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Life remains in the study of aluminium in rivers

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This commentary flags the role of groundwater and biological drivers within catchments in determining aluminium (Al) concentrations in rivers. It concludes my studies, focusing on UK catchments with typologies ranging from acidic uplands to bicarbonate rich rural and urban/industrially impacted lowlands (Neal, 1988; Neal et al., 1987, 2011, 2012).

The study of Al in the hydrosphere has been extensive, inspirational and long-standing (Burton and Liss, 1976; Hem, 1985; Drever, 1977, 1997). From Earth sciences to oceanographic perspectives, issues have centred on the hydrolysis of primary minerals (e.g. feldspars) in the crust to secondary minerals (clays, aluminosilicates and Al-oxides/hydroxides). Here, the nature of dissolved and colloidal/particulate processing through the hydrological cycle from soils and groundwater to the river, estuary and sea has been examined. The issues have expanded to include acidic deposition and mining contamination with the release of Al as an ecotoxicant to surface waters (Exley, 2003, 2012).

Although Al is highly abundant in the Earth's crust (around 8.3%), Al concentrations only average around 50 µg/l in river water and 1 µg/l or less in seawater. This is due in major part to the low rates of primary mineral weathering and the low solubility of the secondary minerals. A critical feature of Al hydrochemistry is its amphoteric character. As such, Al solubility is particularly low at the moderate pH encountered for surface waters, while Al solubility increases at low and high pH due to the respective dominance of Al^{3+} and $Al(OH)_4^-$.

To understand and characterise Al-pH relationships the bench-mark case is $Al(OH)_3$ solubility. With economy and succinctness in view and analysis, this approach has shown great merit over many years. Nonetheless, similar features can occur for other (more complex) secondary minerals with "overlap" due to large differences in solubility between crystalline and amorphous forms of the same mineral and silica concentrations around quartz/chalcedony saturation (Neal et al., 1987, 2011). Figure 1 provides an illustration similar to that given in Drever (1997) for the case of microcrystalline Gibbsite with allowance for Al^{3+}

1

and $Al(OH)_x^{3-x}$ species (x = 1 to 4). Figure 1 (as with Figure 2) is simply illustrative as much more elaborate and broad based thermodynamic analysis is required to fully explore the details of change. For example, Al concentrations and environmental toxicity are strongly influenced by complexation with fluoride, silicon, sulphate and organic matter, colloidal formation, polymeric Al species and temperature (Lydersen, 1990; Poléo et al, 1991; Rosseland et al., 1992; Teien et al., 2006; Exley, 2003, 2012; Xiao et al., 2008). However, temperature variation is included to flag its importance, one which varies according not only to the solubility product, but also to the dominant Al-OH species. Important issues concerning objective tests for assessing Al solubility controls have been flagged previously (Neal, 1988; Neal et al., 1987, 2011, 2012; Christophersen and Neal, 1998). There are a wealth of hydrogeochemical and mineralogical studies spanning over 40 years that link to the widespread and high abundance of the clay minerals as secondary weathering products, with their origin, distribution and solubility linked to neo-formation, transformation and colloidal processing. Hence, it is fundamentally unsound to ignore generally their significance in the hydrosphere to Al solubility even if a simplistic thermodynamic evaluation and viewpoint linked to Al hydroxide solubility seems to suffice.

Set against this backdrop, simple Al equilibrium controls are not generally found in rivers as they contain mixtures of waters from hydrogeochemically distinct sources within catchments and kinetic controls come into play (Neal, 1988; Seip et al., 1989, 1990; Sullivan and Cosby, 1999; Neal et al., 2011, 2012). For a base case, processes occurring within the soil, the groundwater and the river need to be considered separately.

The Soil. Within acid soils, Al levels are determined by a complex set of processes. Via leaching of parent material, these processes include Al binding to organic matter, organic coatings of minerals, dissolved organic carbon and Al-silicon interactions in dissolved and colloidal form (Mulder and Stein, 1994; Richie, 1995; Sullivan and Cosby, 1996; De Wit et al., 2001; Exley, 2003, 2012).

