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Abstract

Dairy facilities and similar confined animal operation settings pose a significant nitrate contamination threat via oxidation of animal wastes and subsequent transport to shallow groundwater. While nitrate contamination resulting from application of animal manure as fertilizer to fields is well recognized, the impact of manure lagoon leakage on groundwater quality is less well characterized. In this study, a dairy facility located in the southern San Joaquin Valley of California has been instrumented with monitoring wells as part of a two-year multidisciplinary study to evaluate nitrate loading and denitrification associated with facility operations. Among multiple types of data collected from the site, groundwater and surface water samples have been analyzed for major cations, anions, pH, oxidation-reduction potential, dissolved organic carbon, and selected dissolved gases (CO_2, CH_4, N_2, Ar, Ne). Modeling of putative geochemical processes occurring within the dairy site manure lagoons shows substantial off-gassing of CO_2 and CH_4 in response to mineralization of organic matter. The gas ebullition appears to strip dissolved gases, including Ar and Ne, from the lagoon water leaving concentrations that are undersaturated with respect to the atmosphere. The resulting fractionated dissolved gas signature serves as an effective tracer for the lagoon water in the underlying shallow groundwater and can be used to constrain inverse geochemical models that assess mixing fractions of lagoon water and local groundwater water. Together with ion exchange and mineral equilibria reactions, identification of lagoon seepage helps explain key attributes of the local groundwater chemistry, including input and cycling of nitrogen, across the site.

Introduction

Background

Management of animal wastes at dairy facilities and similar confined animal operations often entails utilizing manure lagoons to store dairy wastewater which is rich in solids, organic nitrogen, and ammonia. Irrigation with manure lagoon water is a common practice as it provides the dairy operator with a readily available source of fertilizer while reducing the volume of waste stored in the lagoons. However, the transfer of anoxic manure lagoon water to aerated sandy unsaturated zone soils leads to the mineralization of organic nitrogen and nitrification of ammonia to nitrate and thus is a potential source of nitrate contamination to underlying groundwater when nitrogen is added to the fields in excess of the amount that can be assimilated by the crops (Cameron et al, 2002; Karr et al., 2003; Muñoz et al., 2003).

The impact of direct seepage from anaerobic lagoons on the geochemistry of the underlying aquifer is a complex problem that depends upon a variety of geochemical and hydrological factors. As the majority of the nitrogen in manure lagoons exists in chemically reduced forms, water that seeps out of the bottom of lagoons may not necessarily directly increase nitrate concentrations if transport occurs under anoxic conditions. Moreover, ammonium ion (NH_4^+), a major constituent of such waters, may be adsorbed onto clay minerals in sediments during transport, further reducing the dissolved nitrogen load to groundwater (DeSutter et al., 2005). Finally, seepage waters rich in organic carbon may contribute significantly to the creation of anoxic conditions conducive to heterotrophic denitrification driven by microbial oxidation of organic material in the manure lagoon water.

Physical barriers to lagoon seepage are also a key consideration. Leakage from manure lagoons is often impeded either by the presence of engineered clay liners or from the self-sealing effects that may arise from the settling of particulate matter out of the lagoon water (Gooddy et al., 2002; Meyer et al., 1972). However, several studies have suggested that this protection slows but does not stop leakage. For example, J.M. Ham and colleagues (Ham, 1999; Ham, 2002; Ham and DeSutter, 1999; Ham and DeSutter, 2000) have reported seepage from swine and cattle waste lagoons in southwestern Kansas at rates ranging from 0.2 to 2.4 mm/day based upon measurements of evaporation and changes in water depth in response to the addition or removal of waste. They also found that in new lagoons constructed without clay liners, permeability decreased on average by a factor of five after addition of waste to the lagoons, indicating some permeability reduction from organic sludge buildup over time. Harter et al. (2002) inferred manure lagoon leaching rates on the order of 2 mm/day at sites in California's Central Valley from electrical conductivity measurements as well as the presence of reduced nitrogen in wells located near manure lagoon berms. Leakage through manure lagoon clay liners has also been reported by Ritter and Chirnside (1987) and McCurdy and McSweeney (1993).

