

CHARACTERIZATION OF HARDNESS IN THE GROUNDWATER OF PORT-AU-PRINCE. AN OVERVIEW ON THE HEALTH SIGNIFICANCE OF MAGNESIUM IN THE DRINKING WATER

CARACTERIZACIÓN DE LA DUREZA EN EL AGUA SUBTERRÁNEA DE PUERTO PRINCIPE. UNA VISIÓN GENERAL SOBRE LA IMPORTANCIA PARA LA SALUD DEL MAGNESIO EN EL AGUA POTABLE.

Evens Emmanuel^{1,2,3}, Yanick Simon^{1,2}, Osnick Joseph³

Abstract

Water hardness is basically the sum of the concentrations of dissolved polyvalent metal ions which Ca^{2+} and Mg^{2+} are predominant. In recent years it has become an important public health issue. Indeed, it has been reported in the literature a relationship between cardiovascular disease mortality and water hardness used for human consumption. It seems that total hardness of water concentration greater than 200 mg/L with a magnesium concentration less than 7 mg/L can cause adverse effects on human health.

In Haiti, where more than 60% of the territory's geology is dominated by limestone, water resources are known to be very hard. Studies of the sources used to supply the population of the metropolitan area of Port-au-Prince (MAPP), the largest urban area in the country, showed a total hardness greater than 200 mg/L, with magnesium concentration less than 7 mg/L. Otherwise, cardiovascular diseases are the 7th cause of death and represent 3% of total deaths. In the perspective to evaluate the health risk associated with low magnesium concentration in the water used for human consumption, it seems appropriate to proceed with the characterization of the main components of the hardness into groundwater of the MAPP. The aim of this study was: (i) to review the chemistry and toxicology of Ca^{2+} and Mg^{2+} in order (ii) to characterize hardness, with a specific emphasis on Mg concentration, in Port-au-Prince groundwater. Mg^{2+} concentrations ranging from 5.58 to 6.9 mg/L were measured in a private borehole. These results should be confirmed by studies involving a larger sample size during rainy and dry seasons.

Keywords: water hardness, geology and hydrogeology of MAPP, groundwater, medical geology, cardiovascular diseases, health hazards.

Resumen

La dureza del agua es básicamente la suma de las concentraciones de iones metálicos polivalentes disueltos de los cuales Ca^{2+} y Mg^{2+} son predominantes. En los últimos años esto se ha convertido en un problema de salud pública importante. De hecho, se ha registrado en la literatura una relación entre la mortalidad por causa de enfermedades cardiovasculares y la dureza del agua utilizada para el consumo humano. Aparentemente una dureza total superior a 200 mg/L, con una concentración de magnesio menor a 7 mg/L puede causar efectos adversos para la salud humana.

En Haití, donde más del 60% de la geología del territorio está dominada por piedra caliza, los recursos hídricos son conocidos por ser muy duros. Los estudios de las fuentes de abastecimiento a la población de la zona metropolitana de Puerto Príncipe (MAPP), el área urbana más grande del país, mostraron una dureza total superior a 200 mg/L, con una concentración de magnesio menor a 7 mg/L, sin embargo, las enfermedades cardiovasculares son la séptima causa de muerte y representan el 3% de las muertes totales. En la perspectiva de evaluar el riesgo para la salud asociado a una baja concentración de magnesio en el agua utilizada para el consumo humano, parece conveniente proceder a la caracterización de los principales componentes de la dureza de las aguas subterráneas de la MAPP. El objetivo de este estudio fue: (i) revisar la química y toxicología de Ca^{2+} y Mg^{2+} con el fin de (ii) caracterizar la dureza, con un énfasis específico en la concentración de Mg en el agua subterránea de Puerto Príncipe. Se midieron en un pozo privado concentraciones de Mg^{2+} en el rango de 5,58 hasta 6,9 mg/L. Estos resultados deben ser confirmados por estudios con una muestra mayor, durante las estaciones lluviosa y seca.

Palabras clave: la dureza del agua, geología y hidrogeología de la MAPP, agua subterránea, geología médica, enfermedades cardiovasculares, riesgos para la salud.

¹ Laboratoire Santé-Environnement, Université Quisqueya, 218 Avenue Jean Paul II, Haut de Turgeau, Port-au-Prince, Haïti. Tel: (509) 3423 4269 / (509) 3718 4833; Email: evens.emmanuel@gmail.com

² Haiti Chapter of International Medical Geology Association, Université Quisqueya, 218 Avenue Jean Paul II, Haut de Turgeau, Port-au-Prince, Haïti.

³ Laboratoire de Qualité de l'Eau et de l'Environnement, Université Quisqueya, 218 Avenue Jean Paul II, Haut de Turgeau, Port-au-Prince, Haïti.

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1. INTRODUCTION

Hardness is the traditional measure of the capacity of water to react with soap and describes the ability of water to bind soap to form lather, which is a chemical reaction detrimental to the washing process (Rubenowitz-Lundin and Hiscock, 2005). Water hardness water results from the contact of groundwater with rock formations. Hardness is due to the presence of polyvalent metallic ions, predominantly Ca^{2+} and Mg^{2+} (Desjardin, 1988). The sources of the metallic ions are typically sedimentary rocks, and the most common are limestone (CaCO_3) and dolomite ($\text{CaMg}(\text{CO}_3)_2$).

