

Identifying Impacts of Agricultural Waste Storage on Groundwater Characterized by Elevated Background Solute Concentrations

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Abstract

Groundwater quality impacts stemming from agricultural waste handling or storage operations can be difficult to quantify, given the problem distinguishing impact signatures from background fluctuations in indicator analytes such as nitrate, bicarbonate, and other ions. Consequently, reliance on gross intra-well or inter-well water quality statistics – in some instances required by regulatory agencies – can yield misleading conclusions as to whether or not an impact has occurred. A data set from a site in California's San Joaquin Valley featuring an onsite composting operation provides an illustrative example. Although a cursory evaluation of changes in groundwater quality parameter concentrations (e.g., nitrate, potassium) are suggestive of waste-impacted recharge reaching groundwater, an assessment of site groundwater data in the context of regional data (using GIS and data exploration tools), in combination with geochemical scenario modeling using PHREEQC, indicates an alternative explanation entailing variations in background groundwater quality also appears viable. For example, water-aquifer interactions (e.g., gypsum and carbonate-mineral equilibration reactions, ion exchange) in response to groundwater dilution from an external source of water can fully explain recent observations that were initially identified as exceedances by intra-well statistics. These results demonstrate the need to carefully assess trends in site data in the context of all of the possible geochemical reactions that could influence concentrations of individual signature analytes.

Background

Organic agricultural wastes that are processed or stored on the land surface harbor potential threats to underlying groundwater, including increased nitrate, dissolved solids, and changes in oxidation-reduction (redox) conditions that may generate adverse outcomes. Such impacts can occur if a pathway exists for transport of waste constituents or mineralization products through the vadose zone. However, ascertaining whether or not a groundwater impact has occurred is problematic because background concentrations of indicators such as nitrate and other major ions such as potassium, magnesium, or bicarbonate, will be non-zero under ambient conditions, and possibly subject to temporal fluctuations owing to other nearby sources, seasonal effects, and other factors. Despite the implied signal-to-noise ratio problem, regulatory agencies (e.g., in California) often prescribe intra-well or inter-well statistical approaches that simply flag certain

sampling events as “exceedances” relative to perceived background conditions, regardless of whether or not such exceedances are consistent with a site conceptual model.

Groundwater samples from an anonymous site in the southern San Joaquin Valley of California where agricultural wastes are handled exhibited atypical concentrations of certain analytes in sampling events in 2015 (Figure 1); samples include those from a well located upgradient of site operations (Well #1) as well as a downgradient well (Well #2). Elevated 2015 sampling event concentrations included elevated nitrate and potassium, both of which are consistent with impacts from agricultural wastes (Christensen and Peacock, 1988; Van Averbek and Yoganathan, 2003; McNab et al., 2007), along with elevated concentrations of other constituents such as chloride and bicarbonate alkalinity. Whether or not these changes reflect an impact breakthrough event, or represent other processes not directly related to the agricultural waste, is a question that must be understood in the contexts of: (1) regional groundwater quality, and (2) alternative conceptual models that capably explain the observed changes in water chemistry across multiple indicators. Both are discussed below.

Groundwater Quality Examined in a Regional Context

Groundwater quality across the southern San Joaquin Valley (Kern County, in this example) varies as a result of recharge-area geology as well as anthropogenic input. For example, the concentrations of magnesium, sulfate, and other constituents exhibit high concentrations on the western side of the valley, along drainages from the California Coast Range, particularly southwest of the Kern National Wildlife Refuge and southwest of the city of Bakersfield (Figures 2 through 6). The site is located in one of these drainages that is characterized by high concentrations of these analytes.

Given the high degree of temporal variability in the concentrations of various constituents in downgradient site wells, establishing which samples represent water compositions similar to those in the surrounding area and which are anomalies is an important first step in determining possible agricultural waste impacts. Three data analysis approaches indicate that the elevated concentrations observed in the 2015 sampling events are consistent with ambient groundwater in the area, whereas the relatively low preceding these events is anomalous. The data analysis approaches include:

1. Principal component analysis, which indicates that a single factor (e.g., drainage through a certain type of lithology) is associated with the elevated concentrations of many of the water quality parameters along the western side of the valley (Figure 7).
2. Novelty detection, using a support vector machine (SVM) algorithm (Pedregosa et al., 2011), was used to ascertain whether or not the elevated concentration samples collected in 2015 are atypical of regional groundwater. Selected scatter plot slices through multi-dimensional parameter spaces entailing groundwater data from a subset of wells along the Coast Ranges (training data, comprised of a total of 139 samples) as well as site data (test data); delineated into ambient (i.e., not novel) and anomalous (i.e.,

novelty) sets using the SVM algorithm are shown on Figure 8. The algorithm indicated that 9/13 samples from Well #2 prior to the two 2015 sample events (i.e., low-concentration samples, as indicated on Figure 1) are anomalous, whereas 12/14 samples from Well #1 belong to the ambient set, along with the both 2015 sample sets from Well #2. These results imply that it is the dilute samples indicated on Figure 1 that are novelties, rather than the apparent 2015 “exceedances”.

