

Estimation and impact of carbon dioxide capture on drinking water: Tillmans equilibrium diagram

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ABSTRACT

The increase of CO₂ in the atmosphere may produce some effects on drinking water because water tends to naturally capture CO₂ species. The main purpose was the study of the impact of capture of free CO₂ and its transformation to carbonic acid (H₂CO₃) and bicarbonate ions (HCO₃⁻). The study used a Tillmans equilibrium diagram obtained from the modified Mojmir Mach model as a function of water temperature and considered the effects on anion and cation composition. Three wells located in different zones were selected, with similar characteristics (capture of CO₂). Samples were taken in different seasons of the year and the amount of CO₂ in the drinking water was calculated. It was found that with increasing concentrations of free CO₂ the pH decreases, and this process makes the water acid and susceptible to dissolve some elements (Ca, Na, K, Si) and other species (HCO₃⁻). The capture of CO₂ has important effects on the anion and cation composition of drinking water and on the variation of pH by more than one unit, which may affect the health of consumers. The method presented in this study is an excellent user-friendly alternative to determine the impact of natural capture of total CO₂ by water.

Key words | carbonate system, CO₂ capture, drinking water, Mojmir mach, Tillmans equilibrium diagram

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INTRODUCTION

Global or regional climate changes are significant and their origin may be natural or anthropogenic, for example the emissions of CO₂ from drinking water reservoirs (Saidi & Koschorreck 2017). Increasing numbers of studies are under way on the effects of climate changes, mainly in air, but in water few studies have been reported

(Saidi & Koschorreck 2017; Chen *et al.* 2018). In recent years, CO₂ concentrations in water and soil that may come from the atmosphere, and the gas contained in the pores of rocks have increased significantly. This increment could be considered an important impact from climate change.

High concentrations of CO₂ cause the decrease of the pH of water. Drinking water tends to naturally capture CO₂, which raises the concentrations of some ions such as Ca²⁺, Mg²⁺, Si⁴⁺, K⁺, as well as alkalinity, and the dissolution of carbonate minerals. Elevated levels of CO₂ might dissolve some non-potable elements and compounds of host rocks into groundwater resources (Lemieux 2011). The changes of groundwater hydrochemical conditions, such as increase of total dissolved solids, decrease of pH, change of redox potential, and the desorption process of CO₂ from the soil are the consequences of elevated CO₂ concentrations (Peter *et al.* 2012; Cahill *et al.* 2013; Rillard *et al.* 2014; Yang *et al.* 2015).

Most water used for human consumption is of good quality; however, in recent decades it has been demonstrated that it is not immune to pollution (Unión Europea 2008), and to climate changes, due to the increase of CO₂ concentration in water. Current regulations do not yet consider the presence of CO₂ in drinking water and the alteration of its quality by the increase of CO₂. The estimation of free, equilibrium, and total CO₂ in water was done using Tillmans equilibrium diagrams with the modified Mojmir Mach model. With this approach it is possible to determine qualitatively and quantitatively the behavior of free, equilibrium and total CO₂ as a function of water temperature and this model can be a very useful tool for the quantification of total carbon dioxide in water for human consumption (Alvarez-Bastida *et al.* 2013).

The objective of this work was to determine the impact of the natural capture of free CO₂, and its transformation to H₂CO₃, HCO₃⁻ and total CO₂ by using a Tillmans equilibrium diagram obtained from the modified Mojmir Mach model, in water from wells located in urban areas or near a source of carbon dioxide where degradation of organic matter takes place. This model allows us to understand the natural processes and the effect on drinking water with respect to calcium content and considers the modification of the concentrations of Na⁺, Ca²⁺, K⁺ and Si⁴⁺, which may produce adverse effects on health. This is the most important contribution of this work because it is a simple model and useful to determine these chemical species in water; furthermore there are very few studies on this subject.

METHODOLOGY

The aquifer of Toluca Valley (Figure 1) is considered one of the most overexploited in Mexico because of the high rate of groundwater extraction for urban and industrial water supply to Mexico City and Toluca City (Dávila-Hernández *et al.* 2014).

