

# QUANTIFYING ALKALINE PROCESS FLUIDS IN SOILS AND GROUNDWATER FROM LEAKS AND SPILLS

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## Abstract

Presence of alkaline process fluids in soils and groundwater from leaks and spills is commonly associated with elevated alkalinity, pH and related parameters in pore water, extracted from soils, and in groundwater.

Alkalinity and pH, however, can be affected by soil-chemical processes such as oxidation of reduced Fe, elevated CO<sub>2</sub> pressures, and, in soils with appreciable amounts of clay, ion-exchange and clay-alkalinity reactions. In such situations, ranges of Na/Br ratios in pore water or groundwater affected by alkaline process fluids are characteristic of a refinery's alkaline process fluids, where bromide is mobilized in the Bayer process from organic matter in bauxite.

The concentration of Na in soil pore water and groundwater is affected mostly by alkaline process fluids but also by ion-exchange at clay surfaces and alkaline soil reactions plus the pore water extraction process. Although the concentration of Br is not affected by ion exchange or soil reactions, it can be affected by 'salt-sieving' through surface charges in clays in combination with size exclusion of Br ions relative to Cl ions. These processes can result in apparent increases of Cl/Br ratios in groundwater and in pore water, when extracted from clayey soils.

This paper discusses the problems commonly encountered in quantifying effects of alkaline process fluids in soils and groundwater and which require a thorough and careful comparison of resulting changes in pH, alkalinity and both Na/Cl and Cl/Br ratios.

## 1. Introduction

Investigations of the presence of alkaline process fluids in soils and groundwater from leaks and spills commonly employ analyses for alkalinity, pH and related parameters in pore water, extracted from soils, and in groundwater. However, alkalinity and pH can be affected by soil-chemical processes such as oxidation of reduced Fe, elevated CO<sub>2</sub> pressures, and, in soils with appreciable amounts of clay, ion-exchange and clay-alkalinity reactions (Gerritse and Thomas 2005). In such situations, and with the knowledge that bromide is mobilized in the Bayer process from organic matter in bauxite, ranges of Na/Br ratios in pore water and groundwater affected by alkaline process fluids can be characteristic of a refinery's processing of bauxite. Mass ratios of 0.56 and 290 commonly apply to Na/Cl and Cl/Br respectively in background water, giving a Na/Br ratio of about 160, reflecting the (marine) ratio in rainfall. Contributions to concentrations of Na and Br (=ΔX) from leaks and spills of process fluids then follow from:

$$[\Delta X] = [X] - R_o [Cl] \quad (1)$$

where: [X] is solution concentration and R<sub>o</sub> the marine X/Cl ratio (Gerritse *et al.* 1990)

Bromide and thus Na/Br mass ratios in process fluids from Alcoa's refineries in Western Australia have decreased over the years from about 800 to 100 with increasing organic matter content of the bauxite ore (Gerritse & George 1988).

This paper describes and discusses results of analyses of alkalinity, pH, Na, Br and Cl in relation to effects of process fluids on soils and

groundwater as part of two investigations to assess the integrity of the clay liners of two bauxite residue storage areas (RSAs) at Alcoa's operations in Western Australia. Concentrations of other elements such as As, Mo and F are also affected by process fluids either directly through accumulation from process fluids or indirectly through dissolution from soil and aquifer materials at elevated pH (Gerritse & Thomas 2005). These and other indicators of the presence of process fluids are not investigated in this paper.

## 2. Residue Storage Area - Case 1

### 2.1 Description

Eighteen drill holes were recently made on the embankments or dykes of an RSA at an Alcoa refinery in Western Australia into the underlying upper and lower superficial formations and soil and water samples were obtained. As shown on Figure 1 the drill holes were made close to or inbetween the locations of existing pairs of monitor bores into the upper and lower superficial formations. The results of this investigation are discussed in the next section. Locations in relation to the RSA and neighbouring RSAs and existing monitor bores are shown in Figure 1

Subsequently ten monitor bores were installed on the dykes of the southern section of the RSA into the underlying upper superficial formation close to the existing monitor bores (Figure 1) and groundwater was sampled from these bores. The results of the analyses of these groundwaters are discussed in Section 2.

