



Vulnerability of groundwater to iron and manganese contamination in the coastal alluvial plain of a developing Indonesian city

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Abstract

This paper evaluates environmental conditions responsible for the high concentrations of trace metals in Indonesian coastal groundwater. Indramayu, which has significant potential groundwater resources, but for which limited information is available regarding its vulnerability, is selected as our study area. Results show that Fe^{2+} and Mn^{2+} are natural contaminants in the groundwater of the study site. The correlations of trace metals with salinity and redox-sensitive parameters verify that saline water has a significant impact upon the dissolution of Fe and Mn. Furthermore, reductive condition is confirmed to be responsible for Fe and Mn dissolution with a less significant correlation compared to salinity. Moreover, the high concentrations of trace metals are coupled with high dissolved organic carbon (DOC), which indicates that reductive environment may arise because of organic-matter decomposition. Finally, the impact of human activity upon Fe and Mn dissolution is identified at the northern tip of Indramayu, where trace-metal contents are significantly elevated. Further, in the southern part, the groundwater condition is relatively more natural; thus, the impact of human activity upon the presence of Fe and Mn is lesser in this region.

Keywords Trace metals · Salinity · Redox condition · Natural groundwater · Indramayu

1 Introduction

Groundwater quality is presently vulnerable to contaminants from natural and human activities [1]. Among many contaminants, iron (Fe) and manganese (Mn) are present in chemicals derived from both natural sources, such as soil and rock, and human activities, such as industrial wastewater and the overexploitation of groundwater, and can eventually pollute groundwater [1–4]. These trace metals are undesirable in clean water due to aesthetic problems, the deterioration of distribution networks, and health issues. In terms of aesthetic problems, Fe and Mn generate an unpleasant taste and odor in water [5]. Groundwater

extraction can generate Fe and Mn precipitates that color an undesirable reddish-brown. These metals can also build up in plumbing systems and cause scaling [6]. Their deposition in pipes both reduces water flow pressure and eventually damages the tubing. Several studies have noted that adverse non-carcinogenic problems, such as nervous system disorders, and respiratory, neurological, and digestion issues, particularly to adults, can arise from Fe and Mn ingestion [7–9].

Fe and Mn are metals with similar geochemical behavior in aquatic environments and exist in dissolved (Fe^{2+} and Mn^{2+}) and suspended (Fe^{3+} and Mn^{4+}) forms [3, 9–11]. They can occur naturally as a result of water–sediment

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interaction which induce their dissolution [12]. Dissolution processes are controlled by several environmental factors, primarily redox conditions [13, 14]. Reductive conditions commonly occur in groundwater systems, which therefore commonly contain elevated Fe^{2+} and Mn^{2+} concentrations [6]; this is recognized as a worldwide issue [8, 11, 15, 16]. The World Health Organization (WHO)'s maximum thresholds for Fe^{2+} and Mn^{2+} in drinking water are 0.3 and 0.4 mg/L, respectively [5]. In Indonesia, the government designs regulations based on the purposes of water use, with the highest priority placed on drinking water [17]. The Fe^{2+} and Mn^{2+} concentrations within this guideline are 0.3 and 1 mg/L, respectively [17].

This study is conducted in Indonesian coastal alluvial plain where the groundwater is potentially vulnerable to Fe^{2+} and Mn^{2+} contamination. Alluvial plain generally has high organic-matter content, which facilitates microbial activities that, in turn, generate a reducing environment promoting the dissolution of Fe^{2+} and Mn^{2+} [6, 13]. Moreover, coastal groundwater is vulnerable to salinization, and previous investigations have found that high salinity is also responsible for the dissolution of metals [11, 18, 19]. The coastal alluvial plain is also a target of urbanization, which has been confirmed to be correlated with elevated Fe^{2+} and Mn^{2+} contents in the groundwater [1, 4, 20]. These issues are mostly attributed to the perturbation of hydrogeological conditions due to human activity. However, limited information is available regarding the natural conditions that are responsible for elevated concentrations of Fe^{2+} and Mn^{2+} . The environmental management required to control Fe^{2+} and Mn^{2+} contamination is also diverse based on the sources of each metal [15]. The mitigation of Fe^{2+} and Mn^{2+} in contaminated areas can be performed by containment and remediation [21], and their removal from water can be performed via filtration and oxidation followed by sedimentation processes [2, 22, 23]. The aims of this research are to evaluate the distributions of these trace metals in the groundwater at the study site and to identify the environmental factors contributing to their presence. This information will be necessary for the sustainable management of clean groundwater in Indonesia.

2 Study area

The area under study is Indramayu, which is located on the north coast of Java Island ($107^{\circ} 52' - 108^{\circ} 36' \text{ E}$ and $6^{\circ} 15' - 6^{\circ} 40' \text{ W}$). The total area is approximately 2100 km² with approximately 1.72 million people and the population growth of 0.54% [24]. The temperature is relatively high, from 22.9 °C to 30 °C. During the last ten years, the total average rainfall was 1649 mm, with a total annual of 108 rainy days in average [24, 25]. Economic activities

in the region are mainly related to agriculture, fishery, and animal husbandry. The Indonesian government is focused on developing Indramayu because the region is vital for rice and fish production, particularly for West Java Province.

2.1 Hydrogeology of Indramayu

Indramayu is a lowland area (Fig. 1a) with a low topographic gradient of approximately 0%–2% [24]. The geology of Indramayu comprises young river deposits (Qa), coastal deposits (Qac), deltaic deposits (Qad), flood-plain deposits (Qaf), tuffaceous sandstone and conglomerate (Qav), and beach-ridge deposits (Qbr) (Fig. 1a). Qa is situated along the Cimanuk River and comprises sand, silt, and brown clay. Qaf, characterized by sandy-humic clay, clayey sand, and partly topaceous soil, is the largest formation of Indramayu. Moreover, the northern region comprises (i) Qac, (ii) Qad, and (iii) Qbr in the form of: (i) silt, clay, sand, and mollusk-shell fragments; (ii) silt, brown clay, and some mollusk shells; and (iii) coarse to fine-grained sand and clay with abundant mollusk shells. Furthermore, the southern region comprises Qav.

