The Adoption of the Soil Chemical Equilibrium Approach to Solving Hydrogeochemical Problems

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Abstract While hydrogeochemical reactions are well documented, focus is on thermodynamics of the aqueous phase, especially as it pertains to precipitation-dissolution reactions. Except in highly permeable systems, groundwater has sufficient time to react with minerals within solid phases that take in consideration other reactions including ionic excahnge. Generally these reactions occur at far from equilibrium and in relatively dilute aqueous solutions similar to unsaturated soil conditions. The Proactive Monitoring approach of Mulvey (1998) was modified to include soil chemical equilibria reactions, including using both pe and pH to specify the redox status of aqueous systems. Understanding the hydrogeochemical environment in a proactive manner allows for more appropriate decision making with respect to management, treatment and regulatory issues.

Keywords hydrogeochemistry, proactive monitoring, redox

Introduction

Numerous graphical and numerical interpretation are basic tools in hydrochemical studies (Zaporozec 1972) to describe groundwater chemical behavior as determined by initial water sources, the medium through which it travels and subsequent reactions. Mulvey (1998) proposed that these can be described in terms of soil chemical reactions, especially ionic exchange. Ion exchange reactions reduce the concentrations of some ions, introduce new ions and leave others to migrate unimpeded, producing a leachate front that can potentially provide a more accurate monitoring methodology of leachates at mine sites that are generated within tailings facilities and waste rock dumps. Key to this approach is the use of ratios rather than absolute ionic concentrations, especially where mine leachate (ML) differs from native exchangeable or groundwater cations (N), expressed as:

$$ML/N \qquad (1)$$

where ML = 100 × 3 most dominate, lease reactive cations within the mine leachate

N = 3 most dominate groundwater or soil/rock exchangeable cations.

When this approach was applied to an open-pit mine site that had been subsequently backfilled with organic material prior to the cessation of dewatering, it was found that a modification was required to take into account redox reactions. Following the guidelines of Mulvey (1998) soil chemistry fundamentals were employed to describe groundwater hydrogeochemistry.

Site Description

The site (Fig. 1) covers an approximate area of 3.2 ha located in the Perth suburb of Maddington, Western Australia. The site is located on the eastern edge of the Swan Coastal Plain, within the Guildford Formation geological unit (Gozzard 1983). The Guildford Formation comprises of sediments deposited during the Quaternary Pleistocene period (10–20 Ma) and is described as sandy clay, white grey/brown, with fine to coarse grained sub angular to rounded sand, with component clays of moderate plasticity. The water table is approximately 1.0-4.0 m below the surface and re-

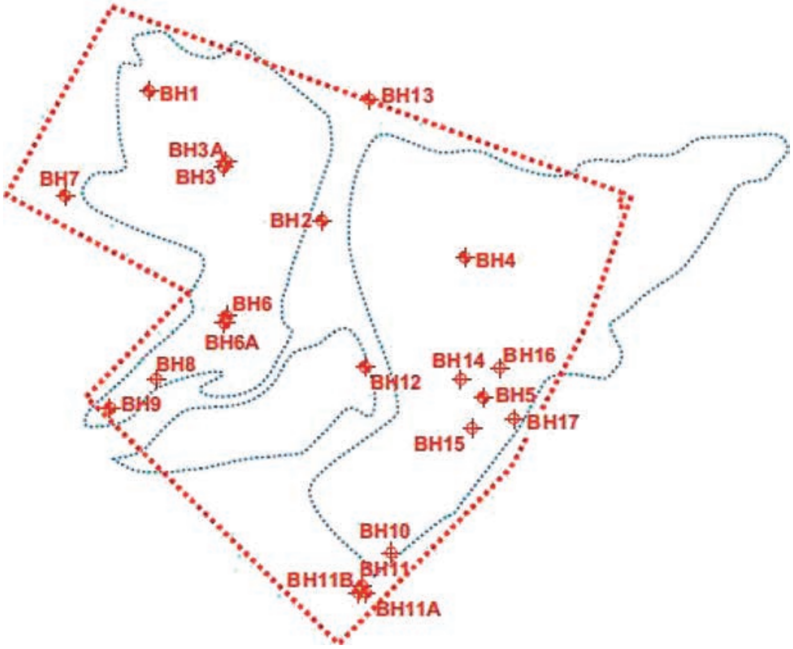

***Fig. 1** Site layout showing location of monitoring wells. Red outline delineates area of investigation. Blue outline delineates extent of open pit mining.*

gional groundwater quality (Davidson 1995) is characterised as having:

- TDS concentrations greater than 2,000 mg/L;
- nitrate (NO_3^-) concentrations greater than 1 mg/L;
- sulfate (SO_4^{2-}) concentrations less than 100 mg/L with Cl/SO_4 ratios of between 20 and 30.

Groundwater quality is a reflection of previous agricultural activities (including dairy farming) and the presence of sulfides within the Guildford Formation.

Groundwater bores surrounding the site have water levels ranging between 2.5 and 3.5 m below the surface. Available information regarding water quality indicates that total dissolved solid (TDS) values range from 170 – 4,000 mg/L.

Clay was extracted from the site between 1946 and 1985. At the completion of brick making operations, the pits were reportedly backfilled with inert construction waste by the landowners at that time. However uncontrolled deposition of drums, timber, vegetable matter and garden waste material also occured creating a complex source of contaminants to enter the groundwater system.

Field Investigation and Observations

Seventeen borings, including 3 nested wells, were installed. Boreholes located within the natural sediments of the Guildford Formation had the following stratigraphy:

- generally unconsolidated clayey fill material across the site to depths of approximately 0.5 and 2.5 mbg (metres below grade), overlying alluvial sediments of predominately stiff grey to white sandy clay, with varying amounts of sand and gravel and varying degrees of stiffness;
- laterite gravel layers varying in colour from red to yellow up to 200 mm thick at depths between 4.0-6.0 mbg;
- a white medium grained saturated silty sand at approximately 7.0-8.0 mbg; and
- grey to white sandy clay to clayey sand below 8.0 m.

Boreholes located within the clay pits had the following stratigraphy:

- generally unconsolidated clayey fill material across the site to depths of approximately 2.5 mbg;
- waste fill material within the clay pits comprising organic matter and rubbish (bricks, concrete, wood, plastic, metal);
- natural materials below the base of the pits were stiff, grey with yellow mottled sandy clay, encountered at various depths.

Groundwater levels were approximately 16 m AHD. Overall groundwater flow is approximately west southwest to southwest at a gradient of 0.001. Groundwater samples collected within the clay pit indicated the presence of pesticides above site criteria, while samples collected outside the clay pits had no detectable pesticide concentrations.

Conceptual Site Model

Concentrations of several analytes allowed for the principles proposed by Mulvey (1998) to be used to develop a monitoring program. However, use of the proposed ML/N formula of Mulvey (1998; Equation 1) did not provide sufficient interpretation of the groundwater monitoring data. Further examination of the data and use of ratios has been used to develop a conceptual model of groundwater beneath the site, including the quality and movement of the leachate, as discussed below.

To highlight the breakthrough of displaced native cations, Equation 1 was modified to include only two ML cations:

$$ML/N = \frac{K + NH_4^+}{Mg + Ca + Na} \times 100 \qquad (2)$$

Given the complexity of the of the site chemistry, the use of Equation 2 was still insufficient to adequately describe all the variability in groundwater chemistry observed at the site. Lindsay (1979) describes the use of pe + pH as a convenient single-term expression for defining the redox status of aqueous systems. The use of pe (-log of electron activity) allows for electrons to be treated as reactants and products so that both chemical and electrochemical equilibria can be expressed by a single equilibrium constant. When ML/N is plotted against pe and pH (Fig. 2), a series of classes of groundwater in the vicinity of the site can be described, including three leachate classes and four background classes.

