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In situ and laboratory treatment tests for lowering of excess manganese and iron in drinking water sourced from river–groundwater interaction

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Abstract Manganese and iron are essential nutrients at low doses. However, long-term exposure in high doses may be harmful. Human activities and natural sources are responsible for manganese and iron contamination in water. This study aimed to investigate the source of high manganese and iron contents in shallow groundwater, where the groundwater is used for drinking purpose, and to decrease the excess manganese and iron from shallow groundwater. Based on the on-site analytical results taken from the wells in the study area, iron contents in water samples varied between 30 and 200 µg/L, which were under the allowable limits of Turkish Drinking Water Standards (TDWS) (Water intended for human consumption, <http://rega.basbakanlik.gov.tr/eskiler/2005/02/20050217-3.htm>, 2005). However, manganese levels varied from 30 to 248 µg/L, which some of them are higher than the allowable limits of TDWS (Water intended for human consumption, <http://rega.basbakanlik.gov.tr/eskiler/2005/02/20050217-3.htm>, 2005) (50 µg/L), and EPA (<http://water.epa.gov/drink/contaminants/index.cfm>, 2006) (50 µg/L). The source of excess manganese is originated mainly from geogenic source besides Porsuk River interaction in shallow aquifer in the specific section of the study area. To decrease high manganese content from the well water and reservoir water, laboratory and in situ treatment tests were applied. Among these tests, chlorination, associated with filtration (by fine sand, active carbon and zeolite) and the use of

different filtration procedures by cation exchange resin were determined as the most effective methods, which was not previously applied on-site as a combinative approaches to reduce the excess manganese in water.

Keywords Drinking water · Reduce excess manganese and iron · Filtration · Groundwater

Introduction

In our century, about one-third of the world's population depends on groundwater to meet their drinking and irrigation water demands (Alley et al. 2002). Alluvial aquifer is the main source of drinking water for many European countries (Kedziorek and Bourg 2009). Many shallow wells have been drilled near river bank due to having high infiltration rate into alluvial aquifer. However, as reported in the literature, groundwater becomes undrinkable due to many different reasons (e.g., land degradation, deforestation, poor agricultural activities, overpopulation, inaccurate exploitation, and management of the water resources).

Environmental pollution due to natural (including geogenic) or anthropogenic reasons occurred in surface water resources is relatively more common in proportion to groundwater (May et al. 2011; Petitta et al. 2011; Rao et al. 2012; Reddy 2013; Choi et al. 2013), this makes groundwater an attractive source for drinking water. However, water usage and management in upstream area impact water quality and quantity in downstream area. Hence, the protection of the quality and quantity of freshwater resources gains a great importance to sustain its utilization (Kumar et al. 2010). In this respect, river–groundwater interaction can alter water quality and quantity by reciprocally (Mohammadi 2009; Gao et al. 2010; Baalousha

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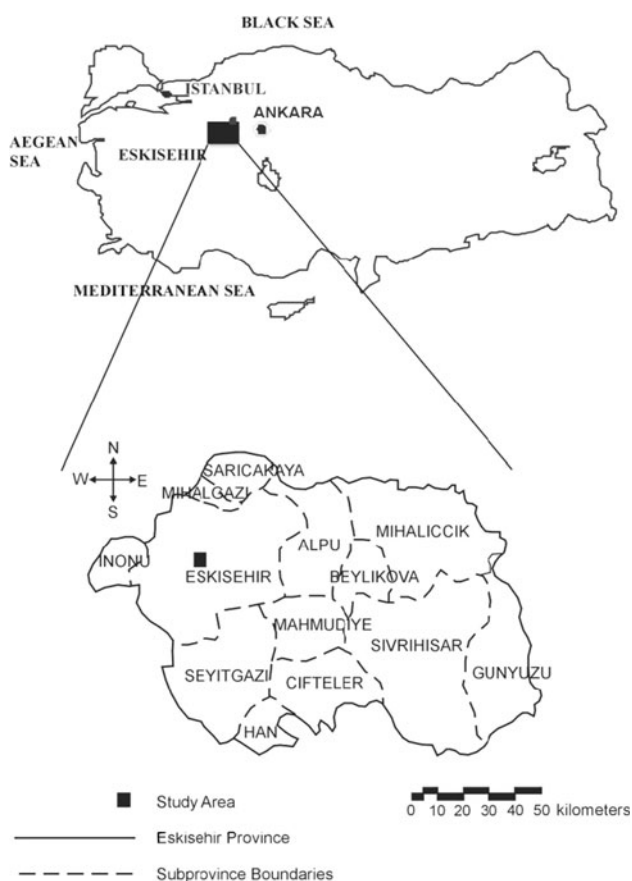


Fig. 1 Location map of the study area

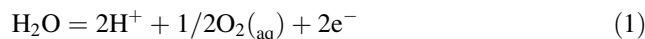
2012; Edet et al. 2012; Delfs et al. 2012; Borrelli et al. 2012; Garcia et al. 2012).

The shallow groundwater in the study area is exploited to meet domestic water for the Meselik Campus of Eskisehir Osmangazi University. The campus is located in close proximity to the course of the Porsuk River (Eskisehir, Turkey). The most common pollutants in the Porsuk River, which also cause deterioration of groundwater quality, are mainly manganese and iron as much as nitrogen, phenol, and trace elements (Yuce et al. 2006). Previous research indicates that the Porsuk River interacts with the shallow groundwater system (Kacaroglu 1991; Kacaroglu and Gunay 1997; Yuce et al. 2006). As a result of this interaction, shallow groundwater is widely contaminated by the Porsuk River (Yuce 2007). The reductive dissolution of Mn and Fe oxides has caused increase in the Fe and Mn concentrations in groundwater of the shallow aquifer. Consequently, high dissolved manganese and iron in drinking water provided from the shallow wells may cause health problem. For this reason, reducing the manganese and iron concentrations in the shallow groundwater is the essential.