Sampling and physicochemical characterization

A two-year sampling program was developed. Ten water samples (S1–S10, in April 2015, June 2015, October 2015, November 2015, January 2016, March 2016, April 2016, June 2016, August 2016 and October 2016, respectively) were taken from three wells, W1, W2 and W3 (Figure 1), which supply water to part of the population of Toluca City.

Water was collected in polyethylene containers for physicochemical characterization. Physicochemical parameters were measured *in situ*: pH, ambient and water temperature, electrical conductivity and total dissolved solids by using a Hanna potentiometer model H199130. Laboratory analyses were performed to characterize water according to Standard Methods (2005).

Transient parameters were determined *in situ* and in the laboratory based on standardized and international techniques (Standard Methods 2005; USEPA 2009).

Na, K, Ca, Mg, and Si were determined by atomic absorption spectroscopy (Agilent model 280FS AA).

The free and total carbon dioxide concentrations in the water were calculated by using Tillmans equilibrium diagram obtained from the modified Mojmir Mach model, and the chemical equilibrium constants involved as a function of water temperature (Masschelein 1992). The application of this model was done by using the software AgrInc_Agua 2.6 (Alvarez-Bastida *et al.* 2013). This model is based on Tillman's equilibrium diagram (Figure 2) (carbonic acid molar concentration [H₂CO₃] vs. bicarbonate molar concentration (1/2 [HCO₃⁻])). The molar concentrations of [H₂CO₃] and 1/2[HCO₃⁻] were obtained from the acidity and alkalinity and other ions (Na⁺, K⁺, Mg²⁺, Si⁴⁺, Cl⁻, SO₄²⁻, NO₂⁻ and NO₃⁻) present in drinking water. Under the equilibrium curve, CO₂ is present as carbonate in the water and pH is higher than 8.3. Above the curve, the

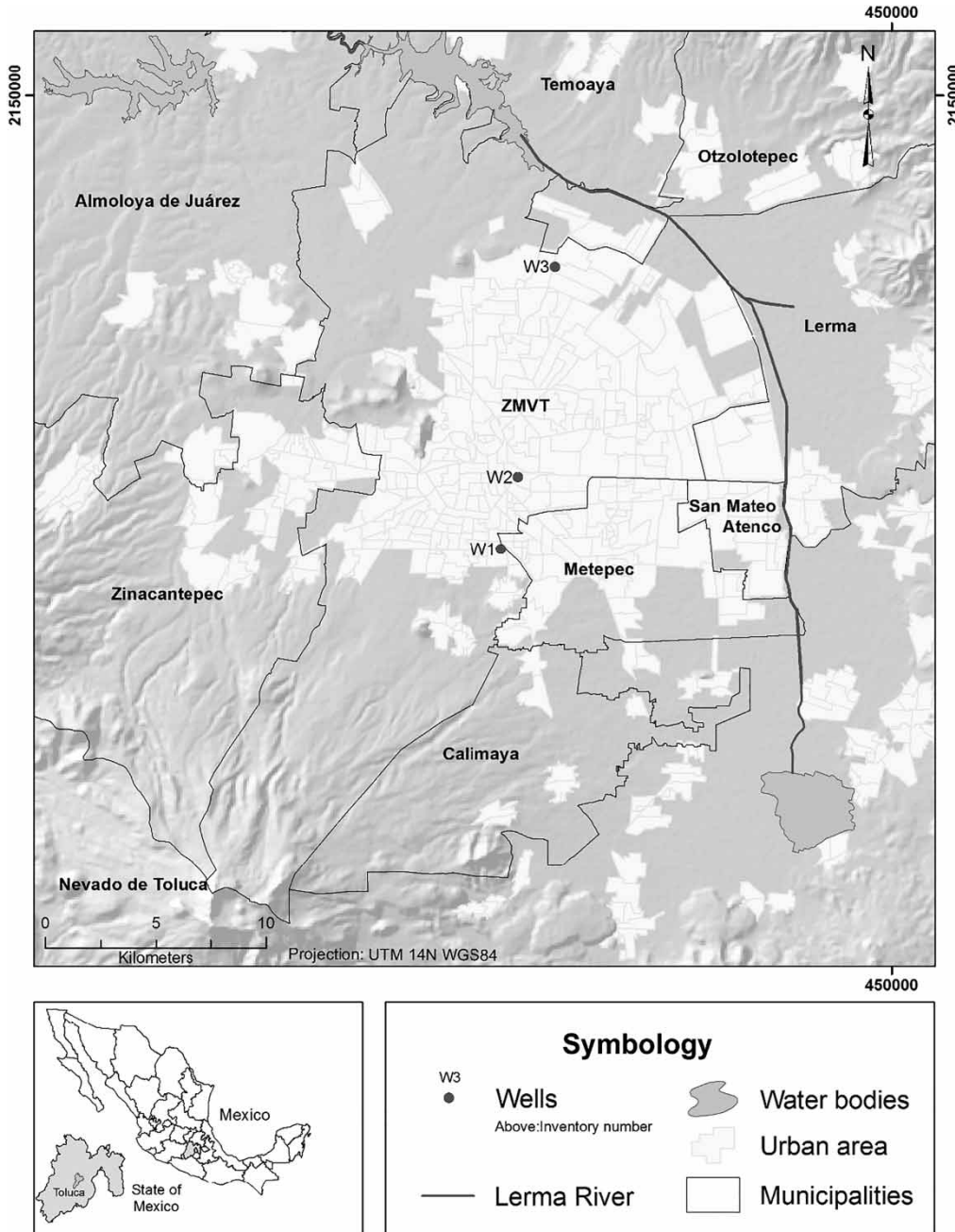
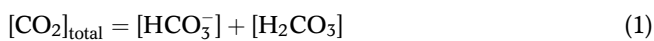