Leachate Classes

- **Class 1** The groundwater from BH1 in the western edge of the western clay pit has the lowest ML/N ratio of the leachate due to the lower NH_4^+ concentration.
- **Class 2** Boreholes located in the middle of the western clay pit (BH3A, BH3, BH6) have the lowest redox values and higher ML/N ratios (6.19-9.98) due to higher NH_4^+. BH3 and BH6, in the lower portion of the clay pit, have K and NH4 concentrations lower than borehole BH3A screened in the upper portion of the aquifer, indicating either earlier disposal or more putrescible matter.
- **Class 3** he eastern clay pit has a different leachate signature than the western clay pit, with higher ML/N ratios due to higher K and NH4. The higher ML/N ratios indicate that the western pit was either filled after the eastern pit or contains more putrescible matter.

Background Groundwater Classes:

- **Class 4** BH2 is located between the eastern and western landfill, showing characteristics of leachate, with a negative redox and nitrate levels < 0.1 mg/L. NH_4^+ and HCO_3^- concentrations were lower than the than leachate concentrations. TDS is at the lower range of leachate. Dewatering during mining may have generated sulfate and bicarbonate. Alternatively, groundwater may be impacted by the precursor of fermentative leachate
- **Class 5** Surface groundwater within the Guildford Formation indicates the influence of leachate within the pit, although redox values are positive. Groundwater collected from BH7 and BH11, down gradi-

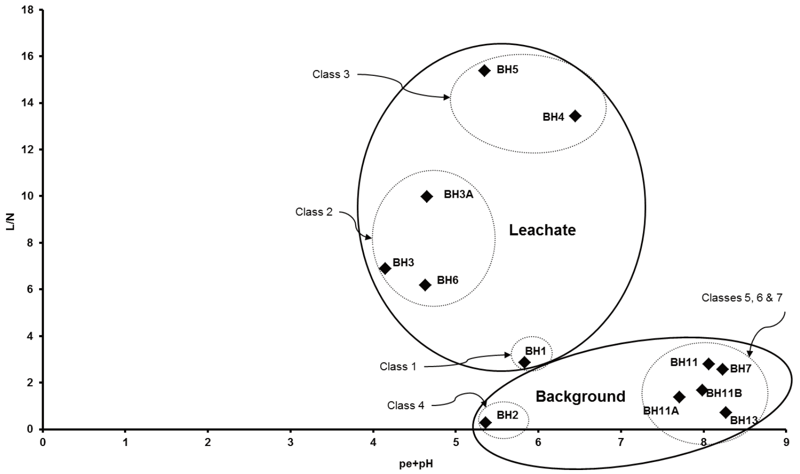

***Fig. 2** Groundwater Classes.*

ent of the clay pits have higher NH_4^+ and HCO_3^- and lower nitrate levels than BH13, upgradient of the clay pits. The Cl/SO_4^{2-} ratios indicate that pyrite has been oxidised during the dewatering process associated with mining. TDS concentrations are elevated due to high bicarbonate and sulfate, or the precursor to landfill leachate (the fermentative phase) is passing these bores.

- **Class 6** Shallow background bores BH13 is up gradient of the clay pits intersecting the water table and BH11 is cross gradient, screened between 6.0 and 8.0 mbg. Both wells have TDS values less than 1,000 mg/L nominal NH_4^+ and NO_3^- greater than 1 mg/L. Native cation ratios (Cl/HCO_3^- and Cl/SO_4^{2-}) indicate that mine dewatering has influenced the chemistry of these wells.
- **Class 7** The deeper well has the characteristics most typical of groundwater in the Guildford Formation (Davidson 1995)

A conceptual site model is presented in Fig. 3 and is summarised as follows:

- Potential sources of contamination: Three clay pits contain waste fill below the water table provide a source of leachate to groundwater.
- Chemicals of concern: Concentrations of metals, hydrocarbons and pesticides have been detected in soil and groundwater samples collected within the clay pit.
- Potential transport mechanisms and exposure pathways: The site is currently vacant and all infrastructure has been removed. The waste material is covered with a minimum of 1.5 m of fill. The pits have been excavated into clayey material with a clayey sand lens has been observed at approximately 9.0-10.0 mAHD.