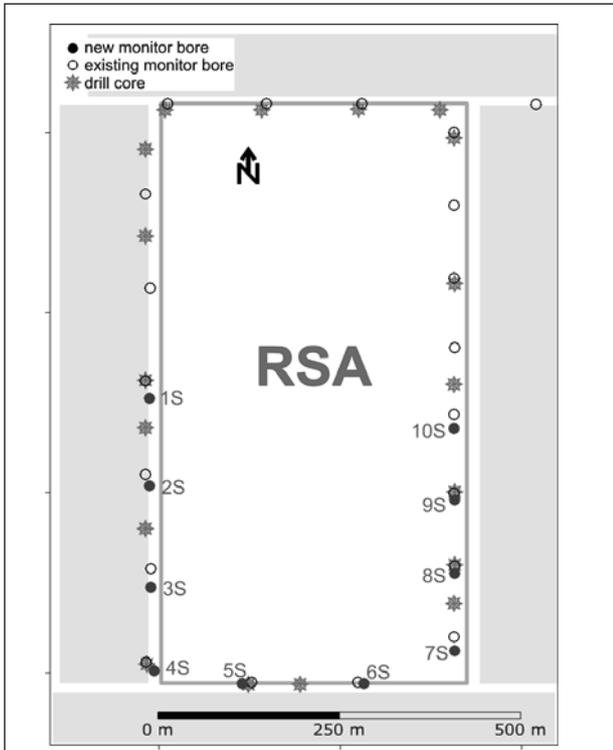


FIGURE 1 Locations of drill holes (stars), made close to or in between existing monitor bores (circles) on the embankments of the RSA at an Alcoa refinery in Western Australia, and new bores 1S to 10S (dots) installed near existing monitor bores in the southern section of the RSA. The grey area adjoining the RSA indicates neighbouring RSAs.

## 2.2 Results for Pore Water

Groundwater and extracts in water (10 g soil in 30 mL water) of pore water from soil sampled from drill holes on the dykes surrounding the RSA (Figure 1) were analysed for pH, Electrical Conductivity (EC), total alkalinity, Na, Cl and Br. Moisture content of soil samples was determined before extracting in water.

Na/Cl ratios in water extracts of materials containing clay increase significantly with increasing dilution through a shift in the ion exchange equilibria (Gerritse & Thomas 2005). The effect of increasing dilution through a shift in the ion-exchange equilibria on ratios of Na/Cl in water extracts of samples from soil cores from dykes and in groundwater from drill holes into the lower superficial formation at the RSA can be clearly seen in plots of Na/Cl ratios against Cl concentration in Figure 2, assuming decreasing Cl concentration to reflect increasing dilution. Na/Cl ratios and associated 'excess' concentrations of Na in extracts of core materials thus need not reflect the composition of pore water.

Ratios of Cl/Br in extracts are not affected by ion exchange and do not appear to be affected by dilution, though scatter of data increases at lower Cl concentrations. Cl/Br ratios in extracts can, however, be affected by 'ion size-exclusion' in clays. It is then possible that the larger Br ions are excluded from clays, while Cl ions are not. Thus upon extraction in water of clayey soil samples more Cl ends up in the extract relative to Br, when compared with the original pore water.