The groundwater level is generally 3.5 m.a.s.l and flows toward the sea (Fig. 1a). The simplified cross section in Fig. 1b shows a thick clay in the north, which comprises a slight to dense carbonate clay with shell fragments. The clay in the southern region, however, is not as thick as that in the northern area. It comprises silty and sandy mixed with rounded sand. Moreover, the aquifer is relatively shallow in the southern region. Despite being a large groundwater resource, it cannot be directly used by the population because its water has a high total dissolved solids content (> 2000 mg/L) [29]. In addition, during the field survey, we learned that the groundwater has an unpleasant taste and color.

2.2 Land use in Indramayu

Land use in Indramayu is mostly accounted for by agriculture ($\pm 75\%$), brackish ponds ($\pm 13\%$), and settlements ($\pm 11\%$) (Fig. 2). Another further major land use in Indramayu is water bodies. Indramayu is traversed by the Cimanuk River, the second-longest river in West Java Province, which plays an essential role in its development [30], both as the source of irrigation and ponds, and for raw water to be processed as clean water. Unfortunately, the river cannot be utilized optimally for clean water as its condition is contaminated by organic and suspended solid. The chemical-oxygen demand and total suspended solid reached 70 mg/L and 5900 mg/L, respectively [31].

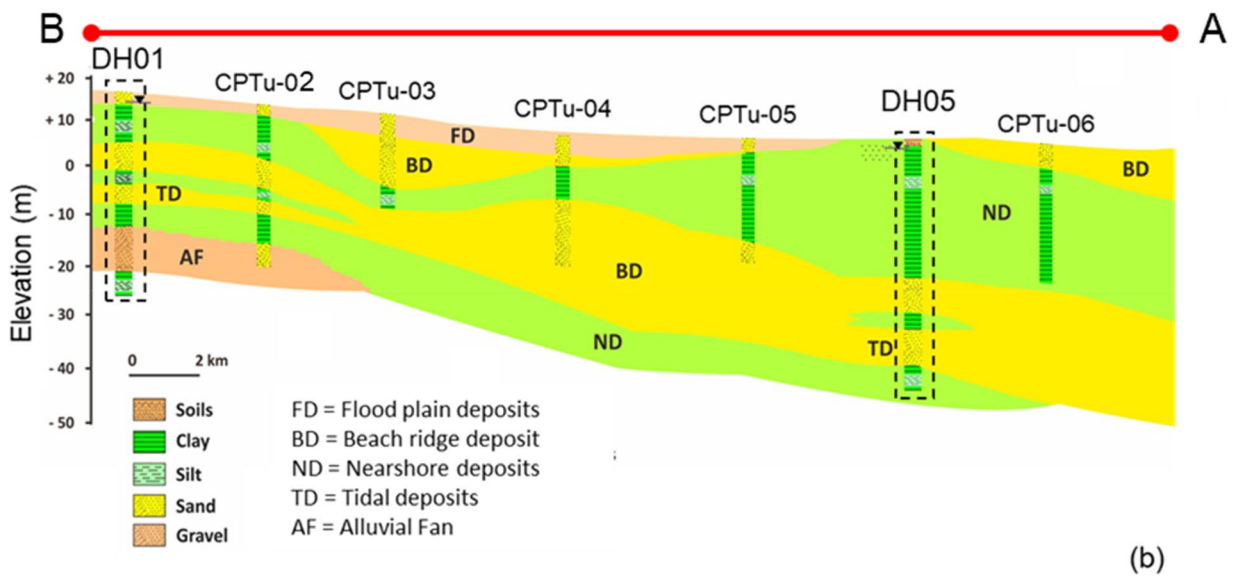
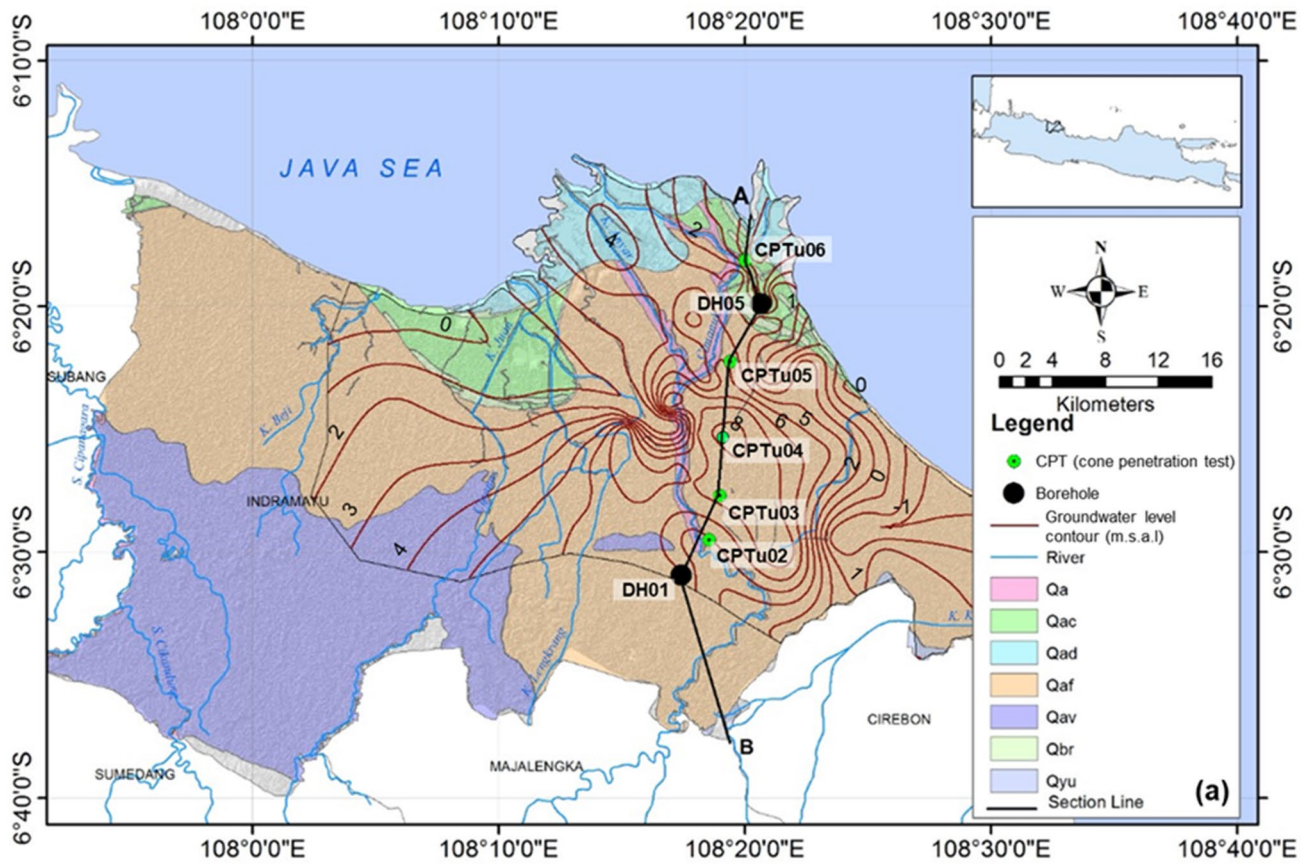
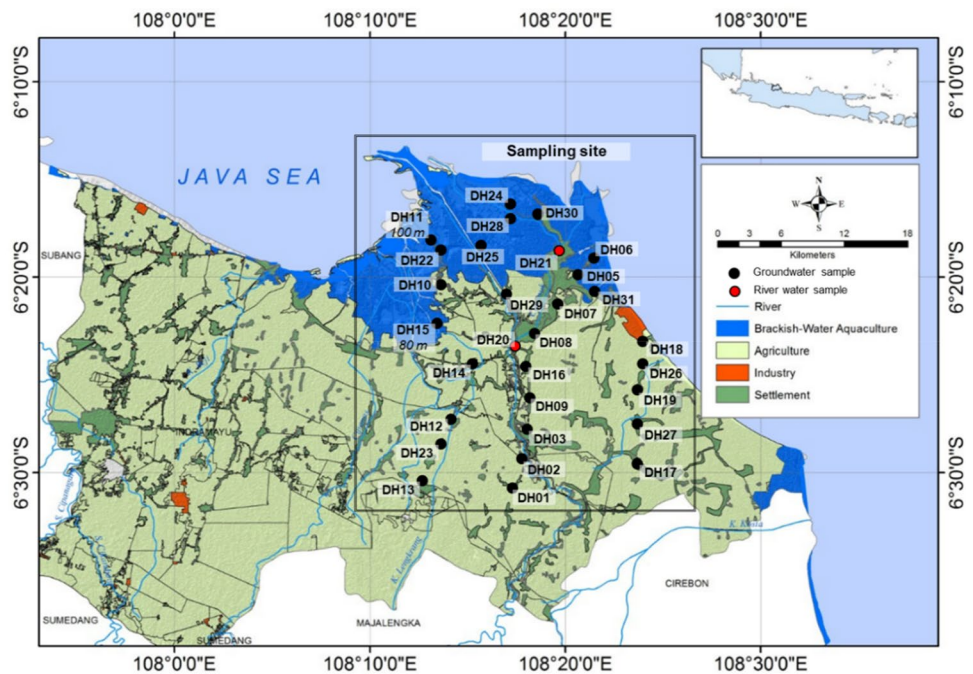