Site Description and Groundwater Analytical Suite

Given prior assessments indicating the potential for manure lagoon leakage, the goal of this study has been to expand upon the understanding of the impact of manure lagoon seepage on underlying groundwater in terms of (1) specific geochemical interactions, (2) alternative means for identifying groundwater affected by lagoon seepage, and (3) quantification of the lagoon water mixing fraction at various distances from an active manure lagoon system. The study has entailed evaluating data collected as part of a broader multi-disciplinary evaluation of saturated zone denitrification at a dairy facility located in Kings County, California in the southern portion of the San Joaquin Valley. The dairy facility operates in a typical fashion for older dairies in Kings County. It has approximately 1,000 cows and three active manure lagoons, two of which have liners with a 10% clay content and the third unlined. The lagoons receive runoff water from animal stall flushing that utilizes water pumped from agricultural wells that are located onsite. The largest of the lagoons measures approximately 200 m x 40 m (Figure 1). Water depth within the lagoons varies temporally but may range up to 3 m or more at certain times of the year.

The site is characterized by a shallow perched aquifer (to 10 m depth) and a deeper regional aquifer (greater than 40 m depth) that are separated by an unsaturated zone. Both aquifers are made up of alluvial fan deposits which contain modest solid-phase concentrations of organic carbon (typically ~ 0.1% weight fraction) and reduced sulfur (1-10 μmol/gm). Recharge to the shallow aquifer is ultimately derived from one or more nearby unlined irrigation canals that carry water from the Kings River. However, local agricultural pumping from the shallow aquifer and infiltration from irrigation water appear to be dominant factors in shaping the shallow hydrologic system. The deeper aquifer is characterized by intensive regional pumping, rapidly decreasing water levels, and the apparent disposition of the shallow aquifer as a perched system for an area exceeding 1 km^2 in the vicinity of the dairy. The air gap separating the aquifers is depleted in oxygen and exhibits gas pressure changes in response to water level fluctuations in the deeper aquifer. Detailed vertical profiles of soil and microbial characteristics, groundwater chemistry, and dissolved excess nitrogen for the shallow aquifer were obtained at 5-ft (1.5-m) intervals at several locations using direct-push sampling technology as well as installed multi-level monitoring wells (Figure 1).

A variety of groundwater geochemical parameters were analyzed from water samples collected over several sampling events spanning a period of approximately two years. These include dissolved gases (O_2, N_2, CO_2, CH_4, Ar, Ne) measured by membrane inlet mass spectroscopy – MIMS (Kana et al., 1994), or noble gas mass spectrometry. Part of the rationale for collecting dissolved gas data was to quantify excess N_2, or the concentration of nitrogen produced as a result of either heterotrophic denitrification,

$$4NO_3^- + 5CH_2O + 4H^+ \rightarrow 2N_2 + 5CO_2 + 7H_2O \qquad \text{(Eq-1)}$$

or, alternatively, autotrophic denitrification,

$$3NO_3^- + FeS_2(s) + 2H_2O \rightarrow 1.5N_2 + 2SO_4^{2-} + Fe(OH)_3(s) + H^+ \qquad \text{(Eq.-2)}$$

Excess N_2 can be distinguished from atmospheric nitrogen by comparison with dissolved argon, the dominant source of which is atmospheric. In addition to the dissolved gases, major as well as trace cations (Ca^{2+}, Mg^{2+}, Na^+, K^+, Li^+, NH_4^+) and anions (NO_3^-, SO_4^{2-}, Cl^-, F^-, Br^-, PO_4^{3-}, NO_2^-) were quantified by ion chromatography using a Dionex DX-600 ®. pH, DO, and oxidation-reduction potential were measured in the field using a Horiba U-22® water quality parameter field meter. Dissolved organic carbon (DIC) concentrations were estimated in the water samples by employing the PHREEQC geochemical model (Parkhurst and Appelo, 1999) to achieve charge balance in the samples by adjusting and speciating DIC at the measured pH values. This approach provides rough qualitative agreement between the implied equilibrium CO_2 partial pressures with those measured by MIMS (Figure 2). Dissolved organic carbon was measured in a subset of samples as CO_2 gas pressure after acidification with orthophosphoric acid. Finally, isotopic compositions of hydrogen and oxygen in water (δ^2H and $\delta^{18}O$) were determined using a VG Prism II ® isotope ratio mass spectrometer, and are reported in per mil values relative the Vienna Standard Mean Ocean Water (VSMOW). Oxygen isotope compositions were determined using the CO_2 equilibration method (Epstein and Mayeda, 1953), and hydrogen isotope compositions were determined using the Zn reduction method (Coleman et al., 1982).