Manganese and iron are the most common trace elements in the aquatic environment. But their concentrations in drinking water are varied in many Guidelines. In this respect, the allowable upper limit of iron content in drinking water is 200 $\mu\text{g/L}$ according to Turkish Drinking Water Standards (TDWS 2005) and Guidelines for European Community Drinking Water Standards (GECDWS 1998) while it goes up to 300 $\mu\text{g/L}$ based on Guidelines for Canadian Drinking Water Quality Standards (GCDWS 1996), and Environmental Protection Agency (EPA 2006). For manganese, this limit is 50 $\mu\text{g/L}$ according to TDWS (2005), GECDWS (1998), EPA (2006), and GCDWS (1996).

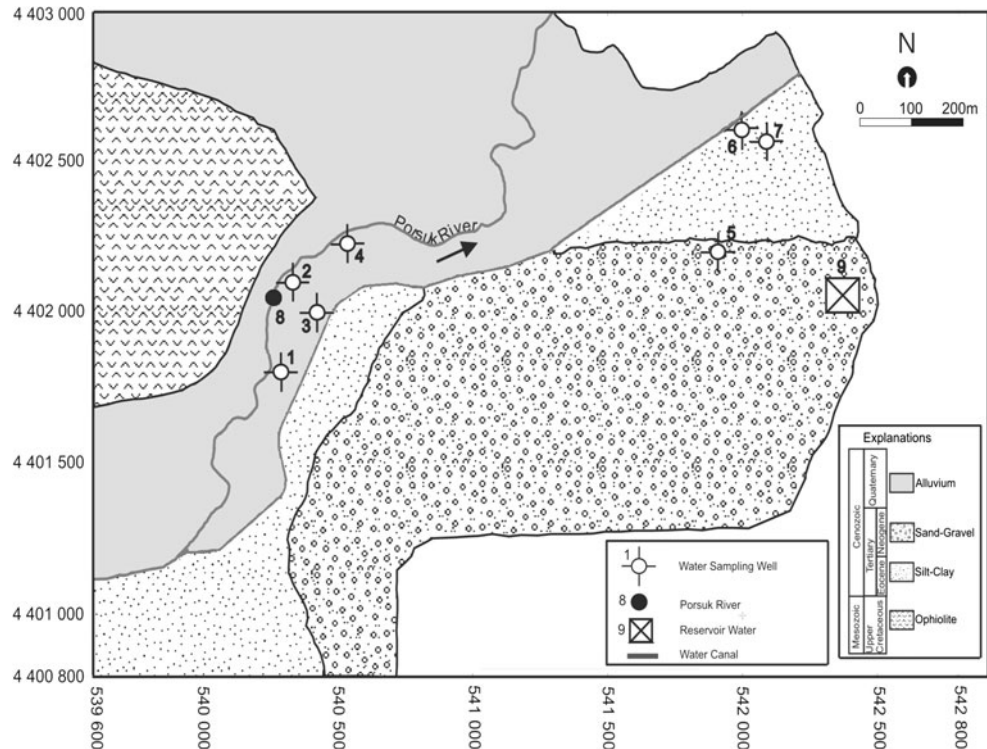
Manganese has usually a divalent ion (Mn^{2+}) in igneous rocks (Bell 1998). Biotite and hornblende are common ferromagnesian minerals in igneous rocks besides pyroxenes, amphiboles; magnetite and olivine are other sources of iron (Appelo and Postma 1992) in rock-forming minerals. Iron and manganese oxyhydroxides may dissolve in surface waters as a result of photo-reduction (Drever 1997). Chemical and bacterial reduction of Mn(IV) to Mn(II) has been seen in groundwater with low oxygen content (Jaudon et al. 1989). The occurrence of the manganese in suspended particles, sediments, and water resources (lakes, rivers, and groundwater) was reported widely (Drever 1997; Berbenni et al. 2000; Barber et al. 1995).

Oxygenated water has lower iron and manganese contents because they form insoluble compounds in water. Generally, uncontaminated surface and groundwater have higher dissolved oxygen content, so iron and manganese are found insoluble forms in water. In surface water, iron and manganese are most likely trapped within suspended organic matter particles. Under anoxic conditions, iron and manganese remain in their soluble forms of Fe^{2+} and Mn^{2+} (Domenico and Schwartz 1990; Appelo and Postma 1992; Fetter 1999). Redox condition in water is mainly characterized by two parameters, redox potential (E_h) and dissolved oxygen (DO). Thus, the oxidizing and reducing conditions are measured as a function of E_h and DO. Higher E_h values correspond to more oxidizing conditions while lower values correspond to more reducing conditions. DO concentration generally is expressed in ppm or % saturation in related with E_h and pH, by the following reaction and equation:



$$E_h = E_0 - 0.059 \text{ pH} + 0.01475 \log [\text{O}_2] \quad (2)$$

On the other hand, a recent study (Kedziorek and Bourg 2009) suggests that the electron trapping capacity of dissolved oxygen and nitrate is a better indicator for manganese and iron dissolution in alluvial aquifers near river.

