Sectorization of environmental risk and human consumption of manganese in groundwater extracted from the Sinaloa River Aquifer

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Abstract

The research reported in this paper had three objectives. The first was to draw a map of the piezometric contours of the Sinaloa River Basin to enable an interpretation of the hydrodynamic behavior of the basin. The second objective was to establish a relationship between the hydrodynamics of the basin and levels of concentration of manganese (Mn), an element which is vital for human survival but toxic at high levels. Given that some of the rural and urban inhabitants of the basin consume untreated groundwater, the third objective was to create a map of the region showing the locations of high manganese level risk in the water. To characterize the hydrodynamics, 40 wells were selected at random. Groundwater depth, ground elevation, hydraulic load and piezometric surface were measured. A water sample was taken from each selected well, and spectrometric laboratory techniques employed to measure manganese and iron levels; the latter as a check on the robustness of Mn measurements on untreated water. The piezometric analysis showed the presence of a regional water source and a local water source, which has protected the basin from saline intrusion for many years. However there are sources of high manganese concentrations in a range of 0.01 to 1.2 mg L^{-1}, which are moving with these two flows at average receptive velocities of 4.2×10^{-3} mh^{-1} and 1.6×10^{-3} mh^{-1}. In an analysis of

groundwater samples, 22 (55%) of the samples exceeded the EPA standard for commercial bottled drinking water and 12 (30%) exceeded the Mexican NOM-127-SSA1-1994-2000 standard for water for human use and consumption. The risk level was very high in two samples (5%), high in 4 (10%), moderately high in 3 (7.5%), intermediate in 9 (22.5%), low in 2 (5%), and zero in 16 (40%). This information can be used for numeric models of Mn transport and flow useful for safeguarding human health and for provision of sustainable management strategies in one of the largest aquifers in northwest Mexico.

1 Introduction

Manganese (Mn) is one of most abundant metals occurring in nature (Jiménez [1]). It shares some properties with iron (Fe) and chromium (Cr). Dissolved Mn is found in subsoil waters in solid compounds of small particles, which, combined with oxygen (O_2), sulphur (S) and chlorides (Cl^{-1}), do not evaporate, degrade or disappear. In underground porous media, Mn tends to accumulate, to adhere, and to be deposited, and levels of concentration tend to vary according to the rate of dispersion (Bianchini [2]). Higher concentrations are generally associated with underground water, in which levels of up to 2.5 mg L^{-1} have been recorded. For such water to be made suitable for use, various treatments are required. Large areas of land may have water with naturally high levels of manganese; if this water is extracted and used without any treatment, it may be toxic to the eosystem or agro-ecosystem (Castro [3]). Effects of using this water can include obesity, glucose intolerance, blood clots, skin problems, low cholesterol levels, skeletal disorders, changes in hair colour, or neurological effects (Manahan [4]). When this water is used for development, untreated water is ingested for prolonged periods, it tends to be a severe health hazard (Freed *et al.* [5]). Because of this, the issue of allowable Mn levels in water has been considered a high priority since 1980, when it was included in various documents and lists of standards (WHO [6]).

  It has been difficult to establish accurate standards for allowable or recommendable Mn limits, as the effects depend on various factors and conditions, as well as the predominant type of organism or ecosystem in a given area or geographic region. The reactions of different organisms to the effects of Mn may vary. Small amounts of Mn are necessary for agriculture and drinking water. It is necessary to know the daily rate of intake per person, given the uncertainty of the risk and the need to prevent potential harmful effects. Since some urban and rural residents of the Sinaloa River Basin use untreated water for drinking, in order to ensure their health, it was considered important to determine the hydrodynamics of the basin and to find Mn concentration levels in the water in order to model the underground flow (ϕ) in the region by sector.