Fig. 1 Simplification of **a** topography, hydrogeology, and groundwater contour, and **b** hydrogeological cross section in Indramayu, Indonesia (Adapted from Achdan and Sudana 1992 [26], Maria et al. 2018 [27], Rusydi et al. 2021 [28])

Fig. 2 Land use and sampling locations in Indramayu, Indonesia



3 Methods

3.1 Groundwater sample collection

We conducted our field survey in November 2019. The average temperature and total precipitation during the period were approximately 30 °C and 68 mm, respectively. It was a dry season following a period of no rainfall in the previous five months. A total of 28 groundwater samples were collected from mostly shallow groundwater (depths of approximately 2–30 m), but two originated from a deep aquifer, DH11 and DH15, (approximately 100- and 80-m depths). In addition, two additional river samples were collected to compare the hydrochemical characteristics with those of groundwater samples. For groundwater samples, water was pumped out for approximately an hour (depending on the volume of water in the well) before being samples with a water dipper. Water samples were placed into polyethylene bottles soaked with 10% HCl solution for 24 h, washed, and then rinsed three times with distilled water. Additionally, these bottles were rinsed three times in the field with well water before collecting the sample.

3.2 Groundwater quality analysis

Water quality properties were analyzed both in the field and in the laboratory. Groundwater temperature (GWT), pH, oxidation–reduction potential (ORP), dissolved oxygen (DO), dissolved iron (Fe^{2+}), and bicarbonate (HCO_3^-) were measured as field parameters using (i) a handheld

EC/pH meter (WM-32EP, DKK-TOA, Japan) for GWT, pH, and ORP, (ii) a portable DO instrument (HQ30d, HACH) for DO content, and (iii) a portable DR900 calorimeter (HACH) with a ferrous iron reagent to determine the concentration of Fe^{2+} . HCO_3^- was measured in the field by titration using a strong acid on the day of sample collection. It is important to note that measured values of GWT, DO, and ORP might be higher than the actual value because field measurements were taken after collection from the well, thus allowing sample contact with the atmosphere. These values can be used as references to understand redox conditions.

Concentrations of dissolved organic carbon (DOC), nitrate–nitrogen (NO_3^- -N), sulfate (SO_4^{2-}), chloride (Cl^-), sodium (Na^+), potassium (K^+), magnesium (Mg^{2+}), calcium (Ca^{2+}), and dissolved manganese (Mn^{2+}) were obtained by laboratory analysis. The DOC value was measured using a total-organic-carbon (TOC) analyzer (TOC- $V_{\text{C}_{\text{PH}}}$, Shimadzu Co.) at the Geothermal Engineering Laboratory, Hirosaki University, Japan. NO_3^- -N concentrations were determined using a continuous-flow automated nutrient analyzer (SWAAT, BLTEC, Japan) at the Biogeochemistry Laboratory, Hiroshima University, Japan. Major cations and anions contents were analyzed by ion chromatography with conductivity detection on an ICS-1100 and ICS-2100 (Thermo Fisher Scientific Inc., MA, USA) with analytical precisions of < 1%, mostly. Mn^{2+} contents were analyzed at the Geothermal Engineering Laboratory, Hirosaki University, Japan, using inductively coupled plasma atomic emission spectrometry (Optima 7000DV, PerkinElmer Inc., MA, USA) with an analytical precision better than 4%.