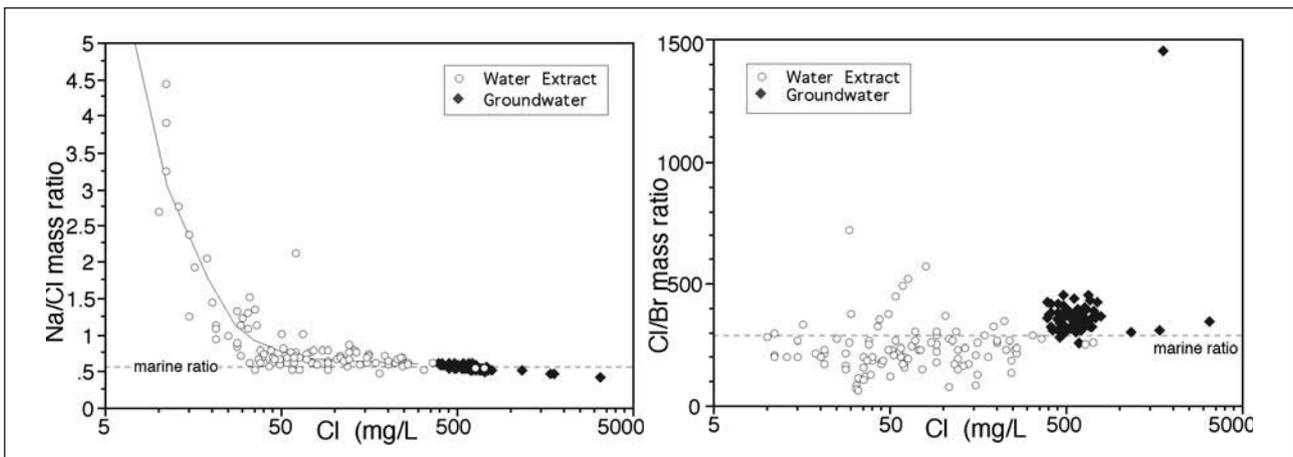


FIGURE 2 Plot against Cl concentrations of Na/Cl and Br/Cl ratios in pore water (from water extracts) and in groundwater sampled from drill holes near or in between monitor bores on dykes at the RSA (Figure 1). Dashed lines indicate the marine Na/Cl ratio.

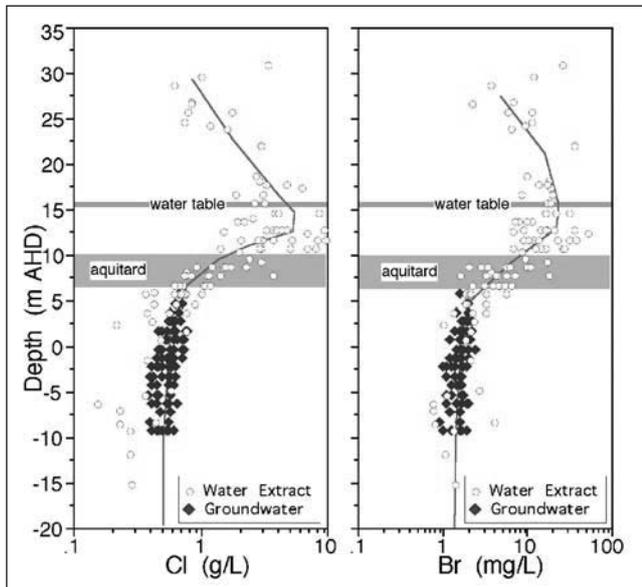


FIGURE 3 Plot against depth of concentrations of Cl and Br in pore water (from water extracts) and in groundwater from drill holes near or in between the monitor bores surrounding the RSA (Figure 1). Location of the aquitard at the dykes is approximate average as estimated from stratigraphic data. Line through data suggests trend