Hardness has been deemed safe for human health, until Kobayaski (1957) showed a relationship between water hardness and the incidence of vascular diseases. Other studies reported the existence of a relationship between cardiovascular disease mortality and water hardness (Schroeder, 1960; Sharret, 1979; Masironi et al., 1981). Hewitt and Neri (1980) noted more than 100 studies on water hardness in association with cardiovascular diseases. Miyake and Iki (2004) observed a lack of association between water hardness and coronary heart diseases (CHD) mortality in Japan. Nonetheless, a large number of studies covering many countries suggest such a correlation and geochemically it is worthy of serious study (Dissanayake and Chandrajith, 2009). Based on available information in the literature on the association of water hardness and the incidence of cardiovascular diseases (CVD), Eisenberg (1992) considered that Mg seems to be the basic element. Indeed, very hard natural water with CaCO_3 concentration higher than 200 mg/L with a magnesium concentration lower than 7 mg/L may affect various organs including the cardiovascular physiology (Rubenowitz-Lundin and Hiscock, 2005).

Hardness is normally expressed as the total concentration of calcium and magnesium ions in water units of mg/L as equivalent CaCO_3 (Desjardin, 1988; Rubenowitz-Lundin and Hiscock, 2005; Dissanayake and Chandrajith, 2009). Ca and Mg are present as simple ions Ca^{2+} and Mg^{2+} with the Ca levels varying from tens to hundred of mg/L and the Mg concentrations varying from units of tens of mg/L (Dissanayake and Chandrajith, 2009). Magnesium is significantly less abundant than calcium in rocks and in most natural waters. In addition, magnesium concentrations are much lower in the water than calcium. They are generally less than 50 mg/L, although values higher or equal to 100 mg/L are stored particularly in cold climates (Rubenowitz-Lundin and Hiscock, 2005).

In Haiti, where more than 60% of the geology is dominated by limestone, water resources are known to be very hard. Studies on the spring waters used to supply a part of the population of the Metropolitan Area of Port-au-Prince (MAPP), the most important urban area of the country, showed a total hardness greater than 200 mg/L, with magnesium concentration less than 7 mg/L (TRACTEBEL, 1998). Otherwi-

se, cardiovascular diseases are the 7th cause of death and represent 3% of total deaths in the MAPP (MSPP, 2003). In the MAPP, groundwater resources are largely used to supply in drinking water to the population (Emmanuel, 2004). The aim of this study was: (i) to review the chemistry and toxicology of Ca^{2+} and Mg^{2+} in order (ii) to characterize hardness, with a specific emphasis on Mg concentration, in Port-au-Prince groundwater.

2. CHEMISTRY AND TOXICOLOGY OF Ca^{2+} AND Mg^{2+}

2.1. Water Hardness

Water hardness has been defined in the literature in a variety of ways with multiple units being used to express it, such as German, French and English degrees, equivalent CaCO_3 and CaO in mg/L. Water hardness is not caused by a single substance but by a variety of dissolved polyvalent metallic ion – predominantly Ca^{2+} and Mg^{2+} – although other ions, for example, aluminium, barium, iron, manganese, strontium, and zinc also contribute (Rubenowitz-Lundin and Hiscock, 2005).

Hardness (in mg equivalent CaCO_3 /L) can be determined by substituting the concentration of calcium and magnesium, expressed in mg/L, in the following equation (Eaton et al, 1995):

$$\text{Total hardness} = 2.497 (\text{Ca}^{2+}, \text{mg/L}) + 4.118 (\text{Mg}^{2+}, \text{mg/L}) \quad \text{Eq.1}$$

Each concentration is multiplied by the ratio of the formula weight of CaCO_3 to the atomic weight of the ion; hence, the factors 2.497 and 4.118 are included in the hardness relation (Freeze et al Cherry, 1979). Table 1 summarizes the general guidelines for classification of water hardness (INERIS, 2004).

Table 1. General guidelines for classification of water hardness (INERIS, 2004)

Hardness in mg/L CaCO_3	Degree of hardness
0 – 30	Very soft
31 – 60	soft
61 – 120	Moderately soft/ moderately hard
121 – 180	Hard
>180	Very hard

2.2. Physical and chemical properties of Ca^{2+} and Mg^{2+}

Magnesium and calcium are silvery gray alkaline earth metals which are very abundant in the earth's crust (Pettit, 1998 ; Fridli, 2002). Table 2 shows certain physical and chemical properties of Ca^{2+} and Mg^{2+} (Fridli, 2002).