3.3 Statistical analysis

The spatial distributions of Fe²⁺ and Mn²⁺ were mapped by ArcMap version 10.6 using the inverse distance-weighted (IDW) interpolation method [32]. The correlation coefficient (*r*) was used to describe the correlation between Fe²⁺ and Mn²⁺ with redox-sensitivity and salinity parameters. Thereafter, the significance of the correlation was described by *P*-values. A small *P*-value (< 0.1) indicates significance between parameters [33]. Finally, Fe²⁺ and Mn²⁺ from the natural origin were evaluated using probability plots [34].

4 Results

4.1 Physicochemical parameters related to redox condition

The groundwater temperature (GWT) ranged from 28.0 °C to 32.0 °C (Table 1). The average and standard deviations were 30 °C and 1.0. According to Boyd (2000) [35], water temperature has a limited impact on potential redox. Because the values of GWT at the research site are generally similar, we assume that GWT has no significant effect on redox conditions in the aquifer. Furthermore, the groundwater has low ORP values, i.e., between -84 and -6 mV, with an average of -34 mV and standard deviation of 20 (Table 1). ORP is an indicator of

Table 1 Groundwater physiochemicals data in the study area

Parameters	Unit	N	GDWQ	N>GDWQ	Min	Max	Avg	SD	Percentile		
									25th	50th	75th
<i>Groundwater</i>											
WT	°C	28			28	32	30	1.0	29	30	31
pH		28			6.4	8.2	7.3	0.4	7.1	7.3	7.5
EC	µS/cm	28			546	38,600	8994	11,751	1426	2955	11,308
ORP	mV	28			-84	-6	-34	20	-43	-29	-20
Fe ²⁺	mg/L	28	0.3*	13	0.10	252	10.3	47	0.1	0.2	1.5
Mn ²⁺	mg/L	28	1*	18	0.02	21.6	3.6	5.6	0.6	1.7	3.2
DOC	mg/L	28			0.45	19.0	3.2	3.7	1.3	1.8	3.9
DO	mg/L	28	6*	27	0.0	6.0	2.2	1.6	1.0	1.7	3.4
NO ₃ ⁻ -N	mg/L	28	10*	0	0.01	5.2	0.4	1.1	0.03	0.04	0.06
NH ₄ ⁺ -N	mg/L	28			0.07	13	3.3	3.7	0.8	2.1	3.4
Cl ⁻	mg/L	28	250**	19	10.6	16,100	3372	5012	134	1274	3893
SO ₄ ²⁻	mg/L	28	400*	12	0.2	3117	469	711	55	126	528
HCO ₃ ⁻	mg/L	28			144	1112	569	244	412	529	718
Na ⁺	mg/L	28			62	7780	1686	2360	151	840	2015
K ⁺	mg/L	28			1.05	213	38	53	9	14	44
Mg ²⁺	mg/L	28			16	1320	283	397	33	81	316
Ca ²⁺	mg/L	28			23	1330	295	343	75	98	401
log pCO ₂					0.55	2.39	1.41	0.41	1.16	1.49	1.70
<i>River</i>											
Cl ⁻	mg/L	2			20	20.6	20				
SO ₄ ²⁻	mg/L	2			37.7	41.4	40				
HCO ₃ ⁻	mg/L	2			180	187.2	184				
Na ⁺	mg/L	2			26.2	26.5	26				
K ⁺	mg/L	2			4.2	4.8	5				
Mg ²⁺	mg/L	2			15.5	15.9	16				
Ca ²⁺	mg/L	2			30.6	32.6	32				

N, number of samples; *GDWQ*, guideline for drinking-water quality according to Indonesian Government Regulation, 2001 [17][†] and WHO, 2017 [5]^{**}, *N>GDWQ*=number of samples exceeded *GDWQ*, *Min*, minimum concentration; *Max*, maximum concentration; *Avg*, average concentration; *SD*, standard deviation. Major cation and ammonium-nitrogen concentrations in groundwater were obtained from Rusydi et al. 2021 [28]

reduction potential; thus, low ORP values imply a low redox environment [36].

The sequence of redox conditions is explained by DO, NO_3^- -N, SO_4^{2-} , and CO_2 [14, 37]. These parameters are responsible for electron acceptors that exhibit an inverse correlation with Fe^{2+} and Mn^{2+} . Indeed, the disappearance of electron acceptors results in the appearance of trace metals [37]. DO contents are heterogenous at each sampling point with a positive skewness distribution. The studied groundwater samples have a DO range from 0.0 to 6.0 mg/L, with an average value and standard deviation of 2.2 mg/L and 1.6 (Table 1). DO is one of the most sensitive components for redox evaluation [38]. According to McMahon and Chappelle (2008) [14], oxic conditions may occur when DO contents ≥ 0.5 mg/L. In comparison, Boyd (2000) [35] reported a high possibility of reductive environments at DO values less than 1 or 2 mg/L. Similar to DO, DOC contents vary with a right-skewed distribution across the studied locations. DOC contents range approximately from 0.45 to 19.0 mg/L, with an average value of 3.2 mg/L and a standard deviation of 3.69 (Table 1). DOC concentrations of > 1 mg/L are undesirable in groundwater since high concentrations can induce the hazardous mobilization of heavy metals [39].

Furthermore, NO_3^- -N varies from 0.01 to 5.2 mg/L with an average of 0.4 mg/L (Table 1). Concentrations of nitrate are distributed with a positive skewness and a standard deviation of 1.1. Although Indramayu is dominated by agricultural areas, NO_3^- -N concentrations are low (< 1 mg/L); few points have relatively high concentrations, such as DH07 (3.2 mg/L) and DH13 (5.2 mg/L); however, these relatively high concentrations are still below the clean water quality standard, which is 10 mg/L [17]. Our previous studies discovered that ammonium-nitrogen predominated as a dissolved inorganic nitrogen species (Table 1) [28, 40]. Unlike ammonium, which is stable under the reductive condition, nitrate is very stable under oxic conditions [14, 36–38]. Therefore, it is conceivable that the groundwater is undergoing nitrate reduction processes.