Fig. 2 Sampling location and geological map of the study area

Many conventional and improved treatment techniques were searched and applied to decrease or remove iron and manganese in water are based on physico-chemical reactions such as usage of manganese greensands or intense aeration and chemical oxidation or utilization of polyphosphate, ion exchanger (resin or zeolite), microbiological removal, and chlorination (oxidation) plus filtration (Shavandi et al. 2012; Tarasevich et al. 2012; Dubinina et al. 2012; Van Halem et al. 2012; Farnsworth et al. 2012; Tang et al. 2012; Fu et al. 2011; Carriere et al. 2011). All of these treatment techniques are useful, but most of them certainly reproduce some other quality problems. For instance, the application of manganese greensand method (MGM) (<http://www.birmfilter.com/index.asp?p=s10>) requires regeneration process. Potassium permanganate is used in the regeneration process. Since the potassium permanganate is in pink color, it may cause pink stain in water unless the water is cleaned by the filtration membrane. Therefore, MGM is not applicable without an extra process for removing the excess manganese from water. A regular backwashing is also essential for effective filter performance in MGM. Another common approach to reduce excess manganese in water is aeration of water. In order to obtain a full achievement in the aeration technique, after abstracting of groundwater from the well, water must gush onto the surface at the stair-shaped plates as a first step pooling to provide full saturation by air. Following this, the aerated water must be exposed to a second pooling by over-flowing

to collect the water before introducing it to a water reservoir, which mostly consists of a closed system.

In this study, the most efficient methods to reduce excess manganese and iron in water without undesirable remnants were searched and tested as in situ and laboratory experiments by the innovative combinations of different individual treatment techniques were performed for the improving of water quality in the study area.

Materials and methods

Location and geological setting

The study area (6 km²) is located in the northwest of the Central Anatolian Region of Turkey, in the Eskişehir Province (Fig. 1).

The basement in the study area is in Triassic age consisting of schist, limestone, and ophiolitic mélange that overlain by sedimentary (conglomerate, marl, and claystone) and volcano-sedimentary units (agglomerate and basalt) of Eocene, Miocene, and Pliocene (Gozler et al. 1996). Pleistocene and Holocene units are composed of old and young alluvium, respectively. The thickness of young alluvial deposits varies from 5 to 15 m in the wells opened in the study area with 14 and 70 m depths. Old and young alluvial deposits form the main aquifer units. Young alluvium outcropped around Porsuk River comprises loose

Table 1 Water analyses results (September and October 2009) (samples were taken after long period of pumping)

Sample No			Temp (°C)	SC (µS/cm)	TDS (mg/L)	DO (mg/L)	Eh (mV)	pH	In-situ colorimetric analyses results (µg/L)			Analyses results in EMMLs (mg/L)				
									Fe	Mn	Fe/Mn	NH ₄	NO ₃	NO ₂		
	MCL for Turkish Drinking Water Standards (TDWS), 2005								200	50			50	0.5		
	MCL for European Community Drinking Water Standards (GECDWS), 1998								200	50						
	MCL for Canadian Drinking Water Quality Standards (GCDWS), 1996								300	50						
	MCL according to the EPA, 2006								300	50			10			
	Sampling Locations	Sampling from specific depth (m)									Fe	Mn	Fe/Mn	NH ₄	NO ₃	NO ₂
1	The active well			13.7	767	0.50	4.6	375	7.5	40	248	0.15	<0.05	7.06	0.143	
2	The recently drilled well (spare well) (inactive)	Filtered by (0.45 µm)	5	14.4	670	0.44	7.3	365	8.0	120	97	1.23	nd	12.48	0.878	
			10	nd	nd	nd	nd	nd	nd	30	108	0.27	nd	15.70	1.504	
			17	nd	nd	nd	nd	nd	nd	30	78	1.15	nd	17.65	1.452	
3	Spare well (inactive)	Filtered by (0.45 µm)	14	12.0	682	0.44	2.0	175	7.4	160	164	0.98	nd	1.86	0.003	
			20	nd	nd	nd	2.2	181	nd	100	160	0.63	nd	2.92	0.007	
			31	nd	nd	nd	nd	nd	nd	180	152	1.18	nd	1.60	0.025	
4	Well			13.4	694	0.45	3.8	243	8.1	100	30	3.33	nd	3.54	0.002	
5	Well			15.2	1441	0.94	5.8	368	7.7	200	32	6.25	<0.05	36.50	0.010	
6	Spare well-27279 (inactive)			15.3	919	0.60	6.3	366	7.9	90	52	1.73	<0.05	25.35	0.011	
7	Well-27278			15.5	924	0.62	4.3	294	8.1	nd	67	nd	<0.05	22.75	0.011	
8	Porsuk River			15.5	618	0.37	7.8	nd	7.5	50	212	0.24	<0.05	5.66	0.132	
9	Reservoir water			nd	nd	nd	nd	nd	nd	30	148	0.20	<0.05	5.38	0.127	
	Tap water			nd	nd	nd	nd	nd	nd	110	104	1.05	<0.05	7.38	0.016	

nd not detected, nf not filtered, EMMLs Eskisehir Metropolitan Municipal Laboratories

gravel, sand, silt, and clay materials and their mixture. Alluvial deposits are underlain by ophiolitic mélange. The alluvial aquifer is unconfined character in the study area. The yields of the wells range from 18 to 90 m³/h. The study area contained five actively operated wells, which provide drinking water to the University, and two non-operative spare-wells. The active well, No. 1 and the spare-wells (inactive), No. 2 and No. 3 are very close (within 50 m distance) to the Porsuk River. The thickness of recent alluvium in the well No. 2 is 8 m. The depth of this well is 20 m drilled nearby the Porsuk River. The recent alluvium in this well is underlain by ophiolitic mélange in 12 m thick at the bottom.

Selection of sampling locations

In the dry period of 2009, water samples were taken from the water-wells and water reservoir (Fig. 2). The dry period was selected for sampling period because worst-case-based water quality mostly occurs in this period due to the lack of dilution by precipitation (rainfall, etc.). In total, 14 water samples were collected from 7 water-wells in the various depths, Porsuk River, reservoir, and tap water. All sampled-wells drilled in the shallow phreatic aquifer are along the Porsuk River. The locations of the sample wells were specified according to Global Position System (GPS).