Table 2. Physical and chemical properties of Ca and Mg (Cardarelli, 2008 ; Ropp, 2013)

Elements	S ^a	CAS#	Z ^b	A ^b	Density	Electronic configuration	MP ^c	BP ^c	Isotopes
				g/mol	[Kg.m ⁻³]		[OC]	[OC]	
Magnesium	Mg	7 439-95-4	12	24.305	1738	[Ne] 3S ²	649	1090	3
Calcium	Ca	7 440-70-2	20	40.078	1550	[Ar] 4S ²	842	1484	6

^aSymbol, ²Atomic number and atomic weight, ³Melting points and boiling points at atmospheric pressure

2.3. Toxicology of Ca²⁺ and Mg²⁺

Calcium and magnesium are essential for the human body. They contribute to the formation and solidification of bones and teeth and play a role in the decrease of neuromuscular excitability, myocardial system, heart and muscle contractility, intracellular information, transmission and blood contractility (Baker et al., 2002; Rubenowitz-Lundin and Hiscock, 2005; Dissanayake and Chandrajith, 2009). They also play a major role in the metabolism of almost all cells of the body and interacts with a large number of nutrients (Campbell, 1990; Altura et Altura, 1996; Bootman et al., 2001).

In the cardiovascular system, magnesium is the candidate element. It plays an important role as a cofactor and activator of more than 300 enzymatic reactions including glycolysis, ATP metabolism, transport of elements such as Na, K and Ca through membranes, synthesis of proteins and nucleic acids, neuromuscular excitability and muscle contraction (Kožíšek, 2003). That can have hand in various mechanism where the main is the calcium antagonist effect which can be direct or indirect (Berthelot, 2003).

Magnesium and calcium have a cardio-protective effect (WHO, 2005). However, the magnesium's role is predominant. Without optimal amounts of magnesium, heart muscle cells lose the ability to produce the energy they need to contract (Seeling et Rosanoff, 2003). In extracellular level, magnesium is required to maintain the efflux of calcium from the endoplasmic reticulum and comes into competition at the sites of calceins (troponine C,..., calmoduline) which participate in the contractile mechanism (Berthelot, 2003). In extracellular level, magnesium blocks the outward passage of potassium and calcium through the cell membrane and by activating the enzyme Na/K-ATPase and Ca-ATPase (Swaminathan, 2003; Rubenowitz-Lundin and Hiscock, 2005).

The presence of increased amounts of calcium in the heart cells is an early sign of damage that develops in magnesium deficient animals even before the cells break down, or become necrotic. These cellular modifications can lead to cardiomyopathy (damaged heart muscle), ventricular arrhythmia which can result to heart failure. (Berthelot, 2003; Seeling et Rosanoff, 2003).

The magnesium has been known for its vasodilator power. It acts as a natural calcium antagonist by competing for calcium binding sites in the vascular smooth muscle and thus reducing the constrictive effect of calcium in the blood vessels (Reinhardt, 1981). His increasing opposes the effects of vasoconstrictors agents and potentiates the action of vasodilators agents (Berthelot, 2003). Indeed, the normal constriction and dilatation of all arteries are influenced by hormones (angiotensin, serotonin, acetylcholine) the secretion of which is controlled by the amount of magnesium present (Seeling et Rosanoff, 2003; Rubenowitz-Lundin et Hiscock, 2005). Thereby, magnesium's role in keeping the endothelium normal is important in preventing angina and also in protecting against developing high blood pressure (Seeling et Rosanoff, 2003).

The calcium has a vasoconstrictor action and protects also against developing high blood pressure (Dietary Reference Intakes). Metanalysis comprising nearly 40,000 people has shown that a calcium intake lowered both systolic and diastolic blood pressure (Cappuccio et al, 1995; Rubenowitz-Lundin et Hiscock, 2005). Many mechanisms may be the cause of this hypothesis. The one of them is that hypocalcemia inhibits Ca-ATPase activity, which leads to an increase in intracellular calcium and contraction of vascular smooth muscles (Mc Carron, 1985; Rubenowitz-Lundin et Hiscock, 2005). In addition, Dietary calcium suppresses the parathyroid hormone in hypertensive population which causes the blood pressure to decrease (Jhonson et al al., 1985; Rubenowitz-Lundin et Hiscock, 2005).

Magnesium and calcium are necessary to keep the appropriate balance in cardiovascular system. A modification (deficiency/toxicity) of the concentration of one of them in intracellular and/or extracellular level have important effect on cardiovascular system (cardiac excitability and vascular tone, contractility and reactivity) and can lead to high blood pressure, cardiac arrhythmia, acute myocardial infarction. That can increase the cardiovascular morbidity and mortality.

In the human body, the toxicity of magnesium may occur at a magnesemia level greater than 1.2 mmol/L (Ismail et al., 2013). Regarding calcium, the serum calcium level should be maintained in a very narrow

way between values of 2.2 and 2.6 mmol/L (Covili et Jacob, 2001). Above this concentration, there could be several adverse effects in which three effects are biologically important and widely studied. It is the nephrolithiasis, the syndrome of hypercalcemia and renal insufficiency with or without alkalosis and the interaction of calcium with other essential minerals (Carroll et Schade, 2003 ; Crown et al, 2009).

3. MATERIALS AND METHODS

3.1. Presentation of study area

To characterize total hardness, and particularly Mg concentration, in Port-au-Prince groundwater (Fig. 1), a borehole from a private drinking water supply network (DWS) was selected in the Cul-de-Sac Plain (north of Port-au-Prince) as the experimental site. The borehole supplies water to a population of 4000 inhabitants including 1600 infants less than 10 years of age. The geology and hydrogeology of the region in which the borehole is located are dominated by a karstic aquifer (Butterlin, 1960; Simonot, 1982; PNUD, 1991). The rainy periods occur in April, May, June and August, September, October and the dry season from December to March (Simonot, 1982).