SO_4^{2-} concentrations vary between 0.2 and 3117 mg/L with an average of 469 mg/L, and a standard deviation of 711 (Table 1). The Indonesian Government Regulations (2001) [17] state that clean water should have SO_4^{2-} concentrations of ≤ 400 mg/L. Based on this regulation, only a small part of the study locality has concentrations over the threshold. Like nitrate, sulfate is stable under oxic conditions. However, the decreases in sulfate concentration may also be related to other process, for example, dilution and precipitation [37, 41]. Therefore, differing from DO and NO_3^- -N, sulfate concentrations alone are not suitable for a general description of the redox condition.

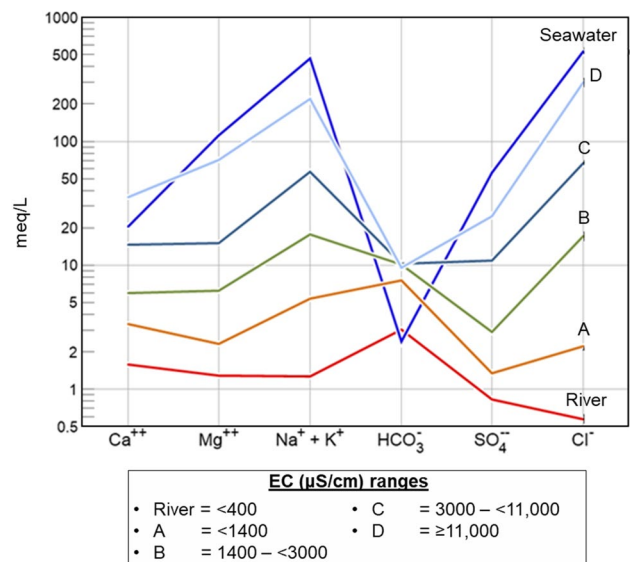


Fig. 3 Schoeller–Berkaloff diagram of the four groups of groundwater samples (A, B, C, and D), seawater, and Cimanuk River water. This diagram was created using Geochemist's Workbench (GWB) version 12.0

4.2 Hydrochemical characteristics

The groundwater samples have EC values varying from 546 to 38,600 $\mu\text{S}/\text{cm}$ with a standard deviation of 11,751 (Table 1). The Schoeller–Berkaloff diagram was created based on the EC's frequency distribution in the groundwater samples (Fig. 3). The groundwater samples of facies C and D (particularly D) have the similar patterns of cations and anions to seawater, which has significantly high concentrations of $\text{Na}^+ + \text{K}^+$ and Cl^- , but low concentrations of HCO_3^- . Moreover, the major-ion patterns of groundwater samples in facies A and B (particularly A) are more likely to be similar to river-water samples. There was an enrichment of $\text{Na}^+ + \text{K}^+$, but the HCO_3^- content is relatively dominant within facies A and B. The seawater influences are arrayed from greatest to lowest in facies D, C, B, and A.

The piper diagram in Fig. 4 supports the previous interpretations. The groundwater of facies A (EC < 1400 $\mu\text{S}/\text{cm}$) shows an indication of freshening; facies B (EC between 1400 and < 3000 $\mu\text{S}/\text{cm}$) implies a mixing between seawater and freshwater, and facies C (EC of 3000– $< 11,000$ $\mu\text{S}/\text{cm}$) and D (EC $> 11,000$ $\mu\text{S}/\text{cm}$) experience seawater influences [37]. Samples from facies A and B are located in agriculture and residential areas; conversely, facies C and D are mostly taken from brackish-water aquaculture sites. In proportion to the EC values, facies C and D also have high Cl^- contents ($> 1,200$ mg/L), which are unsuitable for drinking water. This high concentration of Cl^- can feasibly be derived from marine sediments and brackish-water pond (see Figs. 1 and 2).