2 Methodology

The Sinaloa River Basin (SRB) is a coastal plain with unconsolidated sedimentary igneous deposits caused by erosion and weathering of the Sierra Madre Occidental mountain range. The Mexican Statistical Institute (INEGI) [7], situates it in the RH10-SINALOA hydrological region, and Ávila [8] in hydrological region III. The climate is wet-and-dry (Ar-Aw) and there are four main natural tributaries; the Sinaloa River, the Arroyo De Cabrera, De Ocoroní and San Rafael and one artificial tributary built in the late 1940s, the Valle del Fuerte Canal (Norzagaray [9]). The basin is bordered on the north by the foothills of the Sierra Madre Occidental and on the west by the Gulf of California. The population of the basin is 270,260, and the largest concentrations of population are in the cities Guasave, Batamote, Tamazula and Sinaloa de Leyva (Figure 1).

To fulfill the first research objective of mapping the isopiezic contours of the basin, 40 wells were randomly selected in April 2008 from the universe of all main wells and boreholes utilized for drinking water and domestic use. Positions were taken with a 12-channel Garmin Olathe portable GPS. Elevations above sea level (masl) were measured using an Apex model ET-5 electronic theodolite employing the interpolation method. Soundings of the groundwater level (Nf) were taken monthly for three-day periods using an instantaneous piezometer. A 1978 study by the Técnicas Modernas de Ingenería company states that the SRB aquifer is unconfined; thus it can be assumed that hydraulic load (H) in wells and/or boreholes coincides with Nf levels above sea level. Accordingly, following (Frenegal *et al*. [10]), H was calculated by subtracting Nf from h for each well and/or borehole. The isopiezic map was obtained by interpolating H using the SURFER 8.0 program (Emery [11]) to obtain the piezometric surfaces. This defines ϕ, as it is perpendicular to the izopiezic contours (Hiscock [12]). Physical properties of the porous medium as previously described by Norzagaray *et al*. [9] were interpolated in SURFER 8.0 under the same dimensions of H. Both parameters were then fed into the FlowPATH 6.0 program, and Darcy's Law was used to calculate average ϕ velocity (Fetter [13]). To meet the second study objective, a water sample was taken from each well or borehole. The samples were labeled, prepared and sent to the laboratory for analysis. In the laboratory, the samples were filtered and aliquots were taken. The pH was adjusted according to which element was to be analyzed. The samples were stored in plastic bottles at 4°C until the respective analysis was carried out. Mn and Fe concentrations were analyzed in triplicate by two methods; (a) filtration colorimetry (Silva *et al*. [14]) and ultraviolet spectrometry, cited by the Association of Official Analytical Chemists (AOAC) [15].

For analysis of drinking water by Mn concentration, two references were used; the EPA standard of 0.05 mg L^{-1} for bottled drinking water (ATSDR [16]), and 0.15 mg L^{-1}, the allowable limit set by the NOM-127-SSA1-1994-2000 Mexican standard for human use and consumption of water in general (DOF [17]). Because Fe is associated with Mn in groundwater, Fe was also measured, as a reference to validate the presence of Mn in the samples (Jiménez [1]). The
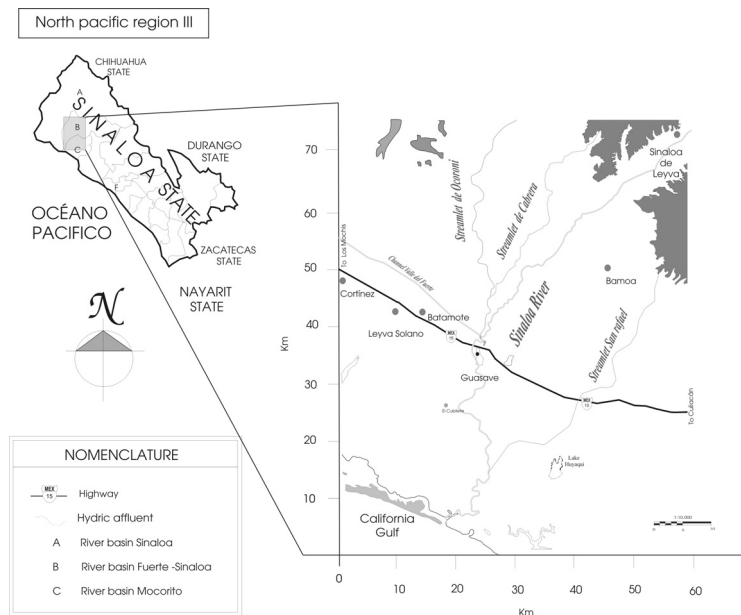
Figure 1:   Location of the North Pacific III Hydraulic Region and the Guasave Valley, Sinaloa de Leyva.