Water levels in wells were measured by a water level measurement unit (hydrometer) and hydraulic heads changed from 801 to 796 m above sea level (a.s.l.) in direction from well No. 1 to well No. 4 while water level in the Porsuk River varied from 803 to 802 m a.s.l. in the sampling section of the study area (i.e., hydraulic head measurements were only available for the wells No. 1 through No. 4 since the rests were equipped with submersible pumps).

Sampling and analytical procedure

Water samples were collected from operating and non-operating well and analyzed in situ for manganese and iron contents. Water samples from the spare (non-operating) wells were collected under stagnant condition by the deep sampling device (hydro-bios) and a portable-pump (Power Pack PP1 with Waterra inertial pump) under the operating (active) condition in varied depths to identify any difference between stagnant and active conditions regarding manganese and iron content. In situ iron and manganese analyses were carried out based on the FerroVer (AccuVac Ampules) and PAN methods, respectively. The detection limits of these methods are 30 and 20 µg/L for dissolved iron and manganese, respectively. An ascorbic acid reagent was used initially to reduce all oxidized forms of

Table 2 Major and minor ion analysis of the active university's well (No. 1)

Ion	Concentrations (meq/L)
Na	0.91
K	0.02
Ca	3.11
Mg	4.44
Total cation	8.48
HCO ₃	6.56
SO ₄	0.92
Cl	0.70
NO ₃	0.02
Total anion	8.20
Ion balance error %	1.67
Trace elements	(µg/L)
Ni	1.48
Al	9.26
Fe	40
Mn	248
Cr	2.08
As	7.04

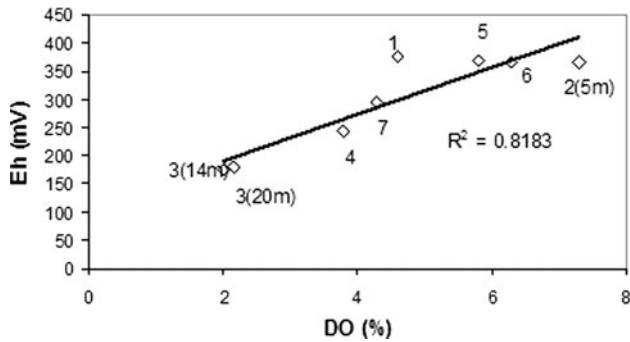


Fig. 3 E_h versus dissolved oxygen (DO%)

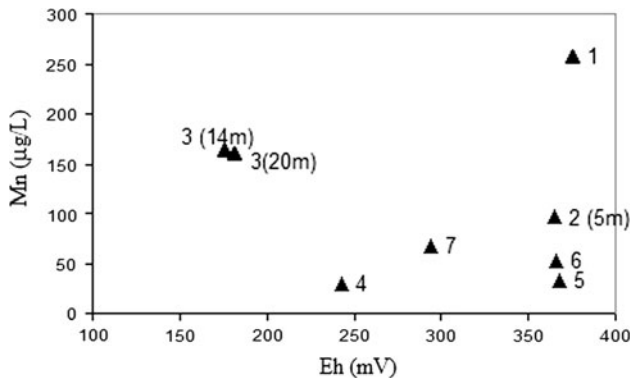


Fig. 4 Dissolved Mn versus E_h

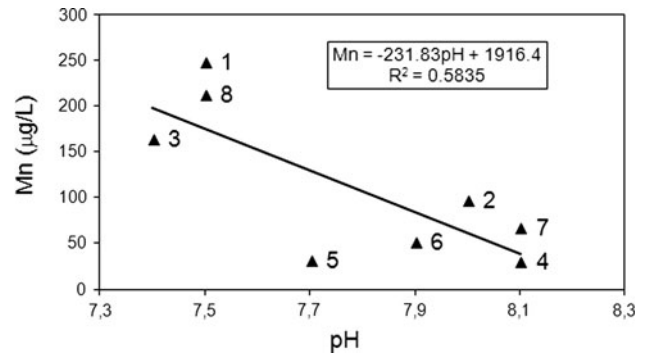


Fig. 5 Dissolved Mn versus pH

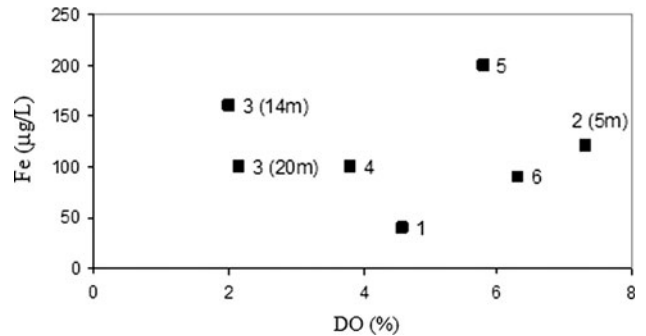


Fig. 6 Dissolved Fe versus dissolved oxygen (DO%)

manganese to Mn^{2+} . An alkaline-cyanide reagent was added to mask any potential interference. PAN Indicator was then added to combine with the Mn^{2+} to form an orange-colored complex. Since unfiltered water samples caused a change in the manganese and iron contents by artificial dissolution in suspended sediments in water, the collected water samples were filtered by 0.45 µm filter before analyzing. Detailed procedure for in situ colorimetric analysis can be obtained from Hach-DR/890, 2007. The NH_3 , NO_2 , NO_3 , and NH_4 analyses were performed in Eskisehir Metropolitan Municipal Laboratories (EMMLs). Major ions and trace elements were analyzed by Ion Chromatography in the EMMLs. The specific conductance (SC), water temperature (°C), total dissolved solid (TDS), pH, and E_h values were measured in situ by YSI-556 Handheld Multi-parameter Instrument. Error limits (accuracy) for water temperature, E_h , SC, and pH were ± 0.15 °C, ± 20 mV, ± 0.5 and ± 0.2 %, respectively. Trace element analyses were performed by ICP-OEM.