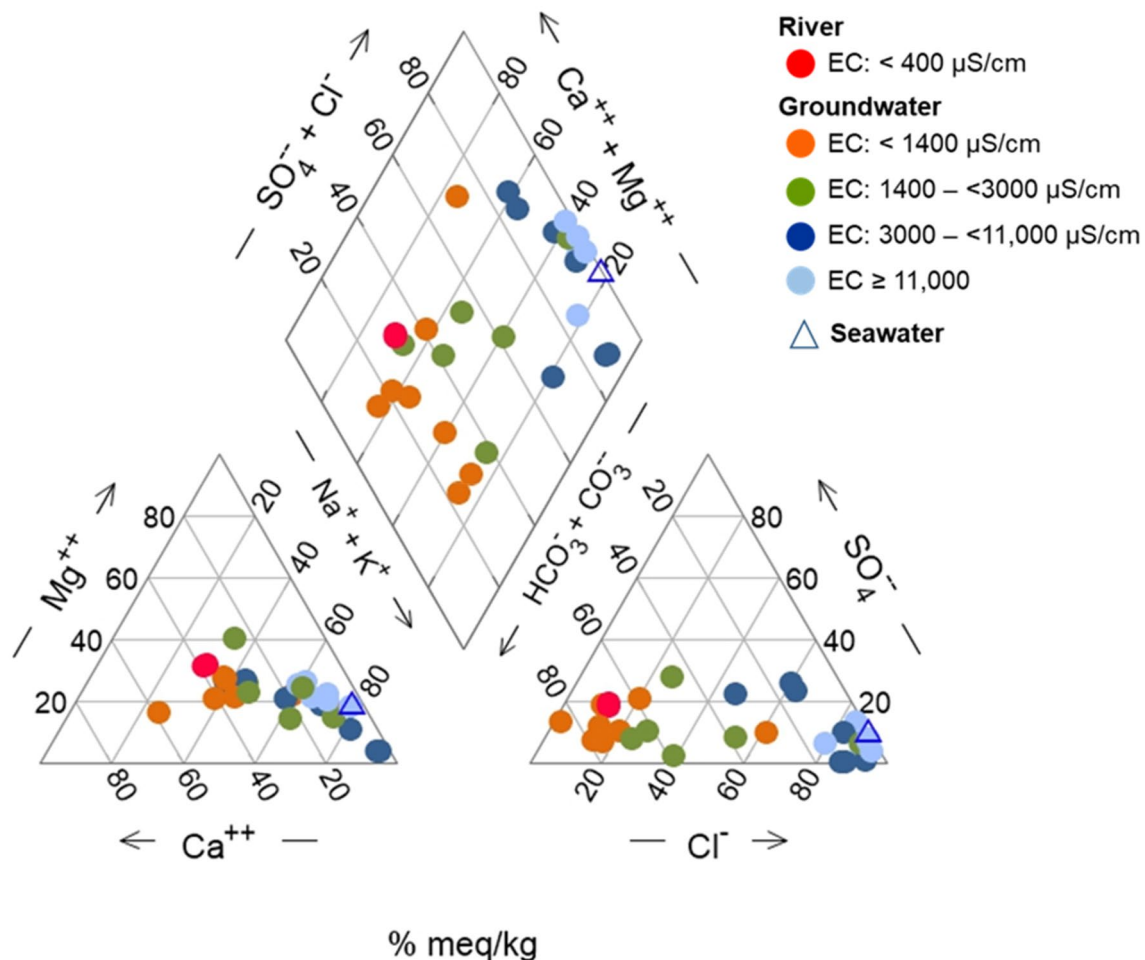


Fig. 4 Piper diagram of groundwater samples (different colors of groundwater samples indicate different classifications of EC. This diagram was created using Geochemist's Workbench (GWB) version 12.0

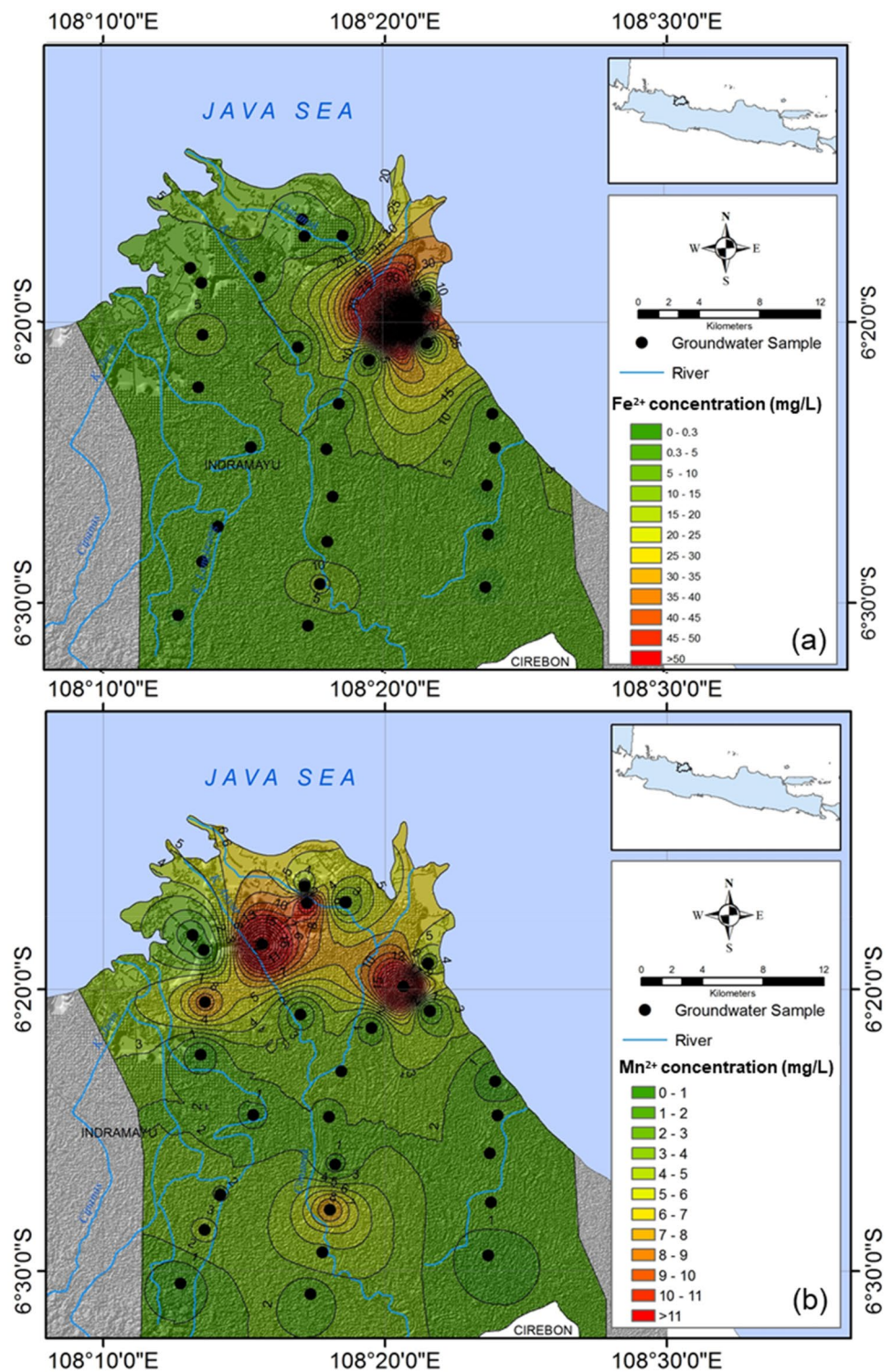
4.3 Fe^{2+} and Mn^{2+} relationship and distribution

The concentration of Fe^{2+} varies between 0.10 and 252 mg/L with an average of 10.3 mg/L and a standard deviation of 47 (Table 1). Likewise, Mn^{2+} contents have a considerable variation from 0.02 to 21.6 mg/L with an average and standard variation of 3.6 mg/L and 5.6, respectively (Table 1). Both elements have a positive skewness distribution. Locality DH05 exhibits significantly higher contents of Fe^{2+} (252 mg/L) and Mn^{2+} (21.6 mg/L) coupled with high concentrations of DOC (19.0 mg/L) and undetected DO (0.0 mg/L); therefore, low redox conditions are very possible. Additionally, following Indonesian Government Regulations (2001) [17], clean water should contain $\text{Fe}^{2+} \leq 0.3$ mg/L and $\text{Mn}^{2+} \leq 1$ mg/L. Thus, < 50% and > 60% of samples exhibit the excess concentrations of Fe^{2+} and Mn^{2+} , respectively. The highest concentrations are primarily located in the north tip of the area (Fig. 5a, b) where coastal and deltaic

deposits and brackish-water aquaculture are the dominant geology and land use, respectively (Figs. 1 and 2).