Wastewaters (domestic and industrial) generated by this urban area are most often discharged into a drainage canal or managed by individual drainage systems. In the Cul-de-Sac plain, two main processes governed the sanitation systems: (i) the pit latrines for low income families, and (ii) for the middle and high income families, individual drainage systems with septic tanks. In the latter, undergo primary treatment that consists in separating large solid materials. The effluents of these tanks are discharged directly into a diffusion well embedded in a matrix consisting of a saturated area and a non saturated area. The groundwater resources are used for drinking water. This aquifer provides more than 50% of the drinking water supply to the population of the Port-au-Prince Urban Community (PPUC) i.e. 3 million people (Emmanuel et al., 2004).

Groundwater resources of Port-au-Prince are vulnerable to contamination related to polluted water infiltration such as leachates, cesspools and septic tanks, stormwater runoff, waste oil discharging, over-irrigation and industrial discharging (Fifi et al., 2010). These sources of groundwater recharge may contain organic and inorganic compounds which can be in dissolved and colloidal forms or associated to particles. Previous researches showed an impact of waters quality due to anthropogenic and geogenic contaminants (Bras et al., 2007; Emmanuel et al., 2007; Bras et al., 2009; Simon et al., 2013) Lead concentrations ranging from 40 µg/L to 90 µg/L were

measured in these groundwater resources (Angerville et al. 2004; Emmanuel et al., 2009). The values, measured for some heavy metals in Port-au-Prince groundwater, are largely higher than threshold values recommended for drinking water (WHO 2004). Therefore, Fifi et al. (2009) studied three sites at Cul-de-sac plain to assess the soil reactivity towards heavy metals. In this study, the authors concluded that heavy metals transfer into soil and groundwater is governed by diversified physicochemical mechanisms. In addition to bacterial and metal contaminations, it was found that Cul-de-Sac aquifers are also exposed to seawater pollution (Simonot, 1982; Bois et al., 1999; Emmanuel et al., 2004).

3.2. Sampling and physicochemical analysis

Five water samples have been collected in April 2005, at the beginning of the rainy season. All the samples were placed in plastic containers with a volume of 1 L. These recipients were rinsed 3 times with the water to be examined. To fill the recipients, we used an improved manual sampling method consisting in preparing an average sample over 100 min (1h40 min) with a sampling time step of 100 ml every 10 min.

Electrical conductivity, pH, calcium and total hardness were retained as the physicochemical parameters for this study. Electric conductivity and pH were measured directly on site after sampling. The recipients containing the water samples for total hardness and calcium measurements were carefully labelled and conserved at 4 °C. Once taken, the samples were transported to the laboratory in less than two hour.

The pH of water samples was measured using a WTW pH 340 ION. This instrument has 2 electrodes: an electrode of reference, metal type and an electrode (specific to the measurement of the pH) out of glass. Electric conductivity was measured on the sampling sites using a WTW-LF 330 multipurpose potentiometer coupled with specific electrodes.

The French protocols, EDTA titrimetric method NF T 90-003 and NF T 90-016, proposed by AFNOR (1997) were used for analysing total hardness Ca^{2+} . Magnesium hardness and Mg^{2+} has been estimated by application of equation 1.

4. RESULTS AND DISCUSSION

4.1. Results of physicochemical analyses of water samples from the private borehole

The results of the physicochemical analyses for the 5 water samples from the private borehole are summarised in Table 3. The values obtained for pH [7.37 - 8.01] indicate a low alkaline range, with a variation of pH lower than 1 unit.

Table 3. Results of the physicochemical characterisation of water samples from the private borehole

Parameters	Unit	Average	Minima	Maxima	Standard deviation	n
pH	-	7.73	7.37	8.01	0.27	5
Electrical conductivity	$\mu\text{S/cm}$	316.2	300	330	12.48	5
Total hardness	mg/L	213.55	205.91	222.84	7.21	5
Ca ²⁺	mg/L	75.56	72.6	79.1	2.47	5
Mg ²⁺	mg/L	6.04	5.58	6.9	0.54	5

Electrical conductivity values varied from 300 to 330 $\mu\text{S/cm}$. The water samples were not salted water. These values were lower than 400 $\mu\text{S/cm}$, i.e., the maximum threshold value for drinking water (ERB, 1999).

High concentrations of calcium [72.6 - 79.1] were obtained, while low magnesium [5.58 - 6.9] values were measured from the water samples. Both concentrations have been obtained on water samples collected during the beginning of April rainy season. The most important concentration of calcium from the borehole [79.1 mg/L] is lower than the highest value from the spring water. The minima value of magnesium from the borehole is equal the magnesium concentration in water sample from the spring water of Tête de l'eau (TRACTEBEL, 1998).

Sprinkle (1989) has identified a sequence of hydrochemical evolution of hardness in groundwater. This sequence starts with calcite dissolution in recharge areas that produces a calcium-bicarbonate dominated water type with a total dissolved solids (TDS) concentration of generally less than 250mg/L. In this study on the water samples from the borehole, TDS were not retained as physicochemical parameters to be determined. However, values can be estimated for TDS from the existing theoretical ratio between TDS and conductivity.