Figure 1 | Toluca Valley aquifer.

CO₂ is present as carbonic acid and bicarbonate and pH is between 4.4 and 8.2. Total carbon dioxide can be obtained as follows (reaction 1):



Tillmans equilibrium diagram allows the calculation of the total amount of carbon dioxide from the carbonate system, which considers CO₂ dissolved in water and the formation of carbonic acid; the carbonic acid corresponds to the free CO₂ which forms hydrogen ions and bicarbonate

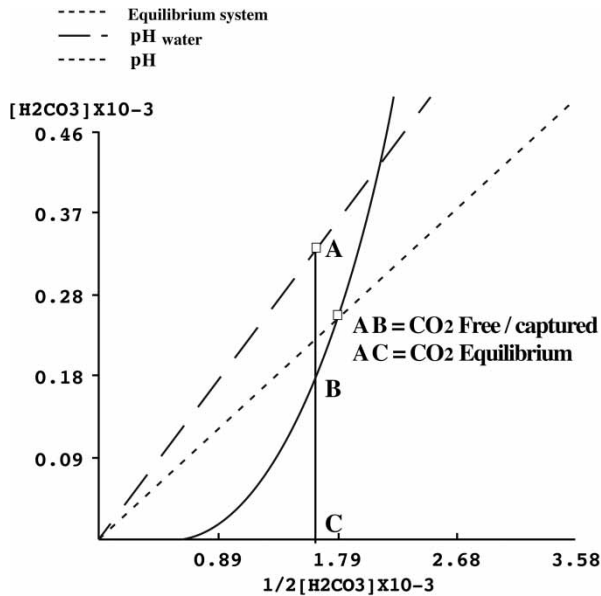
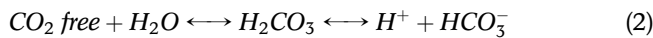


Figure 2 | Tillmans equilibrium diagram.

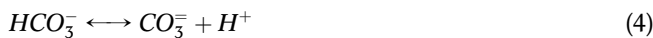
ions (reaction 2):



where, the first dissociation constant of CO_2 is shown in reaction 3:

$$K'_1 = \frac{[\text{H}^+][\text{HCO}_3^-]}{[\text{H}_2\text{CO}_3]} \quad (3)$$

and the second CO_2 dissociation constant is expressed as follows:



$$K'_2 = \frac{[\text{H}^+][\text{CO}_3^{2-}]}{[\text{HCO}_3^-]} \quad (5)$$

The dissociation reaction and equilibrium constant of water are:



$$K'_w = [\text{OH}^-][\text{H}^+] \quad (7)$$

The solubility of CaCO_3 and its constant are shown in reactions 8 and 9:



$$K'_{ps} = [\text{Ca}^{++}][\text{CO}_3^{2-}] \quad (9)$$

The carbonate system was calculated from the Tillmans equilibrium, which considers the contribution of the so-called 'foreign' ions (sodium, potassium, magnesium, chloride, sulfate), which are all cations $[\text{cat}]$ and anions $[\text{an}]$ present in water:

$$\begin{aligned} \mu = & 2[\text{Ca}^{++}] + 2[\text{Cat}^{++}] + \frac{1}{2}[\text{Cat}^+] + \frac{1}{2}[\text{H}^+] + 2[\text{CO}_3^{2-}] \\ & + 2[\text{An}^-] + \frac{1}{2}[\text{An}^-] + \frac{1}{2}[\text{HCO}_3^-] + \frac{1}{2}[\text{OH}^-] \end{aligned} \quad (10)$$

If Equation (10) is multiplied by 2:

$$\begin{aligned} 2\mu = & 4[\text{Ca}^{++}] + 4[\text{Cat}^{++}] + [\text{Cat}^+] + [\text{H}^+] + 4[\text{CO}_3^{2-}] \\ & + 4[\text{An}^-] + [\text{An}^-] + [\text{HCO}_3^-] + [\text{OH}^-] \end{aligned} \quad (11)$$

Equation (11) expressed in molar concentrations:

$$\begin{aligned} 2[\text{Ca}^{++}] + 2[\text{Cat}^{++}] + [\text{Cat}^+] + [\text{H}^+] - 2[\text{CO}_3^{2-}] \\ - 2[\text{An}^-] - [\text{An}^-] - [\text{HCO}_3^-] - [\text{OH}^-] = 0 \end{aligned} \quad (12)$$

where Cat^{++} are the divalent cations, Cat^+ are the monovalent cations, An^- are the divalent anions, and An^- are the monovalent anions.

From Equations (11) and (12) we obtain:

$$\begin{aligned} 2\mu = & 6[\text{Ca}^{++}] + 6[\text{Cat}^{++}] + 2[\text{Cat}^+] + 2[\text{H}^+] \\ & + 2[\text{CO}_3^{2-}] + 2[\text{An}^-] \end{aligned} \quad (13)$$

If Equation (13) is divided by two:

$$\mu = 3[\text{Ca}^{++}] + 3[\text{Cat}^{++}] + [\text{Cat}^+] + [\text{H}^+] + [\text{CO}_3^{2-}] + [\text{An}^-] \quad (14)$$

Mach considers that water generally has a $\text{pH} > 4.5$; this allows us to neglect $[\text{H}^+]$.

$$\mu = 3[\text{Ca}^{++}] + 3[\text{Cat}^{++}] + [\text{Cat}^+] + [\text{CO}_3^{2-}] + [\text{An}^-] \quad (15)$$

If the other ions (Cat and An) are denoted by A then:

$$\mu = 3[Ca^{++}] + [CO_3^{--}] + A \quad (16)$$

If A and D are:

$$A = 3[Cat^{++}] + [Cat^+] + [An^-] \quad (17)$$

$$D = 4[An^-] - \frac{1}{2}[Cat^+] + \frac{3}{2}[An^-] \quad (18)$$

When the pH of the water is < 8.3

$$[HCO_3^-] = \frac{2}{3}(\mu - D) \quad (19)$$

$$[H_2CO_3] = \frac{4K(\mu - A)(\mu - D)^2}{pK_{ps}^1} \quad (20)$$

$$k = \frac{K_2^1}{27K_1^1 K_{ps}^1} \quad (21)$$

The total CO_2 is the sum of bicarbonate ions and carbonic acid as shown in Equation (22):

$$[CO_2]_t = [HCO_3^-] + [H_2CO_3] \quad (22)$$

The following equations allow the calculation of the equilibrium constants of the dissociation of water (Equation (7)), carbonic acid (Equations (3) and (5)), and solubility of calcium carbonate (Equation (9)) at different temperatures (Masschelein 1992).

