Seasonal variation of redox species and redox potentials in shallow groundwater: A comparison of measured and calculated redox potentials

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SUMMARY

The seasonal variation of redox potential (Eh) and redox species such as As(V)/As(III), Cr(VI)/Cr(III), Fe(III)/Fe(II), NO_3^-/NO_2^-, and Se(VI)/Se(IV) were studied in a shallow groundwater for a period of three years (May, 2004–January, 2007). The study area was Chrompet area of Chennai city, India. Groundwater samples from 65 wells were monitored for pH, electrical conductivity, dissolved oxygen (DO), and major ions during pre-(May) and post-monsoon (January) seasons. The objective of the study was to gain insight into the temporal variation of the redox species due to groundwater recharge and to identify the redox reactions controlling the measured Eh of the groundwater. The study revealed that the shallow groundwater was "oxic" with DO ranging between 0.25 and 5.00 mg L^{-1}, and between 0.38 and 5.05 mg L^{-1} during pre-(May, 2004) and post-monsoon (January, 2005) seasons, respectively. The measured Eh (with respect to standard hydrogen electrode, SHE) ranged between 65 and 322 mV, and between 110 and 330 mV during pre- and post-monsoon seasons, respectively. During post-monsoon seasons, DO and Eh increased in most of the wells due to groundwater recharge. The calculated Eh using the redox couples As(V)/As(III), NO_3^-/NO_2^-, O_2/H_2O and Se(VI)/Se(IV) neither agreed among themselves nor with the measured Eh during all the seasons. It shows that in the shallow groundwater, the various redox couples are in disequilibrium among themselves and with the Pt electrode. However, 41% (n = 122) of the Eh values calculated from Fe(III)/Fe(II) couple agreed with the measured Eh within ±30 mV, the uncertainty of Pt-electrode measurement. The post-monsoon seasons showed higher values of As(V)/As(III) and Se(VI)/Se(IV) compared to the pre-monsoon seasons, whereas Fe(III)/Fe(II) behaved in the opposite manner. This pattern of variation is consistent with the increased oxidizing nature, as shown by the higher DO and Eh values observed during post-monsoon seasons. The results showed that the Fe(III)/Fe(II) is the dominant redox couple to equilibrate with Pt electrode. However, the measured Eh can only be used in a semi-qualitative way and can be interpreted with other redox indicating parameters. The measured Eh though represent 'mixed potential', is a useful indicator for characterizing the speciation and temporal variation of redox sensitive species.

1. Introduction

Oxidation-reduction (redox) reactions involve the transfer of electrons from one chemical species to another. Redox reactions play an important role in the chemistry of natural waters and affect the mobility and availability of many inorganic and organic species (Appelo and Postma, 2005). For example, As(III) and As(V) have different adsorption characteristics; Cr(III) and Cr(VI) have different solubilities. Redox processes can alternately mobilize or immobilize potentially toxic metals associated with naturally occurring aquifer materials (Cao et al., 2001; Smedley and Kinniburgh, 2002; Sracek et al., 2004; Wang et al., 2007), contribute to the degradation or preservation of anthropogenic contaminants (Bradley, 2003;

McMahon and Chapelle, 2007), and generate undesirable byproducts such as dissolved ferrous iron (Fe^{2+}), hydrogen sulfide (H_2S), and methane (CH_4) (Barcelona et al., 1989; Ryu et al., 2004). Redox reactions in natural aqueous systems have been the focus of many geochemical studies including groundwater contamination (Nicholson et al., 1983), acid mine drainage (AMD) (Bachmann et al., 2001; Gezahegne et al., 2007; Mok et al., 1988; Nordstrom et al., 1979), and waters associated with marine sediments (Berner, 1963; Vershinin and Rozanov, 1983). Redox reactions and redox sensitive aqueous species differ in nature from most other reactions in aquifer systems. For many reasons, therefore, it is desirable to have an indicator of redox status of the system.

The potential of a platinum electrode (with respect to standard hydrogen electrode, SHE) has been found to roughly obey the Nernst equation in certain natural aquatic systems, including groundwater, AMD and marine sediments. As an alternative to

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electrometric measurement of redox potential (Eh), redox couples could be used to calculate Eh values. The common redox couples useful for this purpose are Fe(III)/Fe(II) (Grenthe et al., 1992; Grundl and Macalady, 1989; Holm and Curtiss, 1989; Matia et al., 1991), As(V)/As(III) (Cherry et al., 1979; Mok et al., 1988) and S^{2-}/SO_4^{2-} (Ioka et al., 2011). Being an intensity factor, Eh characterizes as a summary parameter, the tendency, but not the capacity, of a system for oxidation or reduction. It is a direct potentiometric measurement of the equilibrium established between all oxidized and reduced species in solution and is based on the Nernst equation, which relates potential to the activities of the electroactive species.

In practice, Eh is determined by measuring the potential difference between an inert metal electrode (Pt) in contact with a solution and a reference electrode (Ag/AgCl). Electron exchange with the reduced and oxidized species takes place at the inert metal electrode. The measurement is done at zero net exchange current across metal–solution interface i.e. when electrochemical reversibility is maintained. This reversibility is attained when the individual exchange currents of electroactive redox ions exceed 10^{-6} A cm^{-2}, which corresponds to concentration of $>10^{-5}$ mol L^{-1} of the redox pair (Nordstrom et al., 1979). One of the fundamental requirements for a meaningful Eh measurement in a given time is the attainment of equilibrium between the different redox couples in a solution and the electrode surface, thus resulting in a stable value (Stumm and Morgan, 1996; Whitfield, 1972).