Experimental studies

The iron contents of the water samples were lower than the maximum allowable limit. Thus, much effort has been spent on decreasing the manganese concentration in the water to a safe drinking water quality. To reduce the excess

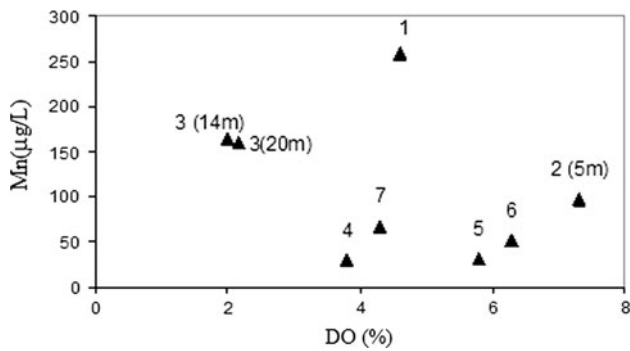


Fig. 7 Dissolved Mn versus dissolved oxygen (DO%)

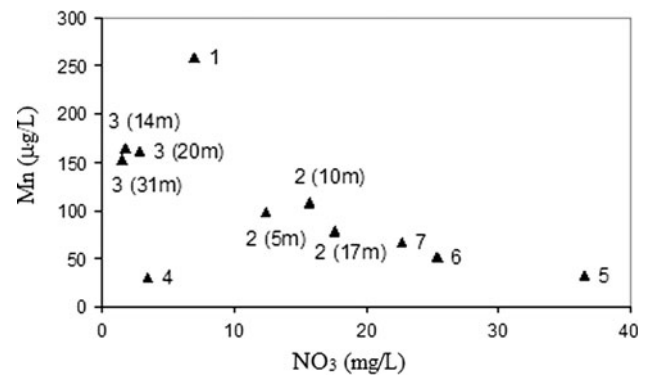


Fig. 9 Dissolved Mn versus NO_3

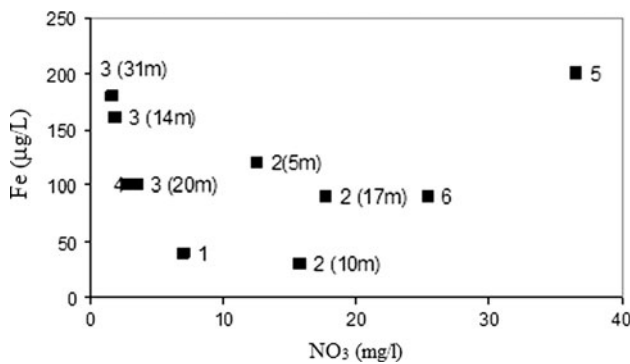


Fig. 8 Dissolved Fe versus NO_3

manganese in water, laboratory, and in situ experimental methods were applied. For the laboratory tests, the sample taken from operating well No. 1 was subjected to four different experiments: (1) one part of the samples was rinsed under aeration (circulation of raw water through cascades to air) and the other part was only aerated without rinsing, the manganese concentrations of both parts in the sample were measured after 18 h of aeration, (2) another part of the sample from the same well was filtered by a $0.45 \mu\text{m}$ and the other part was passed through a smaller sized filter by $0.2 \mu\text{m}$. Both filtered water samples were aerated separately, (3) after application of above-mentioned filtration procedures, the ozonation was performed to the both filtered water samples instead of aeration, (4) in the last experimental method, two filtered water samples were exposed to chlorination. At the end of each method, the manganese contents were measured.

In addition to the laboratory applications, on-site manganese lowering methods were also tested for the same well water sample (i.e., well No. 1). For this purpose, four methods were applied using on-site tests: (1) the combination of chlorination and filtration (sand and active charcoal were tested), (2) the combination of chlorination and filtration (sand, active charcoal, and $0.2 \mu\text{m}$ extra filter were tested), (3) the combination of chlorination and

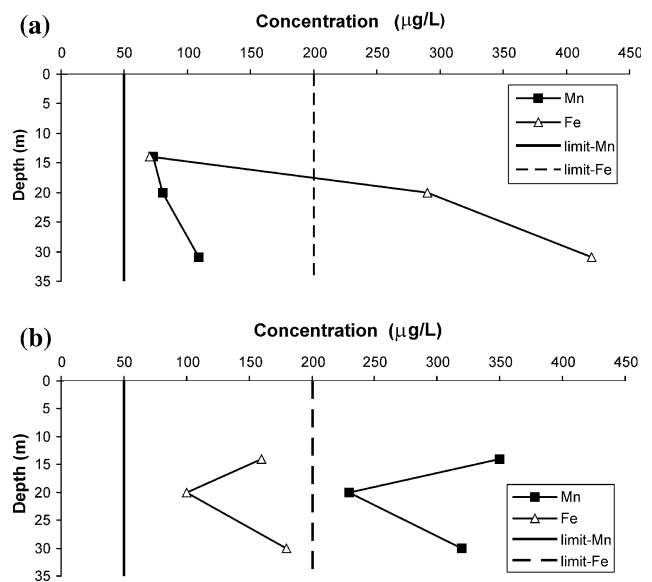


Fig. 10 Variations of manganese and iron concentrations depending on the depth in well No. 3 a before and b after pumping

filtration (sand, active charcoal, and zeolite were tested), and (4) the combination of sand and filtration (only cation exchange resin was used). Water from the well No. 1 was retained for 45 min in aeration following chlorination and then it was filtered. Same procedure was also repeated for water samples collected from the spare wells (No. 2 and No. 3). The water samples from these wells taken at three different depths were analyzed in the laboratory to evaluate the extension of oxidative/reductive environment in the shallow aquifer condition. At the end of each test, the manganese content was measured by colorimetric technique.