Site Groundwater Characteristics

Surface and groundwater samples collected across the site were categorized into groups based on both location and evidence for pertinent geochemical processes. The geochemical compositions for each of these groups are summarized in Table 1. “Lagoon Water” refers to surface water samples collected from three individual manure lagoons at the site. These lagoons, operated in series, receive input from the animal stalls and are tapped to fertilize animal feed crops on site; each is subject to evaporative losses, gas evolution, and some degree of leakage losses. As a result, there is much compositional variability between samples but the Lagoon water remains distinct, particularly in terms of signature elevated NH_4^+, K^+, Cl^-, and PO_4^{3-} concentrations. Lagoon water samples are also characterized by a relatively high pH and low oxidation-reduction potential, high CH_4 and CO_2 partial pressures, and relatively low sulfate concentrations compared to the other sample groups (Figure 3). “Near-Lagoon Groundwater” refers to those groundwater samples collected from wells in the immediate vicinity of the manure lagoons (within approximately 50 meters) from depths greater than approximately 11 meters below the ground surface. These groundwater samples are characterized by relatively low oxidation-reduction potentials, low dissolved oxygen concentrations, high CO_2 partial pressures (equivalent to those of the Lagoon water), and comparatively low sulfate concentrations. As discussed below, fractionated dissolved gas compositions provide an additional line of evidence that these groundwater samples have been impacted by the Lagoon Water. “Deep Field Groundwater” refers to groundwater samples collected across the site (i.e., under the crop fields) from depths greater than approximately 11 meters (exclusive of the Near-Lagoon water and the Downgradient Water, as described below) that are characterized by appreciable excess N_2 in comparison to NO_3^- (Figure 4). In contrast, "Shallow Field Groundwater" refers to those samples collected from shallower depths that generally contain higher concentration of NO_3^- and less excess N_2. Shallow and Deep Field Groundwaters differ somewhat in both oxidation-reduction potential and pH, with the Deep Field Groundwater samples being slightly more reducing and alkaline. Both Shallow and Deep Field Groundwaters are characterized by similarly low CO_2 and CH_4 partial pressures when compared to both the Lagoon Water and Near-Lagoon Groundwater. "Downgradient Groundwater" refers to groundwater samples collected from one location, 2S, southeast of the manure lagoons (Figure 1) below a depth of 11 meters where the water chemistry differs somewhat from that of Deep Field Groundwater (e.g., comparatively low pH and elevated excess N_2) and, as discussed below, dissolved gas compositions indicate a Lagoon Water impact. Finally, "Irrigation Water" refers to the median composition of groundwater samples collected from agricultural pumping wells operated onsite. These wells are screened across a wide depth interval (greater than 10 m) so that produced water is a mixture of the above-defined groups (exclusive of Lagoon Water).

Lagoon Water Chemistry

Dissolved Noble Gases as Tracers

Manure lagoons clearly represent a complex, open system. Major oxidation-reduction indicators such as oxidation-reduction potential, CH_4 partial pressure, and depleted sulfate (compared to other water composition groups at the site) indicate that Lagoon Water samples from the dairy facility reflect chemically reducing conditions, which is consistent with expectation and prior studies (Gooddy et al., 2002). These reducing conditions are ultimately produced via the mineralization of organic matter in the pumped agriculture well water used to flush the animal stalls, a process that may require months of reaction time to reach completion (Van Kessel and Reeves, 2002). Nitrogen speciation is dominated by NH_4^+ (and, presumably, organic nitrogen which was not measured), although geochemical processes in the lagoons such as nitrification, denitrification, and N_2 production from reactions between ammonium and nitrate/nitrite (Thamdrup and Dalsgaard, 2002, Jones et al., 2002) cannot be ruled out, particularly when the potential for oxidation-reduction stratification as a function of depth is considered. Moreover, because lagoon water is ultimately derived from pumped agricultural supply wells, a component of the nitrogen present in the lagoon water may reflect past cycling.