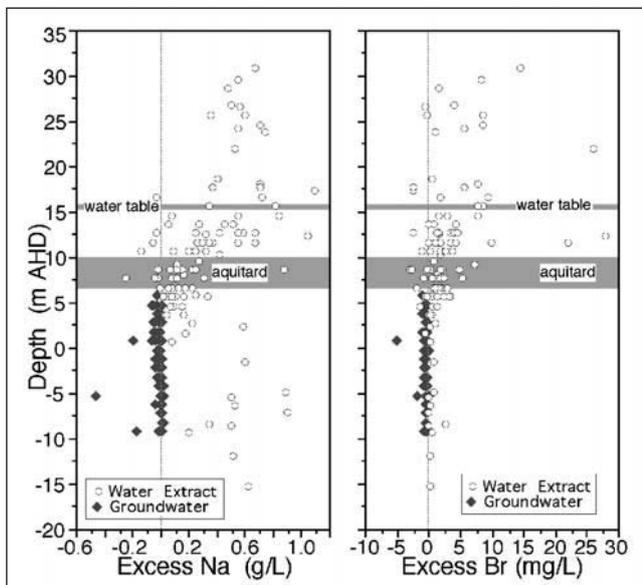


FIGURE 4 Plots against depth of excess concentrations of Na and Br in pore water (from water extracts) and in groundwater sampled from drill holes near or in between the monitor bores on dykes surrounding the RSA (Figure 1). Range of water table is indicated. Location of aquitard is approximate.

'Salt-sieving' is another process that can affect the distribution of Cl relative to Br ions in profiles of clayey soils. 'Salt-sieving' arises from a strong negative charge on the surface of clays, resulting in restriction and thus accumulation of Cl and Br ions and associated cations above the clay layer (Gerritse & Thomas 2008). Depth profiles of Cl and Br in pore waters (from water extracts) of soils and in groundwater from drill holes on the dykes surrounding the RSA are shown in Figure 3. Concentrations of Cl as well as Br peak in pore water in clayey soils above the aquitard. Ratios of Cl/Br are commonly lower above the aquitard than below, resulting in positive excess concentrations of Br above the aquitard and zero to negative excess concentrations below. Spatial variability in clay content would explain the large scatter in data.

Excess concentrations of Na and Br are commonly elevated throughout the profile in water extracts of pore water in soils sampled from the drill holes at the RSA. This is illustrated in Figure 4, where excess concentrations of Na and Br in pore waters, calculated with Equation 1, are plotted against depth of sampling. Concentrations in pore waters in Figures 4 are calculated from

concentrations in water extracts by multiplying with the ratio of water in the extract to moisture content of the soil sample following:

$$[\text{Na}]_{\text{PW}} = 3 [\text{Na}]_{\text{Extr}} / \theta \quad (2)$$

where:  $\theta$  is moisture content (L/kg soil),  $[\text{Na}]_{\text{Extr}}$  is concentration in water extract,  $[\text{Na}]_{\text{PW}}$  is concentration in pore water and '3' is the ratio (L/kg) of water to soil sample when extracting.

Data in Figure 4 also illustrate the effects of ion exchange reactions on concentrations of excess Na in pore water from soils after extraction with water. No effects of ion exchange are observed for Na in groundwater (only available during drilling from the less clayey and more sandy hence more permeable strata of the lower superficial formation), whereas Br is only affected above the aquitard in the more clayey soils of the upper superficial formation by 'size-exclusion' and/or 'salt-sieving'.

Other processes such as weathering of clay materials can also increase Na/Cl ratios, whereas processes involving soil organic matter can change the Cl/Br ratio (Gerritse & George 1988). Interpretation of Na/Cl and Cl/Br ratios and associated concentrations of excess Na and excess Br in terms of pore water or groundwater affected by refinery process fluids should thus always consider possible non-related contributions of ion-exchange and other reactions.

Note that increases in pore water and groundwater concentrations of 'excess Na' and of 'excess' Br from refinery process fluids follow the equation:

$$[\text{DNa}] \approx R \cdot [\text{DBr}] \quad (3)$$

where:  $[\text{DNa}]$  and  $[\text{DBr}]$  are 'excess' concentrations in mg/L (Section 1) and 'R' is their mass ratio in process fluids.

'R' in Equation 3 is about 740 for underdrainage from the RSA and about 110 for underdrainage from RSAs to the south and west of the RSA. Leachate from the RSA is from earlier operations with lower concentrations of Br and dissolved organic carbon (TOC).