limit of 0.3 mg L^{-1}, as specified in the amended NOM-127-SSA1-1994-2000 standard (DOF [17]), was used. The map was prepared using the measured Mn and Fe concentration values, with intermediate values interpolated using SURFER 8.0. Once the hydrodynamics, ϕ velocity, and Mn concentration levels had been established, the map of Mn concentrations was layered on the map of the urban layout of the region, in order to divide it into sectors and map probable Mn dispersion (the third study objective). The ϕ gradients were mapped under the assumption that an intersection of two or more ϕ indicated a convergent gradient, and expansion or loss (drift) of ϕ indicated divergence (Hiscock [12]). To transfer the results to a risk map based on the 0.15 mg L^{-1} Mn standard, risk was divided into seven levels and the drinking water hazard of each level classified. The levels were: 6: Very high (Ma), 5: High (A), 4: Moderately high (Md), 3: Intermediate (I), 2: Low (B) and 1: No risk (N).

3   Results and discussions

H varied from 0.6 to 51.8 meters, with an average of 25.5 masl. Values of H are shown in Table 1; the piezometric map is shown in Figure 2, Section A. The piezometric lines are parallel to the coast and follow similar contours to the topography. The equipotential contours appear perpendicular, and two types of ϕ can be observed (Tóth [18]); a main or regional flow from the northwest

(Figure 2, Part B) and an intermediate flow that enters the basin at the foothills of the mountain range in the southeast (Figure 2, Part C). The average of the regional ϕ velocity as calculated by FLOWpath 6.0 was 4.2×10^{-3} mh^{-1} and of the intermediate ϕ velocity, 1.6×10^{-3} mh^{-1}. The northwest current enters the piezometric surface at 44 masl, and in the course of its flow H drops from 20 to 12 masl. It is fed by the Valle del Fuerte Canal, and its final destination is the Gulf of California. As shown in Figure 2, a major portion of the volume of the northwest current is consistent with that reported by Toutcha *et al.* [19]; of the total volume, 3473.73 Mm^3 converges to the RH10-SINALOA in the state of Chihuahua. The southwest current similarly flows from a piezometric surface of 44 masl, fed from the Sinaloa River. Both currents have, over a long period of time, prevented the intrusion of salt into the basin (TMISA [20]).
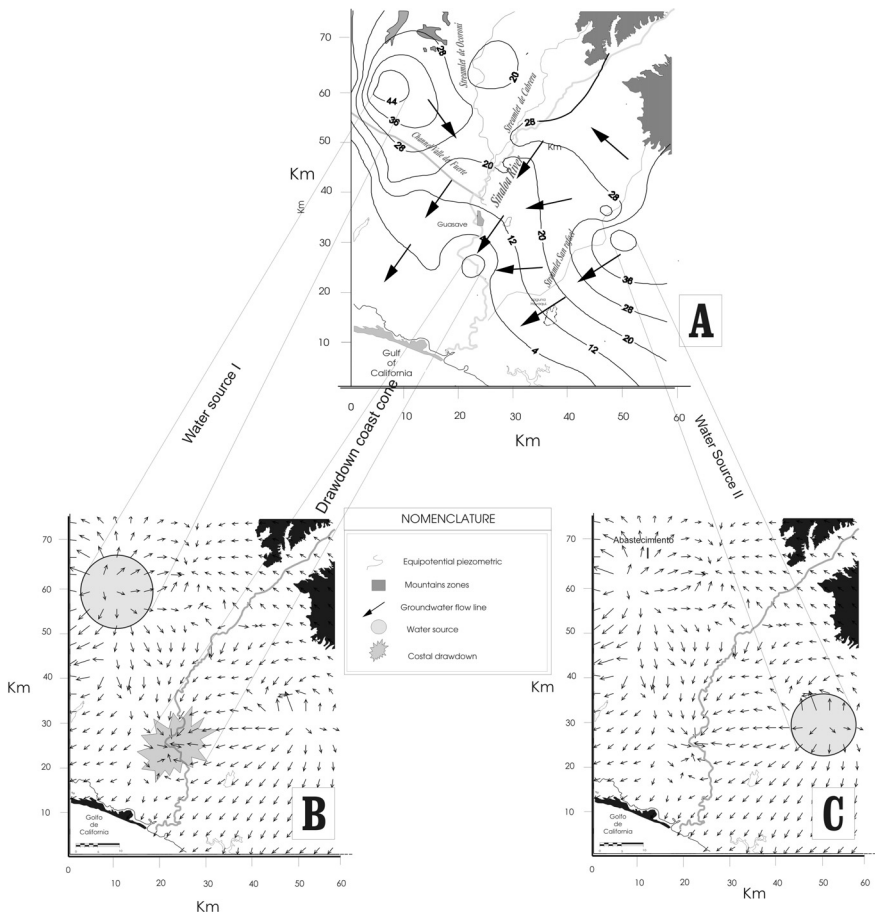