$$pK_1 = 356.3094 + 0.06091964T - \frac{21,834.37}{T} - 126.8339 \log T + \frac{1,684,915}{T^2} \quad (23)$$

$$pK_2 = 107.8871 + 0.03252849T - \frac{5151.79}{T} - 38.92561 \log T + \frac{563,713.9}{T^2} \quad (24)$$

$$pK_w = \frac{4471}{T} + 0.01706T - 6.087 \quad (25)$$

$$pK_s = 171.9065 + 0.077993T - \frac{2839.319}{T} - 71.595 \log T \quad (26)$$

RESULTS AND DISCUSSION

Carbon dioxide (CO_2) is a greenhouse gas that is found naturally in the atmosphere. The atmospheric concentration of CO_2 is increasing due to human activities and contributes to the global warming of the planet. CO_2 emissions arise from burning fuel and also from industrial processes. Water has the capacity to contain different concentrations of CO_2 , which is mainly reflected in acidity (Artoli et al. 2012). As shown in Figure 3, the drinking water samples showed a significant variation of acidity; this behavior could be due to the variation of CO_2 concentrations. Sources of CO_2 include the atmosphere, the aerobic bacterial oxidation of the organic matter contained in the soil, which may migrate to the water, if it cannot escape freely to the atmosphere, and the gas contained in the closed pores of the rocks, which dissolves slowly by diffusion in the water.

Temperature is an important factor that influences the dissolution of the CO_2 and its transformation to carbonic acid. There is a tendency for the acidity of the water to increase with CO_2 gas dissolution (Figure 3) and, in general, the acidity decreases as the temperature increases as observed in Figures 3 and 4. The water from W3 presented the highest temperature (22.6 °C) and the lowest acidity (4.29 mg/L H_2CO_3) of the three wells; this is a common way to diminish the concentration of CO_2 in the water. The acidity of the water decreases in sample 5, because there is more formation of bicarbonates. In the present study, CO_2 gas dissolution has been observed at different water temperatures. These observations support the

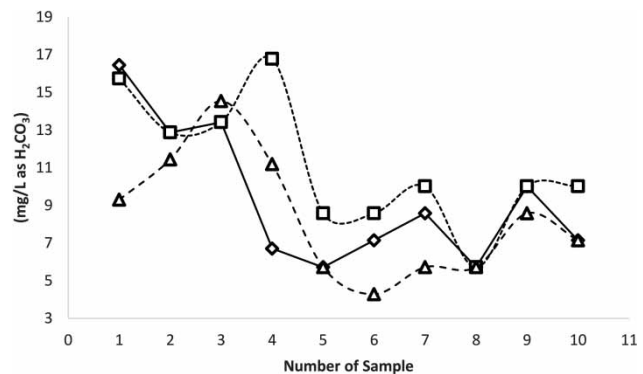


Figure 3 | Acidity of samples (as mg/L H_2CO_3), W1 (◇), W2 (□), W3 (△).

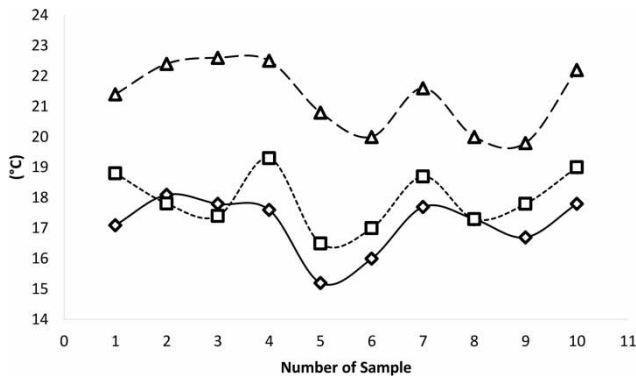
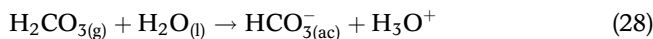
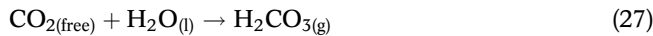


Figure 4 | Temperature of samples (°C), W1 (◇), W2 (□), W3 (Δ).

hypothesis that there are other effects that increase the acidity (16.78 mg/L H_2CO_3) of water and favor the dissolution of CO_2 (such as temperature, chemical composition of water, pH and thus the capture of CO_2).

The CO_2 content in water is related to the alkalinity and free CO_2 , which tends to decrease by the formation of H_2CO_3 (Equation (27)) and the alkalinity increases by its dissociation (Equation (28)). This dissociation process of H_2CO_3 increases the pH value; this behavior indicates a higher CO_2 capture than carbonic acid (Figure 5).