The Groundwater. Groundwater can provide a major input of bicarbonate-bearing water to the river to generate waters of circumneutral to basic conditions. Mixing of groundwater with soil water increases the pH and Al saturation can be reached towards circumneutral pH (Neal and Christophersen, 1989; Neal et al., 1989). While it has often been assumed that such mixing with Al removal from the water column occurs within the river, groundwater provides a major dynamic pathway for soil water transfer even for "hard rock" areas. This is shown directly with

2

groundwater monitoring (Neal et al., 1997) and indirectly by the conversion of variable inputs of chemically unreactive elements in rainfall with a white noise signature to a highly damped and fractal stream response (Kirchner et al., 2000, 2002; Godsey et al., 2010). Apart from times when passage of acidic Al-bearing soil waters dominates, the groundwater environment acts as an Al filter because the pH is constrained around the region where Al solubility is low. This is due to CO_2-HCO_3^- buffering within the groundwater and two opposing processes. Firstly, respiration and organic decomposition processes within the soil and groundwater generate high dissolved CO_2 levels to lower pH within the groundwater zone. Secondly, weathering reactions within the groundwater zone consume H^+, generate bicarbonate ions and increase pH. As the groundwater is not in contact with the atmosphere, CO_2 concentrations remain high and this limits the pH rise via weathering.

The River. On groundwater transfer to the river, pH rises due to a combination of CO_2 efflux to the atmosphere and biotic consumption in the river at times of photosynthesis (Neal et al., 1998, 2011, 2012). However, Al concentrations need not change due to short water residence times and a lack of mineral surfaces to rapidly supply/nucleate Al. Thus, as pH increases the waters are initially undersaturated at low pH to become oversaturated at intermediate pH before returning to undersaturation as pH increases further (Figure 2). In turn, Al concentrations do not reach such high values at low pH, while the minimum solubility extends to higher pH (from 6-7 to 7-9, Figures 1 and 2).

Implications

The research indicates strong but indirect biological influences on Al distributions within rivers linked to inorganic (CO_2) and organic (soil organic matter) processing. In addition, Al filtering mechanisms may occur within riverine and estuarine sediments where CO_2 degassing is restricted and organic matter is high. Al colloids can also be highly significant within rivers inducing further Al filtering via flocculation (especially within estuaries). Indeed, there are issues over the nature and attenuation of Al colloidal materials and their ecotoxicology in relation to liming of acidic waters and estuarine processing (Rosseland et al., 1992; Teien et al., 2006). It is most unfortunate that truly dissolved, colloidal and sediment fractions are not generally determined together. Further, there are issues of the age distribution of the colloids, from long residence times in the soil to recent formation within the river. Colloidal formation within the river may be influenced differently by pH rise via direct

addition of hydroxyl ions and indirectly by CO_2 degassing, while diurnal fluctuations in pH due to photosynthesis/respiration are not generally considered, with skewed measurements due to a general lack of night-time measurements. Nonetheless, Al processing of riverine inputs within estuaries is usually so efficient that the main source of Al in the open ocean is often atmospheric dust and subsequently there is biological removal of Al linked to diatoms and incorporation into biogenic silica (Middag et al., 2009). Thus, biology seems to limit Al distributions across surface waters and probably across many groundwaters as well. Set against the "natural" biotic and abiotic restrictions for Al, anthropogenic activity increases Al concentrations via acidification linked to industry/mining activity and effluent discharge/spillage in rivers.