Figure 2:   Piezometric levels, lines of flow, sources of supply and areas of groundwater depletion.
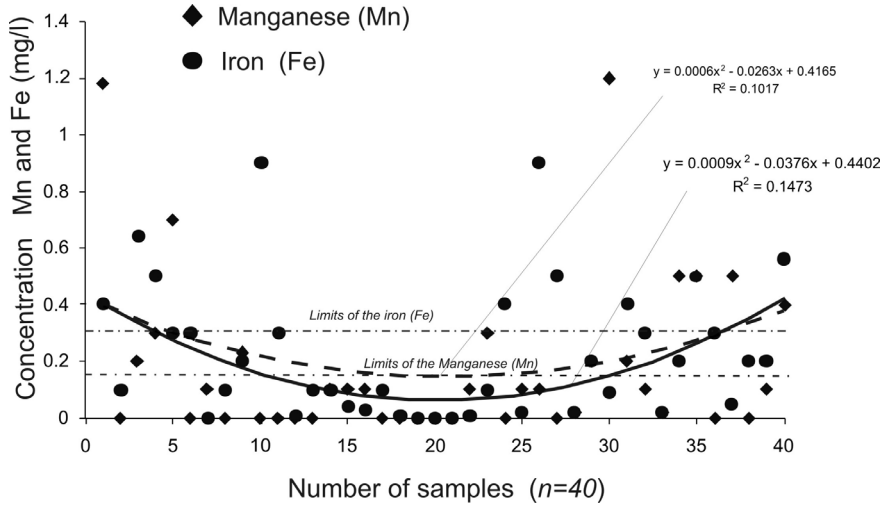
Figure 3:   Distribution of manganese and iron concentrations in groundwater samples from the Sinaloa River Basin.

The distribution of Mn and Fe concentrations in the groundwater samples analyzed is shown in Figure 3. A nonlinear trend, possibly due to variability resulting from the interactions between the flows, can be observed.

Although the ϕ direction has long mitigated the effects of seawater intrusion, apparently in 2008 a 0.06 masl cone of depression appeared, which was due to demand caused by intensive farming, which considerably exceeded the natural recharge (Figure 4, Section A). This runaway demand is attributed mostly to agriculture; in 1967 demand was 430 mm^3/year compared to a 230 mm^3/year recharge; in 1968 130 mm^3/year compared to a 200 mm^3/year recharge, and in 1977 the volume of water extracted was 500 mm^3/year (TMISA [20]). Moreover it has recently become known that 1131.03 Mm^3/year has already been promised to the productive sector (SEMARNAT [21]). This is well above the 510.46 Mm^3/year annual recharge in the Northern Sinaloa State Planning Subregion (PEDUES) [22], of which the aquifer only provides 200–300 Mm^3/year.

Table 1 also shows Mn and Fe concentration levels for the 40 water samples. According to the quality standards used in this study, the concentration of Mn in the 40 samples analyzed was in the range of 0 to 1.2 mg L^{-1} and Fe between 0 and 0.9 mg L^{-1}.