The highest concentrations of free CO_2 were found in the samples taken in 2015 (samples 1–4) (6.35 mg/L), which favored the decrease in pH (6.36); this behavior agrees with studies on the effect of CO_2 in the subsoil.

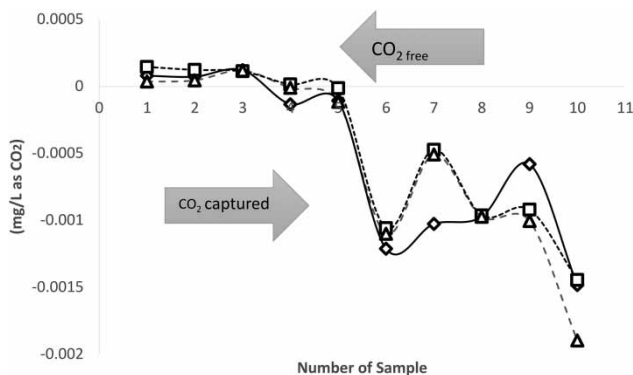


Figure 5 | Free and natural capture CO_2 content, W1 (◇), W2 (□), W3 (Δ).

This species dissolves in water and tends to diminish the pH value; this makes the water acid and susceptible to dissolve other species (Yang et al. 2015). The free and equilibrium CO_2 values were calculated according to the modified Mojmir Mach method.

Figure 5 shows the difference between free and natural capture CO_2 content. Samples 6–10 show a deficiency of CO_2 due to its transformation to bicarbonate, increasing the concentration of this species in the water.

Table 1 shows the amounts of free CO_2 captured by drinking water per year, according to the flow and concentrations of total CO_2 (Equation (22)). The water with the highest concentration of CO_2 is from W2 with 189.89 tonnes of this gas per year.

In this work, different compositions of anions and cations in water were observed due to the natural capture of carbon dioxide. In 2017 El-Naas et al. proposed the modified Solvay method to desalinate water; in this process carbon dioxide is added to reduce emissions and salt concentrations in the water (El-Naas et al. 2017). The natural capture of carbon dioxide takes place according to reactions 29, 30 and 31. This is similar to the modified Solvay process; however, there are some differences in the composition of anions and cations in water. Other reactions take place involving the minerals and subsequent precipitation of carbonate and dissolution of silicate ions because of the increase of Si to about 16 mg/L (reactions 32 and 34). Precipitation of Ca or Mg decreases the carbonate ions concentration to about 14 mg/L and 10 mg/L, respectively (reaction 33) (Guyot et al. 2011).

The natural CO_2 captured in the water is transformed to bicarbonates, which react with the calcium, forming calcium bicarbonate (reaction 29). The presence of sodium in water favors the formation of CaCl_2 and NaHCO_3 (reaction 30). The CO_2 dissolves minerals such as $\text{CaMg}(\text{CO}_3)_2$ and

Table 1 | Concentration of natural CO_2 in drinking water per year

CO_2 (tonne/year)	W1	W2	W3
Maximum	152.55	189.89	93.64
Minimum	87.57	41.76	16.98
Average	124.66	148.17	74.72
Flow (L/s)	25	35	17
Depth (m)	189	250	85