One of the goals of this study is to understand the impact of the manure lagoons on nitrogen chemistry in shallow groundwater at the dairy site. However, tracking manure lagoon seepage is problematic because the lagoon water applied to field crops is chemically identical to seepage from the lagoons prior to oxidation in the soil zone. Ammonium ion is a logical tracer candidate but is only found in groundwater proximal to the lagoons because of the low mobility induced by its propensity for ion exchange. Other natural tracers of lagoon water include high concentrations of organic carbon, Cl^-, and the stable isotopic makeup of the lagoon water. Dissolved organic carbon, while measured in Lagoon Water at hundreds of parts per million (ppm), is found in comparatively low concentrations (generally on the order of 10 ppm) from samples collected from site monitoring wells. Since some solid-phase organic material has been found in sediment samples across the site, the provenance of dissolved organic material in groundwater is somewhat ambiguous. Lagoon water samples have high concentrations of Cl^- as result of salt in cow manure and urine and evaporation of lagoon water. Lagoon water samples also have elevated H_2O-$\delta^{18}O$ signatures as a result of evaporation. In dairy site groundwaters, a correlation exists between chloride content and water $\delta^{18}O$ that is consistent with mixing between local un-impacted groundwater and a high-chloride, evaporated water component characteristic of Lagoon Water (Figure 5). Such mixing is consistent with either field application of Lagoon Water or seepage of Lagoon Water directly from the lagoon. In both cases, the high-chloride and evaporated isotopic composition character of the Lagoon Water will be preserved.

To more definitively distinguish lagoon seepage from surface application, a tracer species that is unique to the lagoon environment and is mobile in groundwater is required. Biogenic production of methane and carbon dioxide in anaerobic manure lagoons may provide such a tracer. Specifically, significant ebullition of these gases as CH_4 and CO_2 concentrations exceed their solubility limits will induce exsolution fractionation (or "stripping") of other gases present in the lagoon water (e.g., N_2, Ar, Ne, He, etc.), which partition into the evolving gas phase and deplete the lagoon water of its dissolved gas load. This stripping process should lead to anomalously low and significantly fractionated dissolved gas concentrations in lagoon waters and, by extension, in lagoon seepage. Similar phenomena have been reported for groundwater coal bed methane environments (Zhou et al., 2006) and ocean sediment pore waters (Brennwald et al., 2005). The advantage of utilizing dissolved gas data in lieu of Cl^- or $\delta^{18}O$ is that the gas-depleted signature produced in lagoons is likely to be reset when water is applied to the surface in fields, where it re-equilibrates with the atmosphere, and can thus be distinguished from direct lagoon seepage. Within the saturated zone, non-reactive dissolved gas constituents are expected to be transported conservatively.

The effects of gas exsolution in the lagoon water and re-equilibration during field application can be detected using MIMS measurements of dissolved Ar, N_2, and O_2 which have revealed significant depletions in each of these atmospheric gases relative to air-equilibrated water (although the O_2 gas content by itself is ambiguous because of oxidation-reduction processes). Nearly all ambient groundwater samples have dissolved air concentrations in excess of equilibrium solubility concentrations (Aesbach-Hertig et al., 1999). However, Lagoon Water with low gas contents is also characterized by fractionated gas compositions, as can be demonstrated by plotting the ratios of N_2/Ar and Ne/Ar (Figure 6) determined by noble gas mass spectrometry. Neon has a lower solubility and higher diffusivity than Ar, and is more likely to partition into the gas phase during bubble formation. As a result, Ne/Ar ratios are highly sensitive to addition of excess air or gas stripping. Mixing of groundwater with lagoon seepage shifts the dissolved gas compositions to lower Ne/Ar ratios, whereas denitrification in the saturated zone increases the N_2/Ar ratio via production of N_2. Water in equilibrium with air would fall on an equilibrium line, with its precise position determined by the recharge temperature. Water compositions having Ne/Ar ratios lower than the equilibrium solubility value at this temperature are likely impacted by lagoon seepage. Addition of excess air during recharge will shift the dissolved gas compositions to higher N_2/Ar and Ne/Ar ratios, but this effect is confined to one of the excess air addition lines, with its starting position dependent on recharge temperature (shown as 15°C as an example on Figure 6). The water samples with the highest N_2/Ar (i.e., exhibiting the strongest evidence for denitrification) are also generally characterized by the lowest Ne/Ar ratios (i.e., exhibiting the strongest evidence for impact by lagoon seepage), suggesting a link between the two processes.