Different types of environmental systems will require different emphases, but the relevance of biology needs to be considered along side inorganic processing. As such, in order to properly understand the Al distribution and biological impacts in surface waters, cross-disciplinary views are required that incorporate processes across the hydrological cycle via biotic, abiotic and colloidal processing, with cross linking to ecotoxicology.
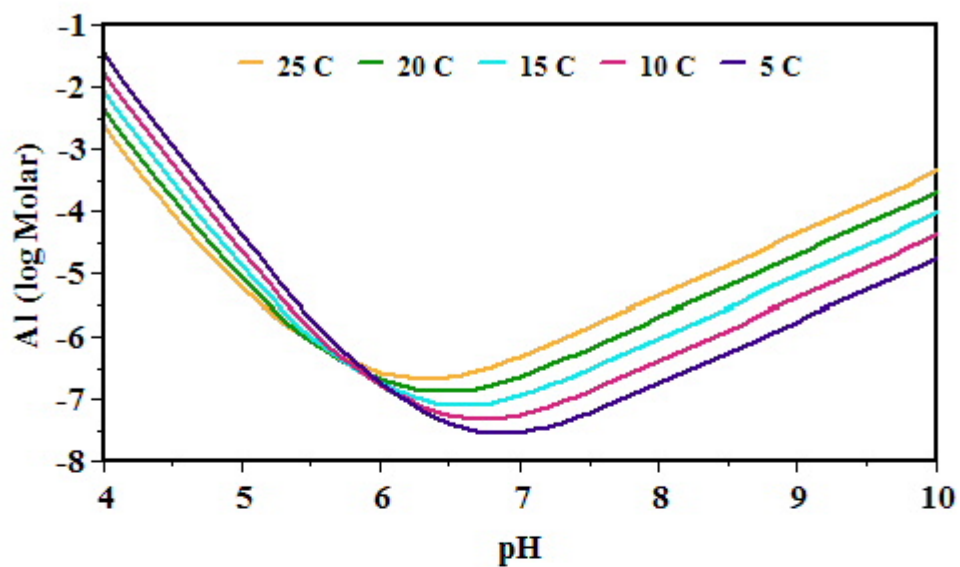
Figure 1. Al-pH relationships for microcrystalline Gibbsite: a reference baseline case. Allowance is made for Al hydroxide species and the inorganic CO_2 system as well as temperature.
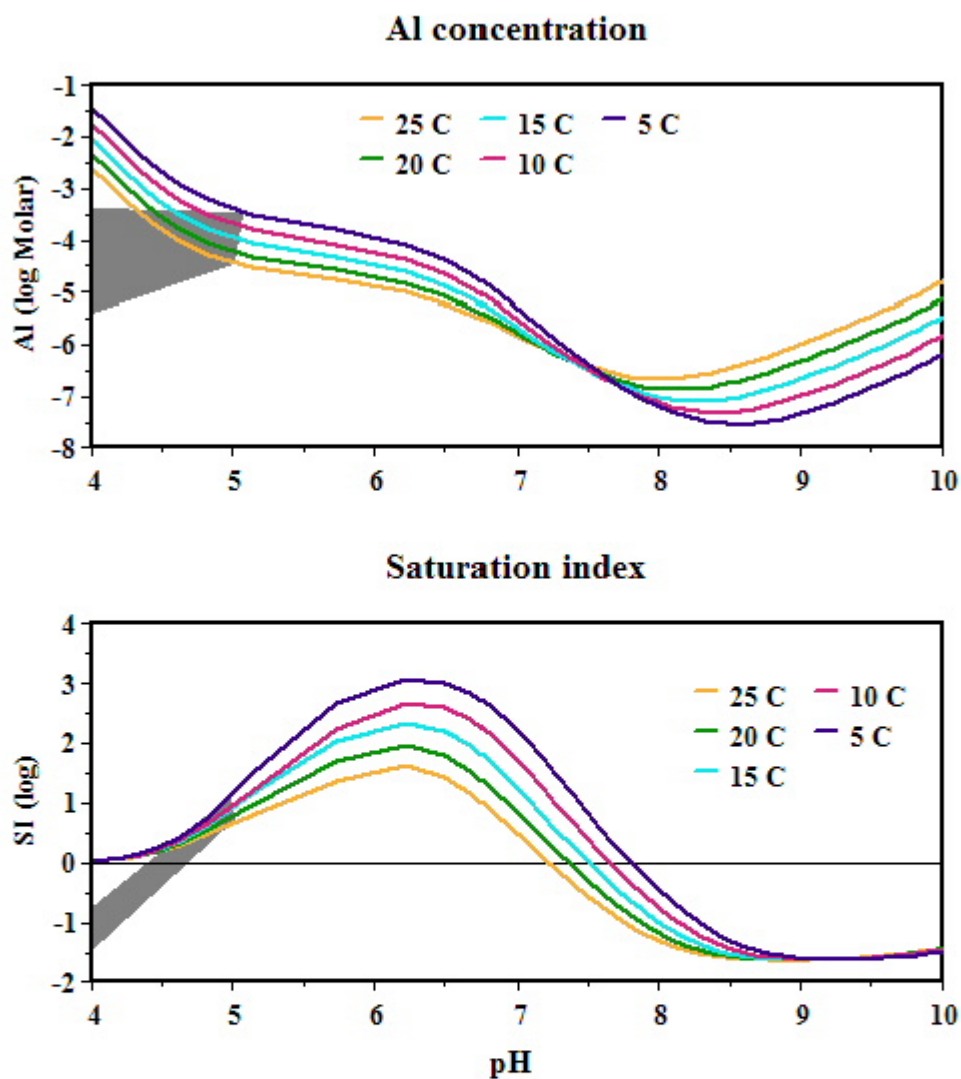
Figure 2. Al-pH and Al saturation-pH disequilibrium relationships for river water. For the analysis, Al in the groundwater is taken as being controlled by microcrystalline Gibbsite solubility. However, degassing of

CO_2 from groundwater at 50 times to atmospheric pressure in the river results in a pH rise but Al/alkalinity is conserved. The shaded area denotes deviations at low pH due to acid soil water inputs.

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