Theoretically, this ratio is an empirical factor that can vary from 0.55 to 0.9 depending on the soluble components of the water and on the measurement temperature. Relatively high factors may apply to saline or boiler waters, whereas lower factors may apply where considerable hydroxide or free acid is present (Eaton et al., 1995). Since pH in this study varied from 7.37 to 8.01, which indicated the presence of hydroxide, probably at low concentration, and the electrical conductivity (EC) from 300 to 330 $\mu\text{S/cm}$, it is obvious that the samples studied were fresh water. In this context a low factor or ratio (TDS/EC = 0.65) has been retained to estimate the TDS values, which varied from 195 to 215 mg/L lower than 250 mg/L. The criteria used to estimate the TDS and the results obtained from the ratio TDS/EC seem to explain the beginning of the process of dissolution of calcite during the first rains of the wet season.

Important concentrations of total hardness were measured on water samples from the private borehole.

Total hardness value varied from 206 to 223 mg/L (as CaCO₃), which are higher than 180 mg/L. Water samples from this aquifer are very hard (Desjardins, 1988; INERIS, 2004; Dissanayake and Chandrajith, 2009).

The combination of geology and hydrology of a watershed is important in determining the hardness of water resources (Rubenowitz-Lundin and Hiscock, 2005). The geology and hydrogeology of the region in which the hospital in this study is located are dominated by a karstic aquifer. The main characteristics of the karstic aquifers, which are dominated the region of Port-au-Prince, are that they have irregular pores, cracks, fractures and conduits of various shapes and dimensions. This type of physically and geometrically heterogeneous structure gives rise to complex hydraulic conditions, with hydraulic parameters subject to considerable variations in time and space. After a precipitation, the rapid and turbulent replenishment of the groundwater occurs via the drainage of high volumes of non-filtered water through large channels (Denić-Jukić and Jukić, 2003). As a result in the specific case of the MAPP, it seems that the aquifer attains a high concentration of dissolved solid matters and is characterized as hard water.

Generally, where the soil or the unsaturated zone of the aquifer system is composed only of limestone, the total hardness is equivalent to carbonate limestone and is lower than 120 mg/L. The total hardness values measured on water samples from the borehole indicate the presence of other minerals in the unsaturated zone of the aquifer. Indeed, Emmanuel et al (2009) have made investigations of the site in which the borehole examined is situated. They presented data relating to boring a private well to supply a hospital, which is located at 100 meters from the well used in this study. The different geological formations of the non saturated area and the well shaft plan of the hospital borehole are shown in Fig. 2.

4.2. Low Mg concentration: a public health perspective

The crustal abundance of Mg is much lower as compared to Ca and hence to lower abundance of Mg in the natural waters, the average Ca/Mg ratio being 4 (Dissanayake and Chandrajith, 2009). In this stu-

dy, the Ca/Mg ratio varied from 11.06 to 13.58. As shown in table 4 and 5, the values of this ratio for water samples from the borehole, were higher than the values estimated for the samples from the spring

water except for the Tête de l'eau value. Otherwise, for all magnesium concentration higher than 7 mg/L a ratio between calcium hardness and magnesium lower than 4 was observed.

Table 4. Average hardness and Ca²⁺/Mg²⁺ ratio of water samples from 12 spring waters used in the MAPP (TRACTEBEL, 1998; Emmanuel et Lindskog, 2002; Simon et al., 2013)

Spring Water	TH ^a	CH ^b	MH ^c	Ca ²⁺	Mg ²⁺	Ratio CH/MH	Ratio Ca ²⁺ /Mg ²⁺
Chadeau	231.2	191.36	39.84	76.64	9.67	4.80	7.92
Desplumes 1&2	249	204.5	44.5	81.90	10.81	4.60	7.58
Tête de l'eau	204	181	23	72.49	5.59	7.87	12.98
Diquini	225	183	42	73.29	10.20	4.36	7.19
Tunnel Diquini	221.95	178.13	43.82	71.34	10.64	4.07	6.70
Leclerc	280.6	233.6	46.8	93.55	11.36	4.99	8.23
Mahotières	268.67	232	36.67	92.91	8.90	6.33	10.43
Corosol	203.7	165.7	38.13	66.36	9.26	4.35	7.17
Mariani	227.15	184.86	42.29	74.03	10.27	4.37	7.21
Métivi	270	226.5	43.5	90.71	10.56	5.21	8.59
Mme. Baptiste	216.67	187.67	29	75.16	7.04	6.47	10.67
Turgeau	246.99	202.33	44.66	81.03	10.85	4.53	7.47

^aTH: Total Hardness; ^bCH: Calcium Hardness; ^cMH: Magnesium Hardness

Table 5. Average hardness and Ca²⁺/Mg²⁺ ratio of the 5 water samples from the private borehole