Lagoon Water Process Simulation

Simulation of major geochemical processes in the Lagoon Water is useful for understanding the possible extent of off-gassing as well as other mechanisms that could be useful as diagnostic indicators of seepage. To model the Lagoon Water chemistry, PHREEQC was used to simulate the addition of a hypothetical manure composition to the mean irrigation water composition at the dairy site. The chemical composition of dairy manure is variable and depends on a number of factors, including feed composition, degree of mixing with urine, and storage issues that affect both decomposition and preferential loss of volatile components. Most reported manure compositions pertain mainly to nutrient content (nitrogen, phosphorous, and potassium), which is usually provided on a per weight basis. The total nutrient mass is typically listed as less than five percent for dry manure, with roughly equivalent portions of nitrogen and potassium and a much smaller phosphorous component (Van Averbeke and Yoganathan, 2003, Christensen and Peacock, 1998). For a hypothetical manure composition, we assumed that all of the nitrogen may be represented as NH_3, phosphate as P_2O_5, and potassium as K_2O, that taken with an organic carbon component, CH_2O, yields a stoichiometric formula of $CH_2O(NH_3)_{0.025}(P_2O_5)_{0.002}(K_2O)_{0.006}$ ("manure") that is consistent with reported nutrient characteristics. This idealized composition, with a carbon-to-nitrogen ratio of approximately 34-to-1, on a per weight basis, is similar to the value of 28-to-1 listed by Cameron et al., 2002.

A number of reactions are anticipated as the manure composition is added to Irrigation Water. Examples include sulfate reduction, methanogenesis, solid-phase equilibration reactions involving carbonates (calcite, dolomite, siderite), ferric oxyhydroxides, iron sulfides, as well as gas (e.g., CH_4, CO_2, H_2S) evolution reactions. Multiple models can be constructed using different combinations of possible heterogeneous reactions in attempt to reproduce the lagoon water composition. However, because much of the volume of the Lagoon Water is likely not in direct contact with soil mineral assemblages, we assumed that dissolution of mineral phases into the lagoon water during the titration would be relatively unimportant. Therefore, assumed heterogeneous reactions in the titration model were limited to: (1) precipitation of Ca- and Mg-carbonates from the lagoon water upon supersaturation with idealized calcite and dolomite phases, and (2) evolution of CH_4 and CO_2 gases if the respective partial pressures exceeded 1.0 and 0.1 atmospheres. The second criterion is consistent with measured dissolved gas concentrations in Lagoon Water samples (Figure 3).

Titration of the Irrigation Water with the postulated manure composition yields good agreement with major geochemical parameters that characterize the Lagoon Water (Figure 7). According to the model, the characteristic composition of the Lagoon Water ultimately reflects two oxidation-reduction reactions – sulfate reduction and methanogenesis – that would be expected to occur in the lagoon in the absence of appreciable dissolved oxygen:

$$CH_2O(NH_3)_{0.025}(P_2O_5)_{0.002}(K_2O)_{0.006} + 0.5SO_4^{-2} + 0.033H^+ \rightarrow HCO_3^- + 0.5H_2S + 0.025NH_4^+ + 0.012K^+ + 0.004H_2PO_4^- \qquad \text{(Eq.-3)}$$

$$CH_2O(NH_3)_{0.025}(P_2O_5)_{0.002}(K_2O)_{0.006} + 0.5H_2O \rightarrow 0.5HCO_3^- + 0.5CH_4 + 0.467H^+ + 0.025NH_4^+ + 0.012K^+ + 0.004H_2PO_4^- \qquad \text{(Eq.-4)}$$

In a system closed with respect to the atmosphere, methanogenesis would tend to reduce the lagoon water pH. However, in an open system, off-gassing of CO_2 will produce the opposite effect:

$$HCO_3 + H^+ \rightarrow CO_2(g) + H_2O \qquad \text{(Eq.-5)}$$

By considering the escape of CO_2 from the lagoon water, the pH of the modeled system rises from pH 6.83 to pH 7.29 which is roughly consistent with the median observed Lagoon Water pH of 7.46 (i.e., noticeably elevated compared to the Irrigation Water). This rise in pH would tend to supersaturate the Lagoon Water with carbonate minerals, leading to precipitation reactions that deplete the Lagoon Water in both Ca^{2+} and Mg^{2+} relative to the Irrigation Water starting composition; this effect is apparent in the lagoon water data (although the model appears to overestimate the loss of Ca^{2+}, presumably reflecting kinetic limitations or compositional uncertainty of the carbonate mineral phase).

