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Modeling nitrogen species as a source of titratable alkalinity and dissolved gas pressure in water

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ABSTRACT

Alkalinity is a measure of the acid buffering capacity of water that is defined by an explicit chemical model of the acid-base processes involved. This paper presents an alkalinity speciation model using C1, C2 and N1 species to model the measured responses during alkalinity and acidity titrations. Charged species can contribute to alkalinity, and uncharged species can contribute to dissolved gas pressure which can be evaluated using the Ideal Gas Law. Groundwater monitoring programs have demonstrated the importance of dissolved gases and the resulting affects on aquifer properties when gas bubbles form. At one such site, there was more titratable alkalinity than could be produced by the total carbon in the sample if it was all present as bicarbonate. With the hypothesis that nitrogen species were contributing to titratable alkalinity, titratable acidity, and dissolved gas pressure in groundwater, an evaluation of the alkalinity and acidity titration curves was undertaken. Modeling of titration curves indicates the importance of charged and uncharged nitrogen species and the resulting reactions with CO_2 and acetic acid. Two models have been developed: Model 1 uses titration curve data and electrical charge balance to speciate total alkalinity or acidity using normal curves, and Model 2 provides limits on the possible contribution of titratable nitrogen based on total carbon and total alkalinity. These calculations use C1, C2, and N1 which provide limits on the missing electrical charge that could be provided by titratable nitrogen. The hysteresis seen between fast and slow alkalinity titrations is explained in terms of known reactions and degassing. Missing electrical charge calculated in Model 1 is within the limits provided by the ratio of C1:C2 species as evaluated in Model 2, and the maximum gas pressure that could be provided by N1 and C1 gases is within the limits imposed by the Ideal Gas Law. Alkalinity is a non-specific measurement, and the methods applied here are non-specific but provide a conceptual framework to be further developed as suitable specific analytical methods for these N species are applied to water samples.

1. Introduction

Groundwater investigations concluded that a town water supply well was too close to a municipal wastewater treatment lagoon (population served approximately 3000). There was a lack of hydraulic response in monitoring wells near the wastewater lagoon to pumping of the water supply well. This was unlikely based on the expected aquifer properties and the location of the water supply well relative to the wastewater lagoon, but these results are consistent with the presence of gas bubbles, or possibly an inter-connected gas phase, within the aquifer. When total dissolved gas pressure exceeds the confining pressure, a gas bubble can form, and when gas bubbles fill the porous media the aquifer can be described as being 'gas locked'. The presence of gas bubbles changes the aquifer properties of hydraulic conductivity and storativity which are physical properties related to the ability to transmit and release water from the aquifer. The importance of dissolved gas and gas bubbles in groundwater systems has only recently become apparent (Roy and Ryan, 2010), and the significance of this process is not widely appreciated (Roy and Ryan, 2013). Groundwater monitoring programs completed by the author at a variety of sites indicate that water levels can increase in source areas due to biogenic gas production in the saturated zone which can increase the total pressure within the porous media of the aquifer system (Hardy and Wall, 2014).

Gas pressure in groundwater is normally ascribed to carbon dioxide and/or methane, but no gas phase methane was detectable in the headspace of the monitoring wells at the wastewater site. Furthermore, a nearby replacement town water supply well encountered high dissolved gas pressures and flowing artesian conditions without methane or hydrogen sulphide being detectable in the gas phase during the well installation. At another location in the same aquifer approximately 100 km distant, there are also indications of elevated gas pressures without any detectable gas phase methane. Uncharged nitrogen species

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can contribute to dissolved gas pressure, but due to the high Henry's Law constant of N_2, the maximum amount of N that can be dissolved as N_2 in water in equilibrium with the atmosphere is only 0.48 mmol/L (14 mg/L of N), and if higher concentrations of N are present in water it must be primarily present in forms other than N_2.

If the total carbon measured at the wastewater site was present as inorganic carbon, then approximately 2–8 meq/L (100–400 mg/L as $CaCO_3$) of titratable alkalinity was missing and this comprised almost one third of the total alkalinity. Based on this result and the observation of significant acid buffering response near pH = 5.9 in some groundwater samples from the wastewater site, the possible presence of hydroxylamine (NH_2OH) was identified. Hydroxylamine is an intermediate product of both ammonia oxidation (Stein and Klotz, 2016; Vajrala et al., 2013) and nitrate ammonification (Hanson et al., 2013) and could provide a non-carbon source of alkalinity with a pKa = 5.95. Hydroxylamine is known to be reactive in aqueous solution, and the apparently transient presence of this reactive species would be consistent with the formation of hydroxylamine as a product of a related reaction during the titration.

Organic acids such as acetic acid contribute to alkalinity (Hemond, 1990) but have higher equivalent weights than CO_2 and produce a lower alkalinity for a given amount of carbon. The most efficient use of carbon to generate alkalinity is as inorganic carbon (i.e. the maximum alkalinity from carbon expressed as mg/L of $CaCO_3$ = 4.17*total carbon in mg/L). Volatile organic acids (VOA) such as acetic acid were analyzed on various groundwater samples from the wastewater lagoon site using three different analytical methods (Ibrahim et al., 2014; Fernandez et al., 2016): distillation, titration, and GC-MS. However, the results of these various VOA analyses were contradictory. Upwards of 1 meq/L of VOAs (60 mg/L as acetic acid, or 50 mg/L as calcite) were measured by the distillation method, which is noted as having a typical recovery rate of only around 50-30%, so the actual concentration of VOAs *in situ* would likely be on the order of 2–3 meq/L (100–150 mg/L as calcite). Similar VOA concentrations were interpreted using a five point titration method (Lahav et al., 2002; Vannecke et al., 2014) (TITRA5), but subsequent analyses using GC-MS did not show detectable VOAs in any of the samples analyzed. None of these analytical methods for volatile organics are considered to be fully reliable (Raposo et al., 2013), and the contradictory results indicated that there were problems with the application of these methods to groundwater samples from the wastewater lagoon. When titration data from the site was evaluated using the USGS online alkalinity calculator (https://or.water.usgs.gov), each sample generated a warning that non-carbonate sources of alkalinity were present in the water sample.