Sample	TH ^a	CH ^b	MH ^c	Ca ²⁺	Mg ²⁺	Ratio CH/MH	Ratio Ca ²⁺ /Mg ²⁺
1	218,94	190,52	28,41	76,3	6,9	6,71	11,06
2	222,84	197,51	25,33	79,1	6,15	7,80	12,86
3	205,91	181,28	24,63	72,6	5,98	7,36	12,14
4	212,25	189,27	22,98	75,8	5,58	8,24	13,58
5	207,84	184,78	23,06	74	5,6	8,01	13,21

^aTH: Total Hardness; ^bCH: Calcium Hardness; ^cMH: Magnesium Hardness

In the future, it seems important to carry out observations on iron concentration in the study of hardness from Port-au-Prince water resources. Indeed, in its study, TRACTEBEL (1998) showed not merely that the water from all emergencies in northern limestone part of the Massif de la Selle have total hardness greater than 200 mg /L, but reported a level of iron (0.30 mg/L) from water sample from Tête de l'eau spring water.

Magnesium concentrations in samples collected during the rainy season were lower than 7 mg/L. Since Port-au-Prince does not have an efficient urban waste management system (for liquids and solids), the main geological characteristic of this urban area facilitates the transfer of surface pollution to groundwater following storms (Denić-Jukić and Jukić, 2003).

Indeed, groundwater with higher total hardness can also results from contamination (Sprinkle, 1989). In this context, interactions between magnesium and other elements could take place. The establishment of a monitoring system, including the characterisation of hardness during rainy and dry seasons, should allow to observe the variations of magnesium during the different seasons.

The presence of magnesium at lower concentrations in water samples from the boreholes is an important indicator of public health. Indeed, low magnesium concentration in water hardness has been considered as the element responsible of the association between water hardness and cardiovascular diseases. It seems that the hazards for human health are more important when magnesium concentrations are

lower than 6 mg/L. Indeed, Marier and Neri (1985) attempted to quantify the importance of water magnesium using a number of epidemiological studies. They estimated that an increase in water magnesium level of 6 mg/L would decrease coronary heart disease mortality by approximately 10%. In this study 60% of the results were lower than 6 mg/L. In the future, epidemiological data could be collected during sampling campaign of water samples in order to establish the correlation between low magnesium concentration in water hardness and cardiovascular diseases. These results should be confirmed by studies involving a larger sample size during rainy and dry seasons.

CONCLUSION

The aim of this study was: (i) to review the chemistry and toxicology of Ca^{2+} and Mg^{2+} in order (ii) to characterize hardness, with a specific emphasis on Mg concentration, in Port-au-Prince groundwater. Magnesium concentrations in samples collected during the first week of the rainy season were lower than 7 mg/L. It would be interesting to confirm these results by carrying out epidemiological studies on the exposed population. It is also necessary to characterise total hardness, including magnesium concentration, with a larger number of water samples during rainy and dry seasons.