Simultaneously achieving an approximate agreement between the Lagoon Water model and field data with respect to pH, NH_4^+, K^+, dissolved inorganic carbon, Ca^{2+}, Mg^{2+}, and CH_4 and CO_2 partial pressures requires the mineralization of some 0.9 moles of the postulated manure composition per kg of water. Given the final modeled DIC concentration (representing the mineralization end-product) of approximately 0.04 mol/kg, the implication is that the vast majority of the mineralized manure (a fraction greater than 90%) could potentially escape from the system as CH_4 or CO_2 gas. While the modeling does not explicitly address the impact of ebullition on N_2, Ar, or Ne concentrations, as the kinetics of bubble formation and mass transfer between the aqueous and gas phases are unknown, the potential for appreciable gas stripping of these species appears to be very high. This is supported by the relationship between measured partial pressures of CO_2 and Ar in the Lagoon Water and Near-Lagoon Groundwater compositions (Figure 8).

Speciation of sulfur in the Lagoon Water is not well constrained because no data were available for dissolved sulfide concentrations. Aside from potential interactions with dissolved iron to produce iron sulfides, stripping of H_2S in a manner analogous to Ar and Ne is a possible dissolved sulfur sink, given the calculated equilibrium partial pressure of approximately 10^{-2} atm (in the presumed absence of other sinks). Running the PHREEQC model with the H_2S off-gassing set to occur at a lower value – 10^{-3} atm – does indicate that the majority of the dissolved sulfur (on the order of 90%) could be stripped from the Lagoon Water but otherwise exerts little effect on the overall water chemistry (i.e., raising the calculated end-state pH to 7.33).

Impact of Lagoon Water Seepage on Aquifer Geochemistry

Given the geochemically distinct makeup of the Lagoon Water, identifying its footprint in the underlying groundwater requires a definitive tracer as well as a set of plausible explanations for the changes that occur in the water chemistry along the groundwater flow path between the lagoon environment and the measurement point (i.e., a monitor well). Some insight into those geochemical processes that could affect Lagoon Water seepage can be gleaned by directly modeling the transformation of Lagoon Water into Near-Lagoon water. This effort can identify, for example, the potential roles played by ion exchange and carbonate mineral equilibration reactions and whether or not such reactions are plausible. A subsequent step, once these reactions have been identified, is to utilize the reactions together with tracer data, such as Ar concentrations, to identify mixing combinations of different waters that could explain the observed geochemistry at more distant locations using inverse geochemical modeling (Figure 9).

Proximal to Lagoon

Lagoon water seepage into the subsurface will bring about equilibration reactions with soil mineral assemblages, particularly ion exchange reactions, given the presence of clay liners used in the construction of the lagoons and the high concentrations of NH_4^+ and K^+ in the Lagoon Water (Liua et al., 1998). To explore the possible geochemical impacts of the infiltrating lagoon water composition on the underlying groundwater, the flushing of the end-state modeled Lagoon Water through an ion exchanger was simulated with PHREEQC. For this simulation, an ion exchange species characterized by a cation exchange capacity of 0.13 mol charge/kg of soil – a reasonable value for clayey soils (Sposito, 1989) – was assumed to exist in equilibrium with the Deep Field Groundwater composition as an initial condition. Default cation exchange selectivity coefficients utilized by PHREEQC were assumed:

$$Na^+ + X^- = NaX;\ \log K = 0.0 \qquad \text{(Eq.-6)}$$

$$K^+ + X^- = KX;\ \log K = 0.7 \qquad \text{(Eq.-7)}$$

$$NH_4^+ + X^- = NH_4X;\ \log K = 0.6 \qquad \text{(Eq.-8)}$$

$$Ca^{+2} + 2X^- = CaX_2;\ \log K = 0.8 \qquad \text{(Eq.-9)}$$

$$Mg^{+2} + 2X^- = MgX_2;\ \log K = 0.6 \qquad \text{(Eq.-10)}$$

Equilibrium with Ca- and Mg-carbonate mineral phases was maintained during the simulated flushing. The predicted distributions of cations on the exchange sites after one pore volume and ten pore volumes are shown on Figure 10. Model results suggest that high concentrations of K^+