Results and discussion

The analytical results of the water samples are given in Table 1. The minimum and maximum concentrations of

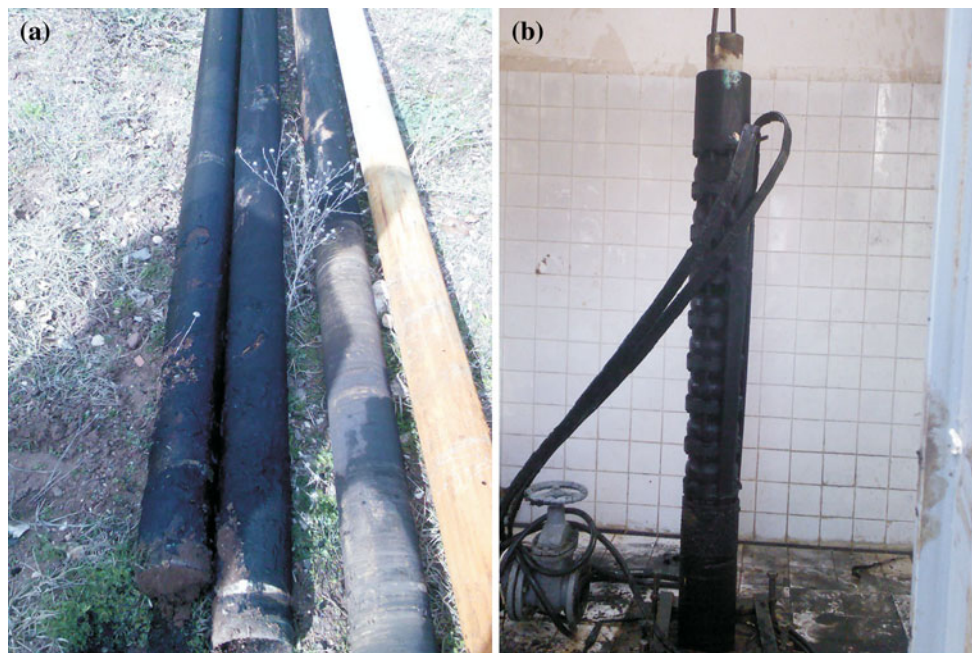


Fig. 11 Manganese coating on the pipes and pump in the active well No. 1

iron and manganese vary from 30 to 200 $\mu\text{g/L}$ and from 30 to 248 $\mu\text{g/L}$, respectively. The results show that the manganese content is higher than the allowable limits for drinking standards. Iron contents of the groundwater samples are generally lower than the maximum allowable value recommended by TDWS (2005), GCDWS (1996), EPA (2006), and GECDWS (1998). However, the manganese content in the water samples is quite higher than the allowable limit (50 $\mu\text{g/L}$) for 12 water samples (Table 1) out of 14. Particularly, the water sample taken from the active well (No. 1) nearby the Porsuk River has the highest manganese content (Table 2).

The manganese and iron contents in the samples taken from various depths of the spare well No. 3 show no remarkable change in the depth. Thus, this indicates that a reductive environment prevails in the environment of well No. 3 and relative decrease occurs in the Fe/Mn ratios (Barber et al. 1995) and nitrate values in comparison with the environment of wells No. 4 and No. 5 (Table 1). This is likely to be the result of nitrate serves as electron acceptor for organic matter in anoxic condition.

The in situ measurements of E_h and DO% show a linear correlation (Fig. 3). By reviewing the analytical results, an inverse relationship between E_h and dissolved Mn is observed (Fig. 4), except for sample 1. In other words, dissolved Mn decreases with oxidation due to conversion of Mn to the insoluble forms. Thus, there is an inverse correlation between higher oxide forms of manganese with an increase in pH (Fig. 5), which is consistent with the theoretical expectations. Samples from well No. 2 in 5 m

depth, well No. 3 in 14 and 20 m depths were used in Figs 3, 4, 5, 6, and 7. Since there is no simple trend between Fe and Mn against DO% (Figs. 6, 7), DO may not be a significant electron acceptor for them. However, NO_3 seems to overtake this role by nitrification process instead of DO (Figs. 8, 9). The occurrence of nitrification process (Fig. 9) in shallow aquifer system is related with the increasing thickness of alluvium. E_h , DO, and NO_3 values in water samples from the wells No. 3 and No. 4, relatively low. A corresponding increase is observed in dissolved iron and especially manganese. According to the obtained data, sample 1 (from well No. 1) showed a relative decrease in DO and NO_3 concentrations, but E_h and manganese concentration increase, which may be resulting in a reductor role of iron for manganese (Appelo and Postma 1992). In contrast to the sample 1, sample 5 (from another well) showed an increase in iron concentration and decrease in manganese concentration which may indicate an oxidative role of manganese for iron (Kedziorek and Bourg 2009). The similar increase in manganese concentration and decrease in NO_3 concentration in well No. 1 and the Porsuk River may result in the bank infiltration from the Porsuk River into shallow aquifer. Thus, recharge/discharge condition between the Porsuk River and shallow aquifer can create the oxidation/reduction process in the aquifer system. Porsuk River water is originated from Porsuk dam's lake located in the upstream area with ca. 20 km distance to the sampling site. Mn and Fe contents in water from Porsuk dam's lake are lower (average 70 $\mu\text{g/L}$ —RDMFE 2005) up to the sampling site. After the outlet of Porsuk