Non-carbonate sources of alkalinity in environmental samples are known, but these are typically characterized as minor contributors to total alkalinity (Hunt et al., 2011). Nitrogen and sulphur were identified as two elements that have titratable species in the pH range of interest. Sulphur can be reliably measured as total sulphur and sulphate, and the results show that sulphate is the dominant form of S and that titratable S could not contribute significantly to the measured alkalinity response in the modeled waters. It is recognized that thiols may be important as catalysts in reactions with N and O species (Hughes, 1999a; Griendling et al., 2016), but on a strictly mass balance basis the potential contribution to alkalinity from S species is minor in all of the modeled waters. In contrast, there is no reliable measure of total N in water samples to quantify nitrogen oxides with commercial total nitrogen instrumentation (Walker, Stojowski, Clifford) typically being limited to the standard four nitrogen species of nitrate, nitrite, ammonia and organic nitrogen. However, numerous N species are titratable and could provide a measurable response during an alkalinity or acidity titration.

Most definitions of alkalinity (Stumm and Morgan, 1981; Drever, 1997; Kirby and Cravotta, 2005a, 2005b) or acidity do not mention organic acids, organic bases (Hernandez-Ayon et al., 2007), or nitrogen species generally. For example, the standard definition of total alkalinity (TA) in seawater is shown as Equation (1):

$$TA = [HCO_3^{-}] + 2[CO_3^{2-}] + [B(OH)_4^{-}] + [OH^{-}] + [HPO_4^{2-}] + 2[PO_4^{3-}] + [SiO(OH)_3^{-}] + [NH_3] + [HS^{-}] + \ldots - [H+] - [HSO_4^{-}] - [HF] - [H_3PO_4] \tag{1}$$

As discussed by Dickson (1992), this definition of alkalinity is based “unambiguously on a chemical model of the acid-base processes occurring in seawater”, and “the alkalinity is defined by a proton condition, which in turn is based on a detailed chemical model of the solution, rather than by an operationally defined end-point”. The ellipses in Equation (1) denote unidentified species that can consume protons during an alkalinity titration, and this would include dissociated organic acids and organic bases such as amines. Furthermore, at the normal pH range and concentrations encountered in groundwater systems, and applying an endpoint of pH = 4.5, several terms in Equation (1) can be ignored including borate, phosphate, silicate, and hydrogen sulphate.

An underlying assumption of Equation (1) is that there are no proton exchange reactions near pH = 4.5, but the work presented here indicates that there are several possible rapid reactions between various titratable species involving C1, C2 and N1 species as indicated by the different responses between the fast and slow alkalinity titrations, and the acidity titrations. The hysteresis seen between fast and slow alkalinity titrations parallels the different titration responses seen between open and closed cell alkalinity titrations of seawater as described in the oceanography literature, and this reflects degassing and other chemical reactions that can occur during the titration.

In this paper, total alkalinity is operationally defined as the equivalent amount of acid required to titrate the water to pH = 4.5 and this is consistent with a definition of alkalinity as the equivalent sum of bases titratable with strong acid. In Model 1, each data point on the titration curve is quantified as the expressed alkalinity at that point in the titration, and all of the titration data points are fit using normal curves. Therefore, the expressed alkalinity at each data point on the titration curve is used to evaluate the water chemistry, and not just the single data point provided by total alkalinity at the endpoint pH. The models presented in this paper also apply to titration data that extend below pH = 4.5, and the methods are insensitive to the use of an alkalinity titration endpoint at or below pH = 4.5 even when volatile organic acids (pKa = 4.75) are present. Therefore, the industry standard interpretation that total alkalinity can be approximated using a fixed endpoint pH = 4.5 is sufficient to apply the methods presented in this paper. Similarly, the interpretation of acidity titrations using Model 1 is not dependent on the applied endpoint of pH = 8.3.

In seawater (Dickson et al., 2007; Ko et al., 2016; Wolf-Gladrow et al., 2007), alkalinity is relatively low both as a concentration (2.34 meq/L, or 117 mg/L as $CaCO_3$) and as a percentage of the total negative charge in solution (0.39 %meq/L, or percent milliequivalents per litre) which is dominated by chloride and sulphate. In groundwater, total alkalinity concentrations can be orders of magnitude higher, and it can comprise over 90 %meq/L of the negative charge in some waters. Groundwater chemistry can be highly variable and the sources of alkalinity can be quite different than what is observed in seawater. The initial observation that there was insufficient carbon in groundwater at the wastewater site to account for the observed alkalinity appears to be relatively unusual even for groundwater, and this provided clear evidence of a significant non-carbon source of alkalinity.

Based on these preliminary evaluations, it appeared that uncharged N was contributing to dissolved gas pressure and that titratable N species were contributing to total alkalinity and total acidity in groundwater at the wastewater site. With this hypothesis, further evaluations of the titration data were undertaken in an attempt to identify possible nitrogen species and to speciate the various contributors to titratable alkalinity and acidity. This approach was then extended to other sites to corroborate the approach using other water chemistries.

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