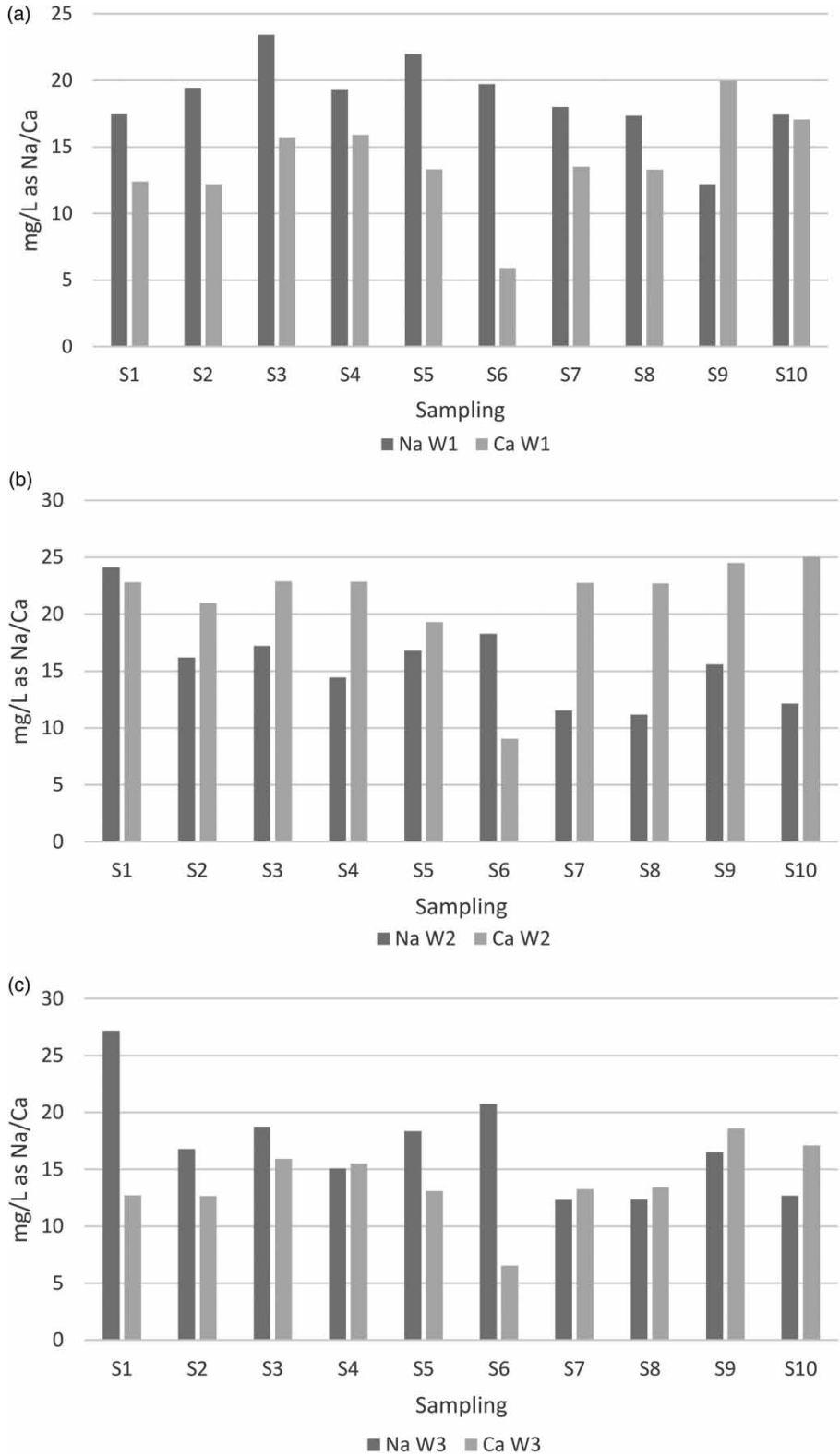
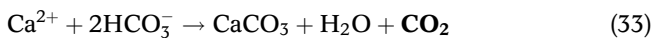
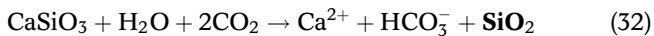
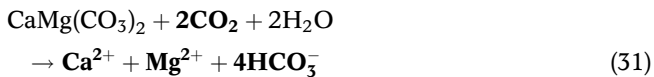
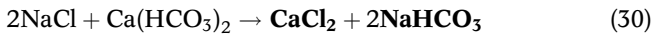
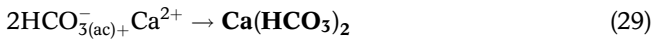


Figure 6 | Relation of sodium and calcium, (a) W1, (b) W2, (c) W3.

CaSiO_3 (reactions 31 and 32). The bicarbonate ions react with calcium and free CO_2 increases (reaction 33) (desorption of CO_2). In reaction 34, the free CO_2 reacts with CaSiO_3 , producing calcium carbonate and silica.



