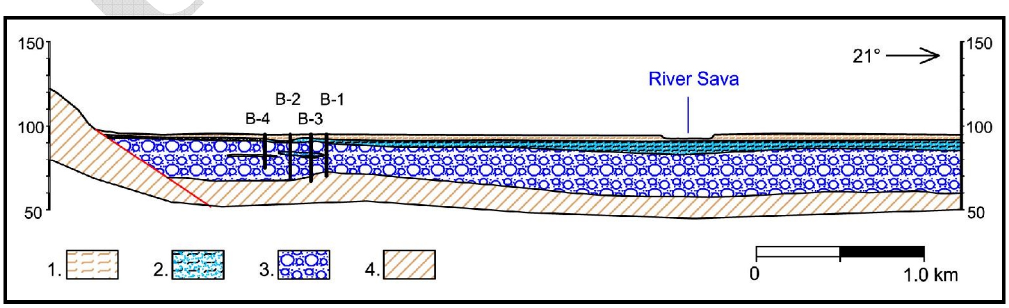

Figure 5. Cross section of spring Medjedja for water supply of Dubica – the whole aquifer in saturacija zone i.e. below the water table; Legend: 1. Clay 2. Clay and sand with clay below the watertable (zone of saturation) 3. Sandy gravel 4. underlie aquifer

Table 1. shows the values of iron and manganese content in groundwater at the fourteen different locations in river basin of rivers Drina, Bosna, Ukrina, Vrbas, Sana and direct basin of Sava. The authors of this work have established the same dependence. The results of correlation with presence, i.e. absence of vadose zone in the aquifer itself shows the clear connection between the lack of vadose zone and higher content of ions in water. This influence is present in such degree that water cannot be used for water supply without previous treatment.

In alluvium of bigger rivers such as the river Sava, the river bed is carved in clay and alluvial gravel and sand which often have no direct connection with significant aquifer in depth of several tens of meters because of clay aquitard layers between them. Recharge of deeper aquifer happens, most frequently upstream, and it is far tens of kilometers from exploitation well. Great lengths of the underground flow from the zone of recharge as well as in regimes of artesian aquifer of peripheral parts of big neogene basins, slow water replacement, biochemical processes and aquifers, and the lack of vadose zone in the aquifer itself are a precondition for higher content of iron and manganese.

The consumption of oxygen in a slow groundwater flow because of biochemical processes happens as well in this type of aquifer, by the bio-degradation processes of organic matters, presence microorganisms in groundwater, and by chemical processes of oxidation in aquifer.Such is the case in most part of Cities of Brcko, Samac, Brod and Gradiska.

This work also shows aquifers from alluvial and terrace's gravel and sand in which vadose zone is present in upper part of aquifer, so the content of iron and manganese in groundwater is in limits of drinking water (PS Mejdan, Čelopek - Zvornik, Grmić near Bijeljine, Rafinerija Modriča, PS Rudanka near City of Doboj).

Table 1. **Display of results of analyses of content of Fe, Mn in quaternary age aquifers in the neogene basins of Republic of Srpska**

Location:	Name of water well/borehole	Age of aquifer: 1. Quaternary (alluvial or terrace sediments) a 2. Pliocene or pleistocene(pl)	River basin	Fe (mg/l)	Mn (mg/l)	Presence of vadose zone in aquifer itself +/-
PS Mejdan at City of Zvornik	B-1	al	Drina	max 0,1	max 0,01	+
Čelopek near City of Zvornik	BČP-1	al	Drina	9,80	4,00	-
Čelopek near City of Zvornik	BČP-6	al	Drina	0,08	0,00	+
Kozluk near City of Zvornik	VEB-1	al	Drina	max 2,80	max 0,10	-
Brodac near City of Bijeljina	B-1	pl	Sava	0,57	0,00	-
PS Grmić near City of Bijeljina	*	al	Drina	max 0,1	max 0,01	+
PS Plazulje near City of Brčko	*	al	Sava	max 2,00	max 0,35	-
EFT Stanari near City of Doboj	BS-12	pl	Ukrina	max 3,27	max 0,30	-
PS Rudanka near City of Doboj	*	al	Bosna	max 0,2	max 0,01	-
PS in City of Brod	*	al	Ukrina	max 4,00	max 0,07	-
PS Rafinerija Modriča	*	al	Bosna	max 0,2	max 0,01	+
"Stirokard" City of Srbac	BS-2	al	Vrbas	1,70	0,05	-
PS Međeđa City of Koz. Dubica	*	al	Sava	max 1,70	max 1,55	-
Mira in City of Prijedor	BM-2	pl	Sana	max 1,74	max 1,75	-

* - group of wells

4.0 Conclusion

By correlation of iron and manganese content in aquifers of quaternary age and sand-point and artesian aquifers in Neogene basins of Republic of Srpska and Brcko district with the existence of vadose zone in the aquifer itself, the authors of this work have made a conclusion that nonexistence of vadose zone in the upper part of the aquifer itself, with the condition of sufficient length of underground flow in such conditions, creates a crucial prerequisite of higher iron content, and occasionally manganese in groundwater.

According to this criterion, the authors of this work stress the following:

- The zone of aquifer with present vadose zone in the aquifer itself (content of iron and manganese in the limits of drinking water),
- Transitional zone, and
- Zone of aquifer without present vadose zone in the aquifer itself (the content of iron and manganese is higher in relation to the drinking water norms).

Contribution to the knowledge of the influence of vadose zone in the aquifer itself to chemical content of water can help researchers with planning, research, predicting, the choice of location and projecting wells for groundwater abstraction and planning treatment plants and total investments.

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