and NH_4^+ from the lagoon water would displace Ca^{2+} and Mg^{2+} from the exchange sites over time, leading to corresponding changes in the aqueous concentrations of these cations. This reaction would have a major potential impact on groundwater quality, albeit a latent effect, since a significant fraction of the nitrogen inventory could be sorbed on aquifer clay minerals. In turn, elevated Ca^{2+} and Mg^{2+} would lead to carbonate mineral precipitation reactions. The result of these precipitation reactions would be a decline in pH which the model matches well with respect to the observations in Near-Lagoon Groundwater (Figure 11). The alternative explanation – that the pH decline results from mineralization of organic carbon in the lagoon seepage – would imply an increase in the CO_2 partial pressure relative to the Lagoon Water, which was not observed (Table 1).

Distal

The lagoon water leaching model predicts changes in water chemistry in the Near-Lagoon Groundwater that are qualitatively consistent with observations. Simulating the effects of lagoon seepage on the Downgradient Groundwater composition (where lagoon impact is suspected owing to low Ar) is more difficult because a much longer flow path is involved which creates more opportunity for mixing with water not derived from the lagoon. To address the mixing problem directly, we utilized the inverse modeling capabilities of PHREEQC to identify mixing proportions of different water compositions, in addition to mineral equilibria, cation exchange, and gas exchange reactions, that could explain the Downgradient Groundwater composition in terms of major cations, pH, Cl^-, SO_4^{-2}, nitrogen speciation, and Ar concentration. Specifically, this inverse modeling was based on the assumption that the Lagoon Water and Deep Field Groundwater compositions were available as components for mixing. In addition, water from a nearby unlined irrigation canal was assumed to also be available (water levels at this location have historically responded strongly to the presence or absence of water in the canal and water samples have generally indicated a relatively young $^3H/^3He$ age). The canal water was assumed to be characterized by low total dissolved solids (consistent with its measured chemical makeup) and an Ar concentration controlled by equilibrium solubility with the atmosphere. Postulated mass transfer reactions available for consideration by the inverse model included cation exchange, oxygenation, and equilibration with calcite and dolomite. A sample variability of 20%

was assumed for all analytes, including argon. The representative end-member argon partial pressure in the Lagoon Water was estimated from the inverse modeling at 4 x 10^{-3} atmosphere (roughly 40% saturated with respect to 1) and is consistent with the lowest MIMS-measured argon partial pressures in the Lagoon Water.

Inverse geochemical modeling generally yields a number of non-unique models, so some care must be exercised in selecting candidate models that represent the most plausible scenarios. For these water compositions, inverse models were excluded that required (1) liberation of significant quantities of CO_2 along the flow path for both waters, which seems improbable given the depth below the water table, and (2) precipitation of carbonate minerals along the flow path for to the Downgradient well location as these water samples have generally been thermodynamically undersaturated with respect to calcite. Given these constraints, reasonable inverse models that could explain the origin of the Downgradient Groundwater, and, for comparison, the Near-Lagoon Groundwater are illustrated on Figure 12, normalized to the respective Lagoon Water components for each model. For the Downgradient water, plausible mixing fractions consist of 11% Lagoon Water, 66% Deep Field Groundwater, and 23% irrigation canal water; the latter required for reconciling the median concentration of Ar with that of Cl^-. For the Near-Lagoon Groundwater, mixing fractions correspond to 60% Lagoon Water and 40% Deep Field Groundwater. For both examples, the normalized mass transfer reactions are consistent with the cation exchange model developed in this study in terms of displacement of Ca^{2+} and Mg^{2+} by K^+ and NH_4^+. The principal difference between the two is the oxidation of some NH_4^+ along the flow path before it reaches the Downgradient location. The result is comparatively less displacement of Ca^{2+} along the flow path, thus reducing the calcite saturation index (consistent with observation).