Table 3 Laboratory experiments for the removal of manganese and iron from water

Element	Unit	Untreated water sample from well No. 1	Aerated 18 h		Aerated		Ozonated by 0.7 ppm		Chlorinated by 1.8 ppm	
			Rinsed	Stagnant	0.45 μm filter	0.2 μm filter	0.45 μm filter	0.2 μm filter	0.45 μm filter	0.2 μm filter
Manganese	$\mu\text{g/L}$	248	51	248	38	28	51	33	71	27
Iron	$\mu\text{g/L}$	40	10	20	20	10	20	10	20	10

dam's lake, Fe and Mn levels increase in the river water most likely to be the result of groundwater recharge having high Fe and Mn from Eocene basalts and ophiolite caused a reductive environment in shallow groundwater at the upstream of sampling site. Hence, DO and NO_3 concentrations decreased in the well samples No. 1, No. 3, and No. 4. Indeed, since the river is in contact with atmosphere, Mn and Fe are expected to be easily oxidized and converted to oxide and oxy-hydroxide precipitates. However, presence of Mn and Fe in Porsuk River water (sample 8) is likely that the river water has not had enough time to fully oxidize the all Mn and Fe influx for this sampling section.

Fe/Mn ratio was low in the samples 1, 8, and 9. In the transition zone (anoxic–oxic), Fe/Mn ratio especially decreases with the precipitation of Fe as it was identified for these samples.

When Fe^{2+} is oxidized to Fe^{3+} and combined with an appropriate anion, it precipitates as iron oxyhydroxide (FeOOH) in water and if manganese co-exists with iron in water, it precipitates as the hydroxyl of Mn^{3+} after the precipitation of Fe^{3+} . This is because oxidation of iron faster than manganese providing that existing of iron bacteria, which catalyze the oxidation reactions under certain conditions of pH and E_h (WHO 2004). Consistent with this, we observed slight lesser amount of iron in water of the well No. 3 (non-operated for a long time) due to exposure in the oxidative condition by pumping and the variations of manganese and iron contents in different depths before and right after pumping were given in Fig. 10 (concentrations shown in Fig. 10 were measured before and right after pumping, therefore they are different than that of given in Table 1). Interestingly, manganese concentration increased

Fig. 12 Manganese and iron concentrations in water (from well No. 1) following laboratory treatment methods

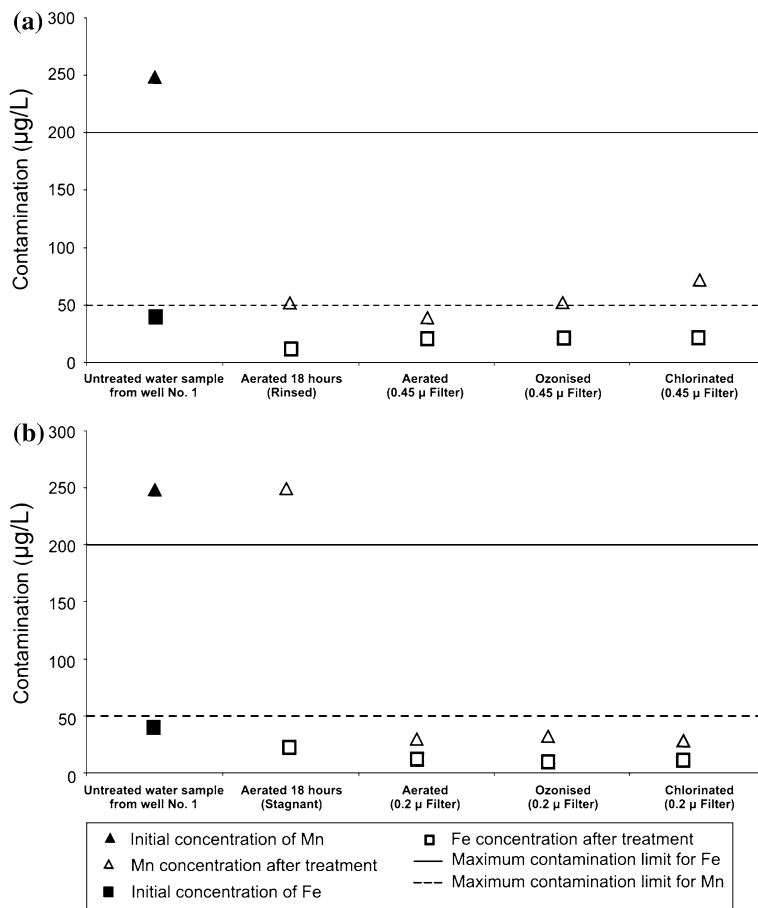


Table 4 In situ manganese removal experiments according to the analyses results

	Untreated water sample from well No. 1	Well water retained for 45 min followed by chlorination Sand + Active Carbon	Well water retained for 45 min followed by chlorination Sand + Active Carbon + Zeolite	Well water retained for 45 min followed by chlorination Sand + Active Carbon + 0.2 μ filter	Raw Well Water Sand + Resin
Manganese $\mu\text{g/L}$	248	210	25	72	0.00
Sodium mg/L	20.9				163

nd not detected, *nf* not filtered, *EMMLs* Eskisehir Metropolitan Municipal Laboratories

immediately following pumping and it is most likely as a result of flushing effect that migrate manganese-rich stagnant water at the deep to the surface by pumping. Furthermore, manganese removal bacteria require completely oxic environment (Johnson et al. 2009). After oxidation, water color became brownish due to the precipitation of the ferric hydroxide and manganese hydroxide in water. Hence, manganese coatings were observed on the inner-walls of water reservoir as well as on the stainless-steel pipelines and the submersible pump (Fig. 11).