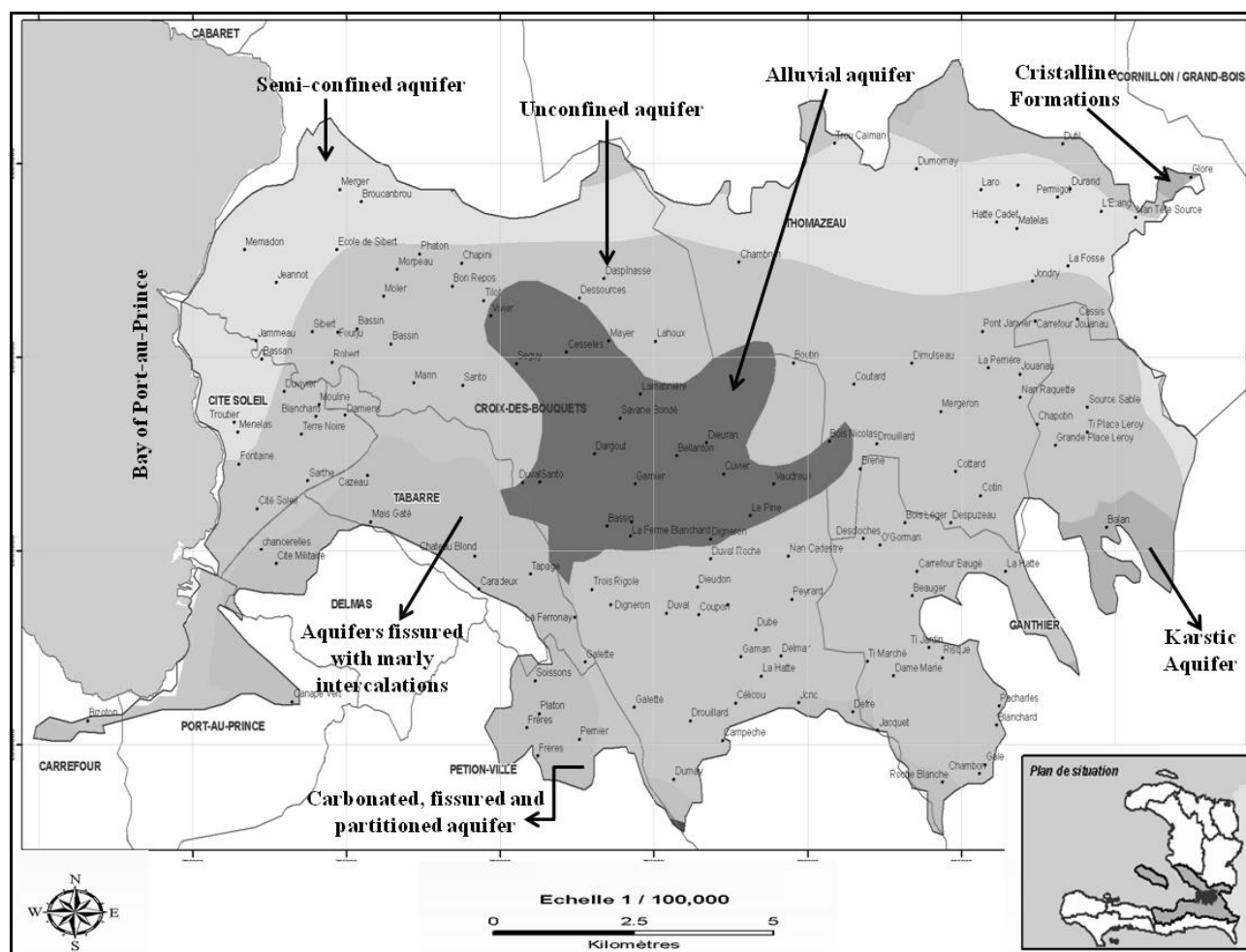


Figure 1: Aquifers systems of plain of Cul-de-sac (Fifi et al, 2010)

Lithological section of the site (meter)		Well casing for drinking water supply	Well casing plan in meters (PVC diam. = 6 inches)		
0 - 1	Agricultural soil		1	0 - 37	Full
1 - 6	Average grade limestone gravel		2	37 - 49	Well screen
6 - 22	Pebbles + limestone sand		3	49 - 52	Full
22 - 26	Average grade gravel + clay		4	52 - 58	Well screen
26 - 29	Clayey gravel + pebbles		5	58 - 64	Full
29 - 32	Yellow sandy clay		6	64 - 70	Well screen
32 - 37	Clayey gravel + calcite		7	70 - 73	Well bottom
37 - 52	Clayey, sandy gravel				
52 - 56	Clayey sand + pebbles				
56 - 58	Clayey gravel				
58 - 62	Clayey sand + pebbles				
62 - 73	Basalt				

Figure 2: Well casing plan for the borehole (Emmanuel et al, 2009)

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RÉFÉRENCES BIBLIOGRAPHIQUES

AFNOR (Association Française de Normalisation) (1997) Qualité de l'eau, Tome 3: Méthodes d'analyse 2, éléments majeurs, autres éléments et composés minéraux. Recueil de Normes Françaises, Paris, p.496.

Altura B.M., Altura B.T. 1996. Role of magnesium in pato-physiological processes and the clinical utility of magnesium ion selective electrodes. Scand. J. Clin. Lab. Invest. 56:211-234.

Angerville R., Rony F.J., Accou K.B., Joseph O., Emmanuel E. and Perrodin, Y. (2004). Assessment of human exposures to lead in drinking water. In AIDIS (Ed.): Proceedings of the XXIX Congreso Interamericano de Ingeniería Sanitaria y Ambiental, San Juan, Puerto Rico, 21–28 de agosto, CDRom.

Baker S.B., Worthley L.I.G. 2002. The essentials of calcium, magnesium and phosphate metabolism: part I. Physiology. Critical care resuscitation. 4: 301-306.

Berthollet A. 2003. Le magnésium: un nutriment important. Forum Med Suisse. 27: 638-640.

Bois M., Emmanuel E., Prévilon E., Laraque E. (1999). Water salinity evaluation from the principal wells of Cul-de-Sac groundwater supplying tank trucks. Proceedings of 8th annual CWWA and 4th AIDIS région 1 conférence. Kingston, Jamaica, October 4 to 8. CDRom.

Bootman M.D., Collins T.J., Peppiatt C.M., Prothero L.S., MacKenzie L., De Smet P., Travers M., Tovey S.C., Seo J.T., Berridge M.J., Ciccolini F., Lipp P. 2001. Calcium signalling—an overview. Semin Cell Dev Biol 12:3–10.

Bras A., Emmanuel E., Lilite O., Brasseur P., Pape J.W., Raccurt C.. Evaluation du risque dû à Cryptosporidium sp présent dans l'eau de boisson à Port-au-Prince, Haïti. Environnement, Risques et Santé, 2007, 6 (5) 355-364.