Conclusions

Dissolved gas measurements in manure lagoon water and underlying shallow groundwater at an instrumented dairy site reflect the ebullition of CO_2 and CH_4 gases from the lagoons that acts to strip gases with respect to equilibrium atmospheric concentrations. Because these gases re-equilibrate with the atmosphere when the lagoon water is used for irrigation, they serve as a unique tracer for the lagoon water in the underlying aquifer and offer a clear advantage over NH_4^+ which is strongly affected by ion exchange. Geochemical modeling results are consistent with the dissolved gas measurements in two ways: (1) simulation of the lagoon water composition (mixing of irrigation water with a postulated manure composition) indicates the potential for substantial off-gassing of both CO_2 and CH_4, which is a necessary condition for Ar and Ne depletion, and (2) measured Ar concentrations are consistent with geochemical models of the impact of lagoon seepage on underlying groundwater that incorporate mixing, ion exchange, and mineral equilibria. As such, this study has definitively shown that leakage from the manure lagoons is manifested in the shallow aquifer geochemistry at the dairy site.

The immediate environmental impact of lagoon leakage on the underlying shallow aquifer is the loading of nitrogen in the form of NH_4^+. As NH_4^+ tends to be effectively bound by cation exchange sites, the shallow aquifer at the site is storing a significant quantity of nitrogen. The possibility of the conversion of the NH_4^+ to NO_3^- via nitrification, and the possible subsequent conversion of NO_3^- to N_2 via denitrification, will depend strongly on local redox conditions within the aquifer, which, in turn, appear to be influenced to some degree by the lagoon seepage itself. However, potential electron donors are also present in the subsurface in the forms of organic carbon and reduced sulfur species in the aquifer sediments. Moreover, both the oxidation of NH_4^+ and the off-gassing of N_2 will depend spatially and temporally on recharge and agricultural pumping, so that the overall nitrogen cycle operating at the site is quite complex. In this study, we have established that leakage from the manure lagoons plays a significant role in this cycle. Further research is needed to better characterize the potential long term impact of lagoon seepage and its effect on the fate of nitrogen at dairy operations.

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Figure 1. Site map of the instrumented dairy site indicating the locations of the manure lagoons and monitoring well locations.

Figure 2. Correlation between carbon dioxide partial pressures calculated using PHREEQC from water sample charge imbalances and the assumption of thermodynamic equilibrium and partial pressures measured using MIMS (MIMS measurements at low concentrations may be characterized by low accuracy).

Figure 3. (a) Oxidation-reduction potential (ORP) versus pH for water samples collected across the dairy site; (b) methane versus carbon dioxide partial pressures, as measured via MIMS; and (c) sulfate versus chloride – the Lagoon and Near-Lagoon sample groups appear to be sulfate-depleted in comparison to the other groups when normalized by chloride.

Figure 4. (a) Variation in nitrate; and (b) excess dissolved nitrogen with depth at each monitoring well location.

Figure 5. The correlation between chloride ion concentration and $\delta^{18}O$ in dairy site groundwaters is consistent with mixing between high-chloride, evaporated Lagoon Water and local groundwater, either through field application of Lagoon Water or through lagoon seepage.

Figure 6. Evidence of gas stripping as indicated by Ar and Ne.

Figure 7. Comparison of key modeled and observed geochemical parameter values in median Lagoon Water (end-state) with Irrigation Water (initial condition).

Figure 8. Relationship between dissolved argon concentrations and carbon dioxide (both expressed as partial pressures) in dairy site water samples. Samples that are undersaturated in argon relative to the atmosphere likely reflect a Lagoon Water signature; supersaturated samples likely reflect air that has been entrapped during irrigation/recharge.

Figure 9. Conceptual model of site geochemical processes and mixing components that drives the geochemical modeling assessment of lagoon seepage.

Figure 10. (a) Modeled changes in cation distributions on exchange sites in soil subjected to leaching by lagoon water; and (b) modeled changes in cation distributions after one pore volume as a result of lagoon water seepage interacting with soil minerals via cation exchange and carbonate mineral precipitation.

Figure 11. Modeled impact on Near-Lagoon Groundwater pH following leaching of Lagoon Water through an ion exchanger initially in equilibrium with Deep Field groundwater and subsequent carbonate mineral precipitation.

Figure 12. Mass transfer reactions that explain Near-Lagoon and Downgradient Groundwater compositions (along with mixing). Moles transferred are normalized to the modeled Lagoon Groundwater contributions (60% and 11% for the Near-Lagoon and Downgradient Groundwaters, respectively).