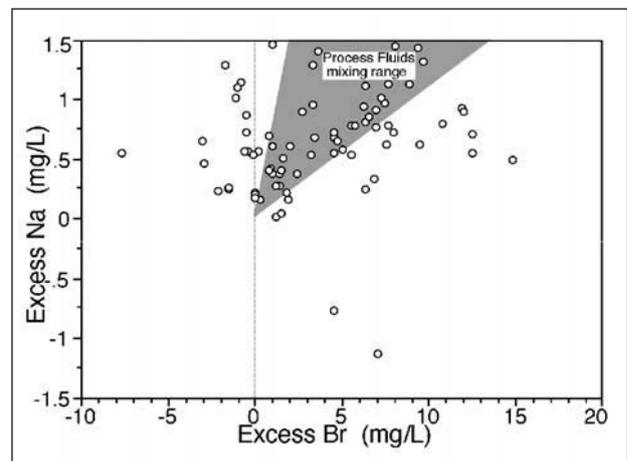


FIGURE 5 Plots of concentrations of 'excess' Na against 'excess' Br in pore waters calculated from water extracts of samples of soil cores (Equation 2) from dykes in the southern section of the RSA (Figure 1). Mixing lines expected for the range of Na/Br ratios in process fluids at the RSA are indicated by the shaded area and follow from Equation 3.

A plot in Figure 5 of 'excess' concentrations of Na and Br in pore water (from extracts in water) of soils at the RSA shows large scatter of data, resulting from the various processes in soils described above. Equation 3 can thus not always be relied on to represent effects of refinery process fluids.

The results of this investigation indicated that there was no detectable effect on groundwater in the lower superficial formation from alkaline process fluids. However, the uncertainties

associated with soil water extract data for soil samples from the upper superficial formation could not afford a definite conclusion about the presence of process fluids in this stratigraphic unit. This latter finding prompted a subsequent investigation discussed in the next section.

### 2.3 Groundwater from Upper Superficial Formation

Figure 6 contains plots of concentrations of Na, Ca, Mg and Br against Cl in groundwater sampled from the ten monitor bores recently installed on dykes in the southern section of the RSA into the upper superficial formation. From these plots it is noted that: groundwater concentrations of Na against Cl plot below the marine ratio in bores on the western and southern dykes, but follow the marine ratio in bores on the eastern dyke (7S, 8S, 9S, 10S); groundwater concentrations of Mg in all bores are well in excess of what would be expected for a marine Mg/Cl ratio; excess concentrations of Mg increase with Cl concentration; groundwater concentrations of Ca are also commonly greater than expected for a marine ratio in all bores and their excess concentrations tend to increase with Cl concentration, though data scatter is large; and ratios of Cl/Br are less than the marine ratio in all bores, except 3S.

Figure 7 shows that alkalinity ranges from 240 to 400 mg/L in groundwater from monitor bores 7S to 10S on the eastern dyke of the RSA (Figure 1) and from 80 to 140 mg/L in groundwater from the other monitor bores (1S to 6S) in the southwest corner of the RSA. However, no link with salinity (Cl) is evident. Salinities are elevated and highest in bores 3S, 4S and 6S.

Increases in groundwater concentrations of 'excess' Na and alkalinity from refinery process fluids follow the equation:

$$[DNa] = [ALK] - [ALK]_o \quad (4)$$

where: [DNa] is the 'excess' molar equivalent concentration of Na, [ALK] the molar equivalent concentration of alkalinity and [ALK]<sub>o</sub> background alkalinity.

Equations 3 and 4 assume conservative (=non-reactive=no adsorption, ion-exchange or precipitation) mixing behaviour. Ion exchange at the surface of clays affects the distribution of major cations in pore water and groundwater. This results in some of Na in solution being exchanged at the surface of clays for Mg and Ca. The sum of 'excess' concentrations of all cations should then be proportional to associated increases of alkalinity and Br.

Alkalinity can be affected by precipitation of Ca/Mg carbonates and oxidation of sulphides (acidification) or (alkalinization) reduction of SO<sub>4</sub> (Gerritse & Thomas 2005).

Equivalent concentrations of 'excess Na+Mg+Ca' are plotted separately in Figure 8 against alkalinity and 'excess Br'. Excess concentrations are calculated with mass ratios to chloride (R<sub>o</sub> in Equation 1) for Na, Mg, Ca and S-SO<sub>4</sub> of 0.56, 0.067, 0.021 and 0.047 respectively (Gerritse et al. 1990).