Twenty-two samples (55%) had levels above the EPA bottled drinking water standard of 0.05 mg L^{-1} and therefore were not suitable for consumption directly from the well or borehole (Table 1). As Table 1 also shows, 12 samples (30%) had Mn levels above the NOM-127-SSA1-1994-2000 standard of 0.15 mg L^{-1}, and 15 samples (37.5%) showed Fe levels above 0.3 mg L^{-1} (Figure 3). If both standards are applied, Mn levels exceeded the standards; the water is unfit for human consumption and would require physical and/or chemical treatment to remove the excess Mn and Fe (Figure 3).
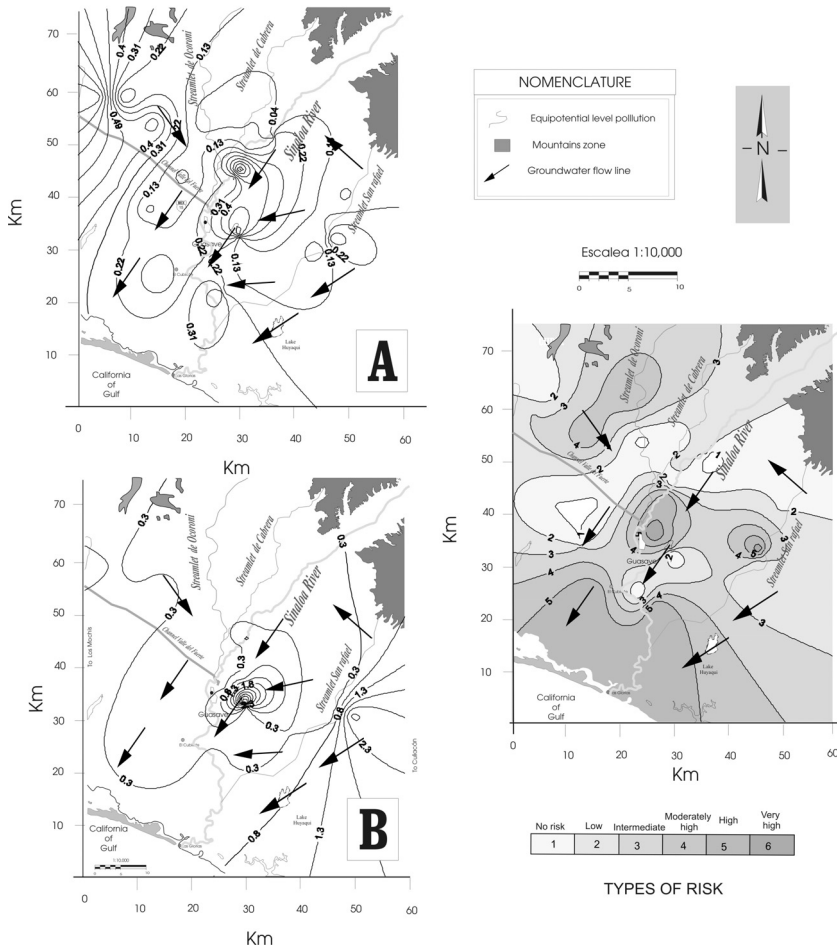
Figure 4:   Spatial variation in the direction of groundwater flow and distribution of concentration levels (mg/l) of manganese (A), iron (B) and risk map for manganese intake (C) in the Sinaloa River Basin.

Populations with Mn and Fe concentrations that are high according to the NOM-127-SSA1-1994-2000 standard are listed in Table 2 in descending order of risk. Sections A, B and C of Table 4 show Mn and Fe concentration levels from Tables 1 and 2 and the associated risk classifications proposed in this study with respect to the direction of ϕ. It can be observed that Mn and Fe concentrations show geometric behavior, with similar coverage areas.

In the northern part of the basin, levels of Mn concentration were similar to Fe concentrations, and were higher than levels specified in the standards. At a distance of 9 km from the coastal cone of depression, Fe was present in the

Table 1: Magnitude of piezometric levels and manganese and iron concentrations (mg L^{-1}).