A bivariate graph of Fe^{2+} and Mn^{2+} (Fig. 6) shows a moderate relationship between their concentrations ($R^2 = 0.41$) with highly significant correlation (P -value < 0.001). This implies non-homogenous geochemical processes, such as different contents of minerals in the aquifer system and different rates of mineral dissolution. Another possibility, suggested by Carretero and Kruse (2015) [42], is the different redox potential of samples; for instance, in a particular redox potential, Mn could be reduced, while Fe remains oxidized. Additionally, Fe^{2+} is generally present at higher concentrations than Mn^{2+} [6, 10]; however, some regions, such as DH03, DH25, and DH28, have significantly higher concentrations of Mn^{2+} than Fe^{2+} . This confirms the heterogenous geochemical nature of the aquifer at Indramayu, in which Fe^{2+} and Mn^{2+} are irregularly dispersed.

Fig. 5 Spatial distribution of **a** Fe^{2+} and **b** Mn^{2+} . Maps were produced using ArcMAP version 10.6 with the IDW interpolation method



5 Discussion

5.1 Effect of reductive condition and salinity

Trace metals and DO have a significant inverse correlation (Table 2). As the preferred electron acceptor, low

DO concentrations imply that oxygen has been used in organic-matter decomposition processes to promote a reduced environment [14, 36, 38]. The reduced environment regulates the dissolution of Fe and Mn-bearing rock and minerals [13, 14, 37]. Similarly, Fe^{2+} and Mn^{2+} exhibit negative correlations with $NO_3^- - N$ but with less significant

Fig. 6 Fe²⁺ and Mn²⁺ relationship (GDWQ accords with Indonesian Government Regulation, 2001 [17])

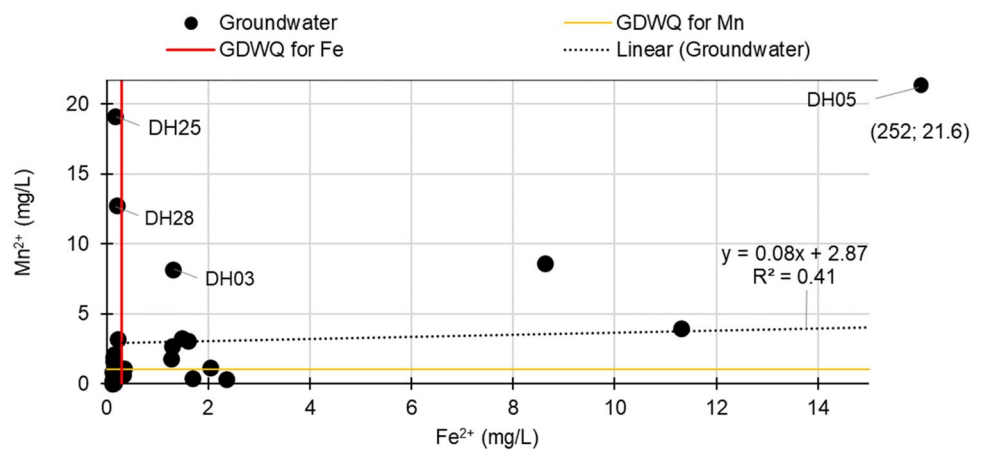


Table 2 Correlation among parameters

	Fe ²⁺	Mn ²⁺	DOC	DO	NO ₃ ⁻ -N	log pCO ₂	Cl ⁻	SO ₄ ²⁻
Fe ²⁺	1							
Mn ²⁺	0.64*	1						
DOC	0.85*	0.64*	1					
DO	-0.28***	-0.42***	-0.27	1				
NO ₃ ⁻ -N	-0.03	-0.16	-0.09	0.24	1			
log pCO ₂	0.48*	0.62*	0.32	-0.58	-0.03	1		
Cl ⁻	0.46**	0.88*	0.63	-0.40	-0.18	0.40	1	
SO ₄ ⁻	0.76*	0.94*	0.72	-0.51	-0.14	0.67	0.81*	1

P-values: * < 0.01, ** < 0.05, and *** < 0.1

correlation compared to DO, probably because nitrate is the second preferential electron acceptor after oxygen. Nevertheless, the negative correlations noted between Fe²⁺ and Mn²⁺ and NO₃⁻-N imply a reduction process that encourages iron and manganese dissolution [14, 36, 37, 43].

The reductive conditions can be a result of organic-matter decomposition by microorganisms that consume dissolved oxygen. Table 2 shows that both Fe²⁺ and Mn²⁺ are significantly correlated with DOC, suggesting that DOC is responsible for elevating Fe²⁺ and Mn²⁺ concentrations. Furthermore, the decomposition of organic matter generates carbon dioxide (CO₂), in this case shown by log₁₀ pCO₂ obtained by Eq. 1:

$$\log_{10} pCO_2 = \log_{10}(\text{alkalinity}) - \text{pH} - (\log_{10} K_1 + \log_{10} K_2) \tag{1}$$

Alkalinity is expressed as HCO₃⁻ in molality. K₁ and K₂ are the equilibrium coefficient for the temperature and salinity of groundwater of the coastal area. Specifically, K₁ is the Henry law's constant for [H₂CO₃]/pCO₂, and K₂ is the dissociation constant of H₂CO₃ ([H⁺][HCO₃⁻]/[CO₃²⁻]). Here, we use 25 °C and 35 ppt as representative values of temperature and salinity, respectively, and K₁ and K₂ are taken as 10^{-1.47} and 10^{-6.35}, respectively [44].

As the third electron acceptor (after oxygen and nitrate), SO₄²⁻ exhibits positive and significant correlations with both Fe²⁺ and Mn²⁺ (Table 2) which indicate no sulfate reduction in the research area. However, two deep wells (DH11 and DH15) have significantly lower concentrations of SO₄²⁻ (both are 0.2 mg/L). Although this condition is accompanied by relatively low concentrations of Fe²⁺ (0.12 and 0.15 mg/L, respectively, for DH11 and DH15) and Mn²⁺ (0.05 and 0.08 mg/L, respectively, for DH11 and DH15), we suspect the sulfate reduction may be present. The iron and manganese could be bound with sulfate as iron and manganese sulfide and precipitated along with sulfate reduction [37].