Natural attenuation involves the net reduction of contaminants in soils and groundwater through dispersion, dilution, (bio)degradation, volatisation, irreversible sorption as well as radioactive decay. Although leachate has been detected in the clay pits and appears to be leaving the site, attenuation is occurring over short distances. Using an average NH_4^+concentration as an analogue for the movement of the leachate out of the clay pit, the rate of attenuation can be calculated to the nearest down gradient monitoring well. The eastern clay pit has an average concentration of NH_4^+ of 17 mg/L, reducing to 5 mg/L in borehole BH7, 10 m outside the pit, indicating that approximately 1.2 mg NH_4^+ is attenuated per metre. Based on this rate, the remaining leachate plume will attenuated within an additional 4.2 m.

Based on the available data, there is chemicals of concern above freshwater guidelines

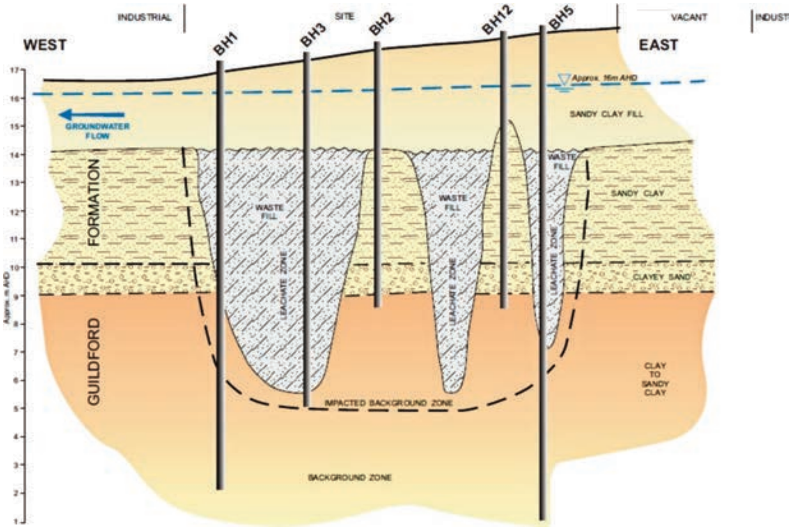

Fig. 3 *Conceptual site model.*

were not been detected in boreholes outside of the clay pit. Further, ongoing impact to the regional aquifer is likely to minimal due to the following factors:

- the leachate has a chemical signature indicative of the long term landfill decay which is in agreement to the time since completion of the landfill (approximately 20 years; Knight and Beck 1987);
- landfill decay will continue, reducing the concentration of leachate components;
- conservative estimate of groundwater flow of 0.001 m/d (0.2 m/a) has been calculated;
- vertical attenuation can also be demonstrated by chemical data collected from boreholes BH11, BH11A and BH11B
- there is no evidence that BH11A has been impacted by leachate, but clearly shows impacts from dewatering and nearby horticultural activities;
- dewatering during mining produced SO_4^{2-} with adequate electron acceptors (concentrations in groundwater > 20 mg/L) for biodegradation (King and Beck 1997);
- nitrate levels in background bores (> 1 mg/L) are also suitable for nitrate reduction (Knight and Beck 1987)

Based on the data collected at this site, the intended land use at the site and current land use in proximity to the site, the environmental impact of leachate identified at the site is not considered to present a risk to the environment. A monitoring program was proposed based on the establishment of groundwater classes. As such basic groundwater chemistry parameters only were measured, greatly reducing analytical costs

Conclusions

A graphical representation of groundwater monitoring data is proposed using basic groundwater parameters expressed as a function of single-term expression for defining the redox status of aqueous systems. Understanding the hydrogeochemical environment in a proactive manner allows for more appropriate decision making with respect to management, treatment and regulatory issues.

Acknowledgements

The author thanks Phil Mulvey, Environmental Earth Sciences, for introducing the concept of Proactive Monitoring and for ongoing discussions around the importance of soil science in hydrogeology.

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