Number sample	Piezometric Head H masl*	Manganese Mg mg/l	SSA1-1994 0.15 mg/l	EPA 0.05 mg/l	Iron Fe Mg/l	SSA1-1994 0.3 mg/l	Number Sample	Piezomtric Head H masl*	Manganese Mg mg/l	SSA1-1994 0.15 mg/l	EPA 0.05 mg/l	Iron Fe mg/l	SSA1-1994 0.3 mg/l
1	14.9	1.18	x	x	0.4	x	21	29.8	0			0	
2	15.8	0			0.1		22	31.0	0.1		x	0.01	
3	14.9	0.2	x	x	6.4	x	23	18.4	0.3	x	x	0.1	
4	19.0	0.3	x	x	0.5	x	24	24.1	0			0.4	x
5	21.2	0.7	x	x	0.3	x	25	47.4	0.1		x	0.02	
6	25.9	0			0.3	x	26	46.3	0.1		x	0.9	x
7	37.1	0.1		x	0		27	49.4	0			0.5	x
8	32.5	0			0.1		28	37.8	0.02			0.02	
9	22.7	0.23	x	x	0.2		29	23.1	0.2	x	x	0.2	
10	21.0	0			0.9	x	30	38.0	1.2		x	0.09	
11	35.7	0			0.3	x	31	37.1	0.2	x	x	0.4	x
12	29.5	0			0.01		32	51.8	0.1		x	3	x
13	32.0	0			0.1		33	9.1	0.02			0.02	
14	33.6	0.1		x	0.1		34	9.1	0.5	x	x	0.2	
15	32.6	0.1		x	0.04		35	0.6	0.5	x	x	0.5	x
16	29.6	0.1		x	0.03		36	8.1	0			0.3	x
17	21.3	0			0.1		37	13.5	0.5	x	x	0.05	
18	11.1	0			0.01		38	13.1	0			0.2	
19	20.0	0			0		39	40.5	0.1		x	0.2	
20	30.9	0			0		40	29.9	0.4	x	x	0.56	x

*masl = meters over the level sea

Table 2: Population and manganese concentration levels in descending order of risk of consumption of untreated water from wells and boreholes in the Sinaloa River Basin, using the classifications proposed in this study.

Number Samples	Population	Manganese Mg mg/l	Magnitude of the rank	Type of the rank		Population	Manganese Mg mg/l	Magnitude of the rank	Type of the rank
30	Palmarito	1.2	7	Ma	32	15 de oct.	0.1	3	I
1	Guasave.	1.18	7	Ma	39	Mesquitón 2.	0.1	3	I
5	Nío.	0.7	6	A	28	Reparo.	0.02	2	B
34	Callejones Tamz	0.5	6	A	33	Tesitos.	0.02	2	B
35	Tamazula.	0.5	6	A	2	Burrión N.	0	1	N
37	Buenavista.	0.5	6	A	6	Cruz Blanca.	0	1	N
40	M. Bernal.	0.4	5	Sa	8	Bamoa pozo.	0	1	N
4	R. Castro.	0.3	5	Sa	10	Lichis.	0	1	N
23	Estación Naranjo	0.3	5	Sa	11	Carboneras.	0	1	N
9	El varal.	0.23	5	Sa	12	Port de Gálve	0	1	N
3	Burrión P.	0.2	4	Ia	13	P. Gálves Nor	0	1	N
29	Serranito.	0.2	4	Ia	17	Utatabe.	0	1	N
31	Entre 26 y 29.	0.2	4	Ia	18	La entrada.	0	1	N
7	Bamoa Llave.	0.1	3	I	19	Nacho Bojórq	0	1	N
14	El Sabino.	0.1	3	I	20	La Trinidad.	0	1	N
15	Carboneras.	0.1	3	I	21	Toruño.	0	1	N
16	León Fonseca.	0.1	3	I	24	Sta. Fe.	0	1	N
22	El Palotal.	0.1	3	I	27	Fco. Villa.	0	1	N
25	La pitaya.	0.1	3	I	36	Retiro.	0	1	N
26	El Coyote.	0.1	3	I	38	Mesquitón.	0	1	N

6: Very high (Ma), 5: High (A), 4: Moderately high (Md), 3: Intermediate (I), 2: Low (B) and 1: No risk (N).

central zone with a source of high concentrations, covering an area of approximately 80 km^2. The source was intersected by one of the flows parallel to the Sinaloa River and its volume increased toward the Gulf of California. The northwest ϕ transported Fe and showed dissolution processes dispersing the mineral in the basin in co-action with recharge in the central west portion near

the Valle Fuerte Canal, carrying it to its final destination, namely the Gulf of California coast (Figure 4, Part B).