3. Water composition speciation modeling conducted using the USGS’s PHREEQC geochemical model, applied to all median well compositions in the Kern County GAMA dataset, indicates that groundwater is saturated (or supersaturated) with gypsum, $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$, in a number of locations on the western side of the valley (Figure 9). As discussed below, most site groundwater are close to thermodynamic equilibrium with gypsum, suggesting its potential influence on site groundwater chemistry is not unexpected.

Geochemical Modeling of Site Groundwater Quality

Historic concentrations from the onsite monitoring wells were divided into “ambient” and “anomalous” data sets in accordance with the results of the SVM novelty detection algorithm, with the anomalous data set exhibiting lower concentrations of multiple constituents (Table 1). Because chloride is presumably a conservative tracer in site groundwater, its low concentration in the anomalous groundwater data set could be hypothesized as indicating substantial, albeit transient, dilution by a much higher quality (i.e., low dissolved solids) water source. However, a simple binary mixing model entailing addition of pure end-member water to match the anomalous-water chloride concentration (Figure 10) yields concentrations of other constituents (e.g., sodium, sulfate) that substantially under-predict observations. This points to a key role for reactions between the aqueous phase and the solid matrix.

Speciation of the ambient (i.e., more highly-concentrated) groundwater composition with the PHREEQC geochemical model indicates near-equilibrium concentrations of carbonate minerals (calcite, or CaCO_3 , and dolomite, $\text{CaMg}(\text{CO}_3)_2$) as well as gypsum (Figure 11). Consequently, the binary mixing model was modified to take into account a series of (equilibrium) reactions:

- Dissolution of calcite and disordered dolomite, if undersaturated
- Precipitation of aragonite (a CaCO_3 polymorph) and magnesite (MgCO_3), if supersaturated
- Equilibrium with gypsum
- Equilibrium with soil CO_2 at a partial pressure of $10^{2.5}$, reflecting microbial activity
- Presence of an ion exchanger, reflecting a cation exchange capacity equivalent to approximately 10 mmol/100 gm soil; the default cation exchange reaction database for major cations (e.g., Na^+ , Ca^{2+} , Mg^{2+}) supplied with PHREEQC’s `llnl.dat` thermodynamic database was assumed

The results of the reactive mixing model exhibit a significant improvement to the match with the anomalous data (Figure 12). These results suggest that much of the difference between ambient groundwater and the anomalous groundwater composition could be explained by dilution and consequent equilibration reactions with aquifer minerals. However, as suggested in Figure 1, the high bicarbonate alkalinity in the 2015 “exceedance” samples does not closely correspond to historic values observed in ambient groundwater (upgradient Well #1). A plausible source of additional inorganic carbon/bicarbonate alkalinity is the mineralization of organic carbon stemming from the agricultural waste. To test this hypothesis, an additional PHREEQC simulation was conducted that assumed the addition of organic carbon (modeled as 30 mg/L CH₂O) to the ambient groundwater composition under a limited oxygen supply and subject to all of the other assumptions used for the reactive mixing simulation. The simulation results are compared to measured concentrations of inorganic carbon, as well as nitrate, on Figure 13. The quantitative agreement between model results and measurements suggest that organic carbon mineralization, coupled with limited denitrification of ambient nitrate, could explain the composition of the downgradient well groundwater measured in the 2015 sampling event.

Discussion

Groundwater chemistry data from the site remain enigmatic. The historic dilute water samples in Well #2, rather than recent elevated samples, represent anomalies in comparison to regional groundwater data. Geochemical modeling with PHREEQC clearly indicates that dilution of ambient groundwater, along with water-rock reactions, can fully explain observed compositional changes. Nonetheless, two questions remain unresolved:

- The source of the substantial volume of dilute water required to explain the observed effects in the downgradient monitoring wells, which remains unidentified.
- Bicarbonate concentrations (expressed as alkalinity) are significantly elevated in the 2015 sample sets in the downgradient wells in comparison to all historic samples at the site.

In summary, the water quality parameters paint an inconsistent picture. As such, a defensible position to assert is that an appreciable portion of the recent observed changes in groundwater quality in the downgradient wells may not necessarily represent an impact from the agricultural waste. This possibility represents a cautionary note against the application of statistical methods as a default means for assessing impacts in the absence of conceptual process models.

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