Since the hydraulic head (801–796 m a.s.l.) in alluvial aquifer in the south of Porsuk River is lower than that of Porsuk River (803–802 m a.s.l.), alluvial aquifer is fed by this particular section. The wells (No. 1, No. 2, and No. 3) drilled near the Porsuk River have excess manganese concentration especially due to the river–groundwater interaction along the section of the study area, except for the well No. 4. This is because well No. 4 is extracted groundwater from the deeper aquifer and well equipped with stainless steel casing, and the annulus between well wall and casing is sealed up to the aquifer level, to protect it against surface contamination. Therefore, river water cannot seep into the well No. 4, but the other wells are exposed to river influence due to the lack of such a protective construction in addition to lower water level in the wells compare to the water level in the river (see Sect. 2.2). Besides river influence, there also exists a lithologic effect since Fe–Mn-rich Eocene basalt and ophiolitic basement, outcropped in the northwest of the study area. Thus, the alluvium contains debris from the ophiolitic basement and Eocene basalt, which is abundant in manganese and iron rich minerals.

Results of chemical analyses show that HCO_3^- is dominant anion in well water (No. 1) and the Porsuk River (Table 2). HCO_3^- and Mn can form MnHCO_3 as a result of chemical interaction. If water is exposed to oxidative condition, then manganese, sourced from MnHCO_3 , can transform into insoluble oxides and this may result in the precipitation of Mn. When manganese bicarbonate is exposed to oxygen, it converts into manganese hydroxide which is less soluble form (Allen and Pelude 2001), and then manganese

hydroxide precipitates as black scale deposits. This is why the inner-walls of the water reservoir are colored in dark.

To achieve satisfactory result for removing manganese and iron from water without problematic remnants, as mentioned in a previous section, four different laboratory tests were applied: (1) aeration, with and without rinsing, (2) aeration followed by filtration using two different types of filters, (3) ozonation, and (4) chlorination following two different sized filtrations (Table 3). The application of the second, third, and fourth laboratory tests provided sufficient decrease in the manganese to meet the acceptable quality for drinking water standards (Fig. 12; Table 3).

On-site experimental methods were the combination of chlorination and filtration that consisted of the different materials such as sand, active charcoal, zeolite, and resin. By application of the on-site tests, manganese concentration of water from the active well No. 1 was decreased below the allowable limit for drinking water. Particularly, by using the third and fourth in situ methods, manganese content was successfully decreased from 248 $\mu\text{g/L}$ to a lower level than the TDWS (2005) (Table 4; Fig. 13). By employing the fourth on-site method, the manganese and iron contents were completely removed from the water. However, the unique disadvantage of the fourth method was the increase in the sodium content of water due to the calcium and magnesium adsorption, besides iron and manganese. In spite of this, the sodium content was still under the allowable limit according to TDWS (2005).

In conclusion, our study provided a better understanding about which methods were the best for reducing of excess

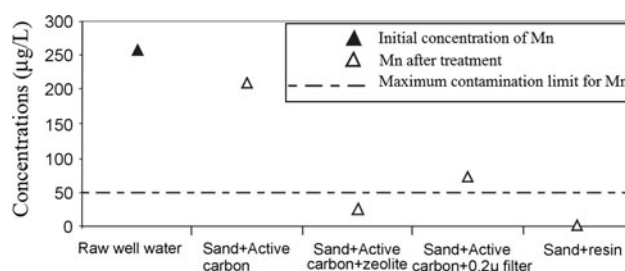


Fig. 13 Manganese concentrations in water (from well No. 1) following in situ treatment methods

manganese in water. As a result, the application of two methods, namely, the filtration by the combination of sand (4th in situ method) and resin without chlorination, and the filtration by the combination of sand, active carbon, and zeolite with chlorination (3rd in situ method) were the most practical and effective methods among the four on-site methods.

Conclusions

We found high manganese content in water samples taken from the wells opened in shallow groundwater system to provide drinking water near the Porsuk River. On the basis of the analytical results of water samples, the manganese content in eight out of ten were over the allowable limit according to national and international drinking water standards. This shallow aquifer system has originally a reductive character (having low nitrate content), converts into an oxidative environment by the infiltration from Porsuk River. This change leads to the alteration of the dissolved Mn and Fe concentrations in the groundwater. Thus, the major reason of the excess manganese and iron contents in shallow groundwater is due to the interaction between Porsuk River and shallow groundwater system. Conformingly, groundwater flow patterns, water chemistry (Yuce et al. 2006; Yuce 2007; Alptekin 2012), temperature, pH, NO₃ data indicate such a mixing from the Porsuk River into the shallow groundwater system. Moreover, lithology of alluvial aquifer is another reason for excessive manganese and iron since aquifer composes particularly of mafic minerals (rich in iron and manganese) associated with volcanic and ophiolitic rocks outcropped in the study area.

To reduce the excess manganese and iron content in shallow groundwater, we applied both laboratory and on-site methods on collected water samples from the wells in the study area. By the application of the laboratory methods, such as the coupled processes of filtration and aeration, filtration and ozonation, and filtration and chlorination, satisfactory results were obtained in reducing manganese and iron content of the well water even well below than the allowable limits for drinking purpose. Filtration by the combination of sand and resin without chlorination, as well as the filtration with the combination of sand, active carbon, and zeolite with chlorination were the most considerable and economic methods among the four on-site methods to diminish excess manganese and iron content in the groundwater. Finally, excess manganese content was decreased to 0 and 25 µg/L by application of these two methods, respectively.

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