Bras A., Berdier C., Emmanuel E., Zimmermann M. Problems and current practices of solid waste mana-

- gement in developing countries – Case study from Port-au-Prince (Haiti). *Waste Management*, Vol 29 (2009) 11 : 2907-2909
- Butterlin J. (1960). *Géologie générale de la République d'Haïti*. Institut des Hautes Études de l'Amérique Latine, Paris, 194p.
- Cappuccio F., Elliot P., Allender P.S., Pryer J., Follman P. A., Cutler J.A. 1995. Epidemiologic association between dietary calcium intake and blood pressure: a meta analysis of published data. *Am. J. Epidemiol.* 142: 935-945.
- Cardarelli F. *Materials handbook : a concise desktop reference*. Springer, 2008, 1378p. ISBN 1846286697.
- Covili F., Jacob L. 2001. Hypercalcémie aiguë. *Conférences d'actualisation*. Editions Scientifiques et Médicales Elsevier SAS, et Sfar, France. p.571-596.
- Denić-Jukić V, Jukić D. Composite transfer functions for karst aquifers. *J Hydrol*, 2003;274:80–94.
- Dissanayake C.B., Chandrajith R. 2008. *Introduction to medical geology*. Springer Dordrecht Heidelberg, London, New York, 297p.
- Eaton A.D., Clesceri L.S., Greenberg A.E. (1995). *Standard methods for the examination of water and wastewater*. 19th edition, APHA, AWWA, WEF, Washington D.C.
- Eisenberg M.J. 1992. Magnesium deficiency and sudden death. *Am. Heart J.*, 124:544-549.
- Emmanuel E. 2004. *Évaluation de risques sanitaire et écotoxicologiques liées aux effluents hospitaliers*, thèse de l'Institut National des Sciences Appliquées de Lyon, Université de Lyon, France. p. 259
- Emmanuel E., Joseph O., Fanfan P.N., Vermande P., Winiarski T. Trend analysis of the groundwater salinity of the Cul-de-sac aquifer in Haiti. *Proceedings of the XXIX Congreso Interamericano de Ingeniería Sanitaria y Ambiental*. San Juan, Puerto Rico, 22–28 de agosto; 2004. CDROM.
- Emmanuel E., Angerville R., Joseph O. and Perrodin Y. (2007) Human health risk assessment of lead in drinking water: a case study from Port-au-Prince, Haiti. *Int. J. Environment and Pollution*, Vol. 31, Nos. 3/4, pp.280–291.
- Emmanuel E., Pierre M.G., Perrodin Y. 2009. Groundwater contamination by microbiological and chemical substances released from hospital wastewater: Health risk assessment for drinking water consumers. *Environment International* 35: 718–726.
- Fifi U., Winiarski T., Emmanuel E. 2009. Sorption Mechanisms Studies of Pb (II) Cd (II) and Cu (II) into Soil of Port-au-Prince. *AQUA-LAC, Journal of the International Hydrological Programme for Latin America and Caribbean*, Aqua-Lac 1 (2): 164–171.
- Fifi U., Winiarski T., Emmanuel E. Impact of surface runoff on the aquifers of Port-au-Prince, Haiti. In.: Eddie N. Laboy-Nieves, Matheus Goosen and Evens Emmanuel (Editors). *Environmental and Human Health: Risk Management in Developing Countries*. London: Taylor and Francis. 2010, pp. 123-140.
- Freeze R. A., Cherry J. A. 1979. *Groundwater*. Prentice Hall, Englewood Cliffs, New Jersey.
- INERIS. 2004. *Devenir et comportement des métaux dans l'eau : biodisponibilité et modèles BLM*. Paris : INERIS 85p. Available on : http://www.ineris.fr/centredoc/03_0693_Rapp_Technique_biodisp_ecot.pdf
- Kobayashi J. 1957. On geographical Relations Between the Chemical Nature of River Water and Death Rate from Apoplexy, Berich. *Ohara Inst. Landwirtsch. biol.* 11: 12-21.
- Marier J.R., Neri L.L. (1985). Quantifying the role of magnesium in the interrelation between human mortality/morbidity and water hardness. *Magnesium*, 4:53-59.
- PNUD (Programme des Nations Unies pour le Développement). *Développement et gestion des ressources en eau. Haïti : Disponibilité en eau et adéquation aux besoins*. Vol. IV, Projet HAI/86/03, New-York, 1991, 50 p.
- Ropp R.C. *Encyclopedia of the alkine earth compounds*. Elsevier Science & Technology, 2013, 1250p. ISBN 0444595538.
- Simon Y., Alfred F., Charles T., Martin M., Emmanuel E., Poitevien G., Balthazard-Accou K., Emmanuel E. Health hazard assessment of water hardness and cardiovascular diseases. Case study from Port-au-Prince (Haiti). In.: *Proceedings of the 5th International Conference on Medical Geology – MEDGEO-2003*. Arlington, Virginia, 25-29th August 2013. Available from: (consulted 10/25/2013) <https://gsa.confex.com/gsa/2013MED/webprogram/Paper218296.html>
- Simonot M. (1982). *Les ressources en eau souterraine de la région de Port-au-Prince. Situation actuelle et recommandation*. Projet des Nations Unies, HAI/79/001, Port-au-Prince.
- Sprinkle C.L. (1989). *Geochemistry of the Florida aquifer system in Florida and in part of Georgia, South Carolina, and Alabama*, United States Geological Survey Professional Paper 1403-1.
- TRACTEBEL (1998). *Définition des périmètres de protection pour les sources exploitées par la CAMEP*. Bruxelles: Tractebel Development, 235 p.
- [WHO] World Health Organization. 2004. *Guidelines for drinking water quality: Volume 1 recommendations*, 3rd Edition [internet]. Geneva. 540 p. Available from: http://www.who.int/water_sanitation_health/dwq/GDWQ2004web.pdf.