The high concentrations of SO₄²⁻ coupled with Cl⁻, thus, positive and significant correlations between trace metals and SO₄²⁻, may be explained in terms of salinity. High salinity is potentially supporting the leaching processes of Fe and Mn from minerals to groundwater, possibly through ion-exchange processes [11, 18, 19]. Salt contents may increase the ionic strength and, according to Debye-Hückel theory, can decrease the ion activity coefficient, such that the dissolution of Fe and Mn in inorganic complexes may occur easily [11].

5.2 Natural and anthropogenic impact

The aquifer in Indramayu is comprised of multiple layers, classified as unconfined and confined groundwater. Figure 1b suggests that unconfined groundwater is discontinued from the south to north and relatively more available in the southern area. Meanwhile, the confined groundwater continues from the south to north region. In the northern part, the confined aquifer is deeper and has more storage than that in the southern part. Furthermore, the piper diagram also indicates a different groundwater type between the south and north region (Fig. 4). Groundwater samples in the southern area, which has most EC values < 3000 $\mu\text{S}/\text{cm}$, are projected randomly in the diamond with the main type of NaHCO_3 and MgHCO_3 , whereas the groundwater in the northern region with higher salinity, which has $\text{EC} > 3000 \mu\text{S}/\text{cm}$, only belongs to NaCl -type.

In the previous subsection, elevated Fe^{2+} and Mn^{2+} concentrations are confirmed statistically related to high salinity and reductive aquifer. Further, the log-normal graph in Fig. 7 helps evaluate Fe^{2+} and Mn^{2+} distribution related to the aquifer system. The transition of the curve's slope in the log-normal graph in Fig. 7 distinguishes whether the trace metals are present in the groundwater with a natural condition or has been impacted by anthropogenic activities [34]. The log-normal distribution of Fe^{2+} and Mn^{2+} samples shows high probabilities of occurring in undisturbed groundwater at the concentrations of < 0.8 mg/L and < 3.8 mg/L (Fig. 7a and b, respectively). This undisturbed groundwater is characterized with relatively lower salinity and located in the southern region. In the case of Fe^{2+} , all samples in the undisturbed groundwater meet the

criteria for drinking water (Fig. 7a), whereas for Mn^{2+} , 50% of the samples from the undisturbed groundwater exceed this threshold (Fig. 7b). Moreover, less than 40% and 20% of the total samples experienced anomalous Fe^{2+} and Mn^{2+} increases (Fig. 7a and b, respectively). This significant increase indicates that the aquifer has been disturbed by human activities [34]. These samples are mostly from facies C and D, which are situated at the northern tip of Indramayu (Fig. 5a and b).

6 Conclusion

Identifying the environmental factors responsible for high concentrations of Fe^{2+} and Mn^{2+} in the coastal alluvial groundwater of Indramayu, a developing city with a relatively natural hydrogeology environment show that the groundwater is naturally vulnerable to Fe^{2+} and Mn^{2+} contamination. The average concentrations of Fe^{2+} and Mn^{2+} are 10.3 mg/L and 3.6 mg/L, respectively. High salinity is suspected of supporting the leaching of Fe^{2+} and Mn^{2+} from minerals and soils through ion-exchange processes. The reduced environment indicated by DO and NO_3^- -N reduction is another crucial factor in the dissolution of Fe^{2+} and Mn^{2+} from soils and minerals to groundwater. This reduction process is possibly promoted by microorganisms and thus occurs as a function of organic matter.

Furthermore, the log-normal curves of Fe and Mn have been successfully used to distinguish two groundwater conditions in Indramayu. The first (dominant) condition is undisturbed groundwater, which has relatively low salinity and is located in the southern part of Indramayu. The

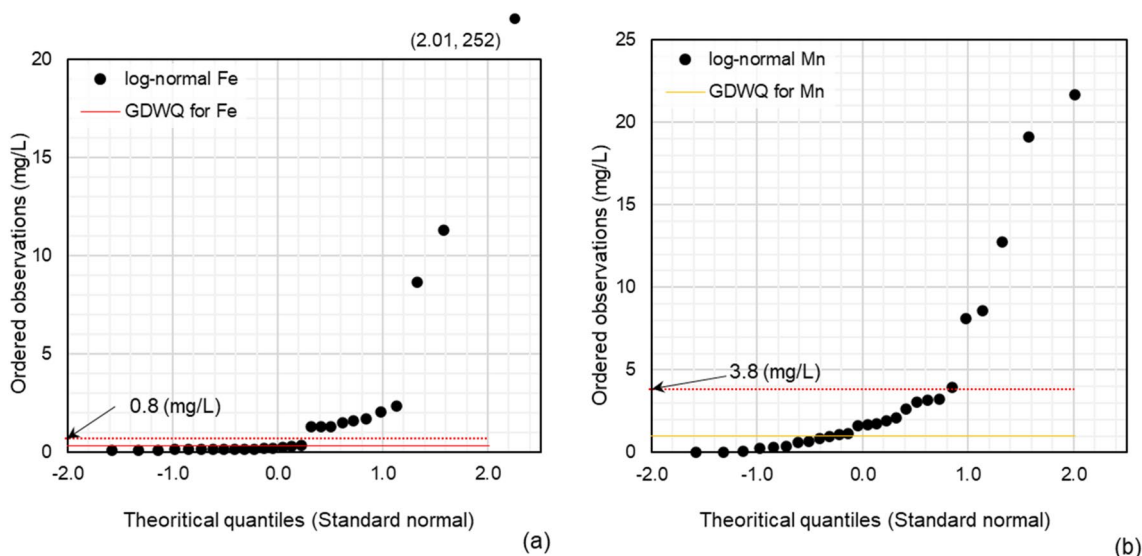


Fig. 7 Probability plots of **a** Fe^{2+} and **b** Mn^{2+} . The regions below and above the red dotted line indicate natural and anthropogenic backgrounds, respectively. GDWQ accords with Indonesian Government Regulation, 2001 [17]

second condition is groundwater affected by human activities, which is found in the northern part of Indramayu. The groundwater in the second condition has significantly high contents of trace metals, exceeding the criteria for drinking-water quality.

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Compliance with ethical standards

Conflicts of interest On behalf of all the authors, the corresponding author states that there are no conflicts of interest to declare.

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