In natural waters several redox couples co-exist; therefore all the redox couples are expected to contribute to equilibrium with defined potential. When at least one redox couple is irreversible, the system cannot arrive at equilibrium. Redox couples involving multielectron transfers and structural reorganization between the reduced and oxidized forms are kinetically slow; hence they do not attain equilibrium even though their concentration exceeds 10^{-5} mol L^{-1} (Grenthe et al., 1992). Consequently, kinetics apart from equilibrium thermodynamics plays a significant role (Frevert, 1984; Grenthe et al., 1992). The measured Eh, as summary parameter, can thus differ significantly from the calculated potentials for each redox couple. Thus, consistent values of measured and calculated potentials serve a convenient way to check the attainment of redox equilibrium. Lindberg and Runnells (1984) concluded from their studies that neither measured Eh, nor any single calculated Eh, represents "a master redox value for natural waters". For many natural systems, low exchange currents over the electrode interface render measurements unreliable.

At disequilibrium, individual redox couples exchange current independently over the solution–electrode interface and the overall potential (measured Eh) is obtained when the sum of all anode exchange currents equal the sum of all cathode currents. This potential is usually referred to as 'mixed potential' (E_{mix}) (Grenthe et al., 1992; Grundl, 1994; Stefansson et al., 2005; Stumm, 1984). In dilute solutions containing redox sensitive species that give rise to an exchange current below $\approx 10^{-6}$ A cm^{-2} (concentration of electroactive species $<10^{-5}$ mol L^{-1}), oxygen begins to be sensed by the Pt electrode and undergo surface redox reactions (Stefansson et al., 2005; Whitfield, 1974). Mixed potentials can disturb redox measurements very much, because they are not reversible and mostly are not constant. Even though Pt-electrode Eh measurements may lack a strict thermodynamic basis, when the major redox couples present in a system have been identified, such measurements may permit the generalization of our understanding of geochemical reaction processes and a system's approach to equilibrium. Indeed Eh measurements were used to interpret several geochemical processes such as mobilization of trace elements (Ahmed et al., 2004; Cao et al., 2001; Hermann and Neumann-Mahlkau, 1985; Wang et al., 2007), speciation of toxic elements (Kim et al., 2002; Zheng et al., 2004), characterization of contami-

nant plume migration (Chapelle et al., 1996; Christensen et al., 2000; Kehew and Passero, 1990), groundwater pollution from landfill (Nicholson et al., 1983), recharge-discharge process in confined aquifers (Barcelona et al., 1989; Champ et al., 1979; Jackson and Patterson, 1982), redox zonation of aquifers (Chen and Liu, 2003; Edmunds et al., 1984; Hsu et al., 2010; Smedley and Edmunds, 2002; Wang et al., 2007), and temporal variation of redox sensitive elements (Groffman and Crossey, 1999; Gruau et al., 2004; Zheng et al., 2004). The present communication is a part of a study regarding the speciation of trace elements in shallow groundwater of a tannery area of Chennai city, India. The aim of the present study was to gain insight into the temporal variation of the species As(V)/As(III), Fe(III)/Fe(II), Se(VI)/Se(IV), and Cr(VI)/Cr(III) due to groundwater recharge and to identify the redox reactions controlling the measured Eh of the groundwater.

2. Materials and methods

2.1. Study area

The study area is a suburban area (Chrompet) of Chennai city, the capital of Tamil Nadu state, India. It lies between N latitude 12°56′12″ to 12°59′56″ and E Longitude from 80°06′14″ to 80°11′30″ and has an aerial extent of 45 km^2. The area forms part of Adyar basin and contains about 15 tanks. Most of the tanks do not possess their command area, because a major part of the area has already been converted to residential/industrial plots over the years. Presently most of the tanks are used as waste disposal sites.

The area is underlain by charnockite rocks of archean age. These rocks are exposed over a wide area and are massive and well foliated. These rocks are absolutely devoid of primary porosity and groundwater occurrence is chiefly confined to the secondary porosity developed by weathering, fracturing, jointing and faulting. Groundwater occurs under phreatic conditions in the shallow weathered and fissured zones and under semi-confined conditions in the fractured, faulted and sheared zones (CGWB, 2003). Groundwater is developed through mostly dug wells as the thickness of weathered zone is sufficiently high ($\approx$15 m). The depth of sampled wells ranged between 3.32 and 14.15 m below ground level (bgl). The depth to water table (DTW) ranged between 0.70 and 13.77 m, and between 0.38 and 8.56 m bgl during pre-(May 2004) and post–monsoon seasons (January 2005), respectively. The wide variation in the water table is due to the topography of the area.

Leather tanning is the major industrial activity in the area. The area was away from residential areas when the tanneries came up nearly a century ago, but now it is densely populated. Before the establishment of common effluent treatment plant (CETP) during 1995, the effluents were discharged untreated into open sewers and low-lying areas. Also, the area lacks adequate domestic sewerage system. Over the years, these factors led to severe groundwater contamination. More details about the study area have been described previously (Kumar and Riyazuddin, 2011a).

2.2. Sample collection and preservation

Groundwater samples were collected from 65 open dug wells representing the phreatic aquifer during the months of May (pre-monsoon) and January (post-monsoon) for a period of three years (i.e. 2004–2007). The sampling wells were selected to represent the industrial and domestic sewage contamination. All the wells are regularly pumped for domestic or industrial purposes. Wells were purged before sample collection and groundwater pH, electrical conductivity (EC), dissolved oxygen (DO) and Eh were continuously monitored. Samples were collected after the stabilization of