Concentrations of Ca and Na were analyzed and it was observed that in the process of natural capture of CO_2 , the main variations were in the concentrations of Ca and Na. According to Figure 6(a) the results show that as the concentration of calcium increases to 19.95 mg/L, the concentration of sodium decreases (11.18 mg/L) due to the ion exchange proposed in Equation (30). The water in W2 contains the highest concentration of Ca (9.05–19.95 mg/L) and always maintains the lowest concentration of Na (11.18–21.99 mg/L) (Figure 6(b)). Conversely, when the

concentration of Ca is lowest (5.89 mg/L and 6.53 mg/L, respectively), the concentration of Na is the highest for wells 1 and 3 (23.42 mg/L and 24.12 mg/L, respectively) (Figures 6(a) and 6(c)). This figure shows that there is a natural change of the soluble ions in water according to the modified Solvay process, which is also carried out with Mg, because it is chemically similar to Ca (Yang et al. 2015) (Equation (32)).

With respect to silicon the results show that high concentrations of CO_2 cause a decrease in the pH of drinking water, which raises the concentrations of Si (reactions 32 and 34) and K, indicating that the dissolution of silicate is a key issue for the conversion of CO_2 into solid minerals (reaction 34), without dissolution of Na (Guyot et al. 2011), as shown in Figure 7. Yang et al. (2015) reported that high levels of CO_2 favor the dissolution of Ca, Mg, K and Si in sediments but do not favor the dissolution of Na. Mean community urinary levels of lithium, magnesium, strontium and silicon showed a direct correlation to the levels of exposure via the drinking water (Dawson et al. 1978).

These changes do not represent a risk to human health according to established regulations for drinking water and human consumption by WHO (2004), USEPA (2009) and Norma Oficial Mexicana (NOM-127-SSA1-2000). However it has been argued that acidic water is corrosive, erodes teeth and bones, filtering calcium and increasing heartburn, can intensify mild hypo due to metabolic acidosis, and aggravate irritable bowel syndrome, while distention of the

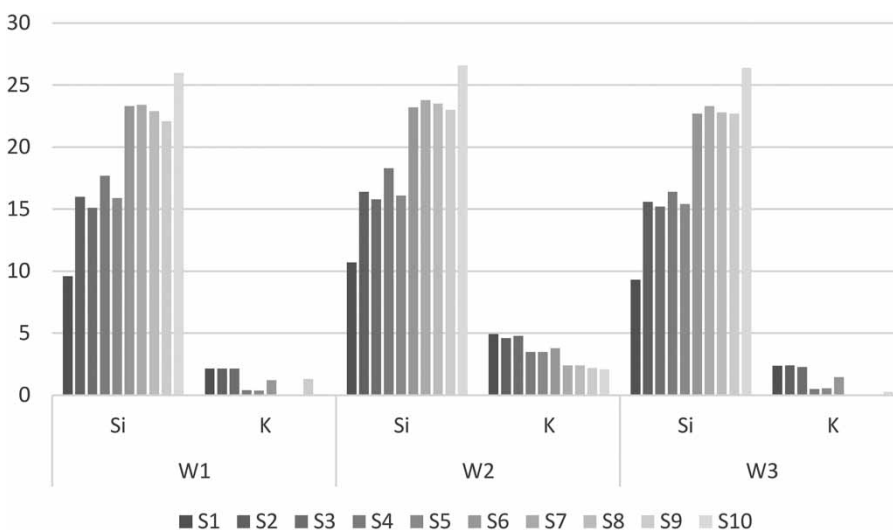


Figure 7 | Relation of silicon and potassium.

stomach may reduce the effectiveness of stomach acid to digest those foods that require higher acidity.

CONCLUSIONS

This study shows a rapid and effective way to calculate CO₂ in drinking water, using the simplified modified Mojmir Mach model. Some important aspects were investigated, such as the capacity of water to contain different amounts of CO₂. Free CO₂ increases the acidity of water and this is responsible for dissolving cationic and anionic species in drinking water, including bicarbonate, silicon and potassium, and reducing the concentration of calcium. Free CO₂ in drinking water was calculated from Tillman's equilibrium diagram; it is a simple and innovative process. The capture of carbon dioxide determined was 189 tonnes per year, which has important effects on the composition of drinking water, as well as variations in pH value of more than one unit (1.1), acidity, decreased calcium, and increased silicon, which may affect the health of consumers. This method is innovative and easy to use to interpret the capture of carbon dioxide in water.

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