Water in the intermediate ϕ in the southwest exceeded both standards for Mn concentration. The northwest current showed the greatest concentration of Mn, with a high concentration (0.49 mg L^{-1}) at the source, which is dispersed in the basin, reaching the coast with a level of 0.22 mg L^{-1}. It seems this behavior is explained by a natural decrease in concentration along the course of the flow. Since Mn in groundwater is not degraded nor does it disappear, it follows that the rest of the mineral, estimated at a concentration of 0.27 mg L^{-1}, attaches to particles of the porous medium and/or is deposited in sedimentary strata in the basin (Bianchini [2]). At its source, the southwest current had a Mn concentration of 0.22 mg L^{-1}, but where it joined the regional current near the cone of depression at a piezometric level of 4 masl, the concentration was 0.09 mg L^{-1}. Another interesting feature of Mn, similar to Fe, was that there was a source of high concentration in the central area, covering approximately 180 km^2. This source moved parallel to the Sinaloa River towards the cone of depression. Consequently, since the area around the cone of depression receives flows with different Mn concentrations, the mineral accumulates so that over time the level reaches high concentrations in coastal areas; as much as 0.31 mg L^{-1}, which is much higher than the standards cited in this study. The risk was classified as very high in two samples (5%), high in four (10%), moderately high in three (7.5%), intermediate in nine (22.5%), low in two (5%), and zero in 16 samples (40%) (Figure 4, Section C).

4 Conclusions

Areas where both of the standards for Mn and Fe concentrations were exceeded may be influenced by environmental conditions at the time of year when sampling was done; in this study 55% of samples exceeded the EPA Mn standard and 30% exceeded the NOM-127-SSA1-1994-2000 standard but the result could have varied according to whether water was sampled in the rainy season or the dry season. Therefore the average of the 40 samples in the present study is only evidence of one particular scenario, although the questionable quality of the groundwater in the Sinaloa River Basin was noticeable. Because of this, it is recommended that further measurements of the selected parameters be made to identify the range of the sources of high concentrations as reported in Sections A and B in Figure 4 more precisely, and to make more specific decisions and corrective action for each case. The high concentrations of Mn in underground water were attributed to the lack of O_2; the Mn can therefore not oxygenate, or precipitate or disappear. As stated by Bianchini [2], it follows that it adheres to particles in the ground and is then deposited in sediments in the basin. With respect to sources of high concentration in Section A of Figure 4, it is recommended that further detailed research be conducted to identify and evaluate the processes of Mn deposition and adhesion to porous media, as these areas could be a source of risk for human consumption, especially if Mn accumulates in the ground. When these areas are properly characterized, more effective

processes can be used to remedy the situation. As the matter stands, given that there are still urban areas lacking water supply and sewage networks, it is suggested that methods be applied to eliminate or significantly decrease Mn and Fe concentration where untreated water is used for human consumption in centers where the concentrations do not meet the quality standards for direct human consumption. Such treatments could include chemical precipitation, pH adjustment, aeration, or ionic exchange. When variations in space and time are analyzed (concentrations might be higher in the dry season than in the rainy season, as the minerals might be dissolved and carried away into the porous medium more in the latter than the former), since this study was conducted during the dry season, it is recommended to also conduct systematic sampling and analysis during the rainy season in order to observe and throw more light on transport processes and identify sites towards which the sources of high concentration could be directed. This would increase information about the areas of risk in Section C of Figure 4. There is no doubt that drinking water must contain Mn. However, despite the benefits it provides, such as aiding rapid growth, nutrition, increasing the body's antioxidant abilities and slowing down anti-inflammatory effects of the damage from continuous exposure that could adversely affect health, such as irreversible damage to brain cells (Freed *et al.* [5]), allowable limits should be added to the World Health Organization Guidelines for Quality (WHO [6]).

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