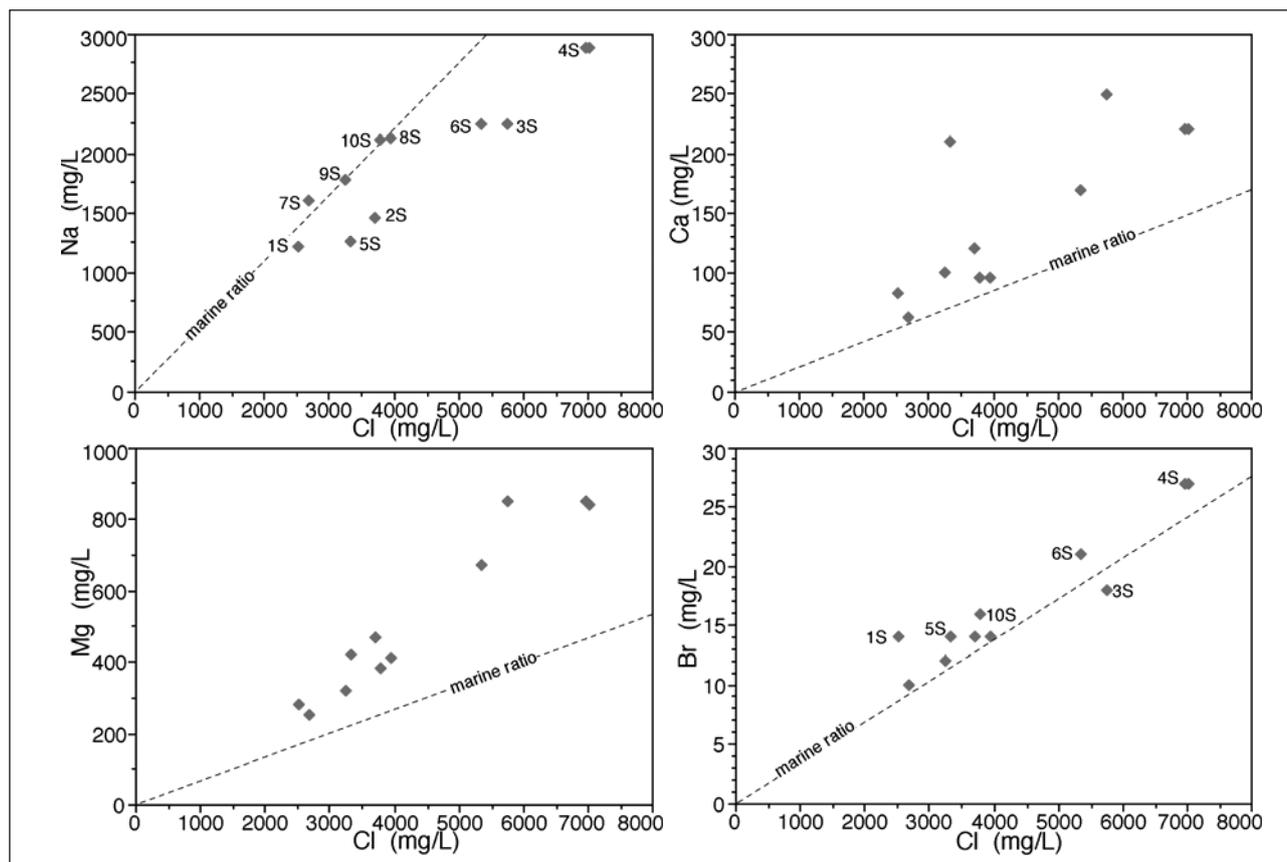


FIGURE 6 lots of concentrations of Na, Ca, Mg and Br against chloride in groundwater sampled from the new monitor bores on dykes in the southern section of the RSA (Figure 1). Dashed lines indicate data positions expected for a marine ratio.

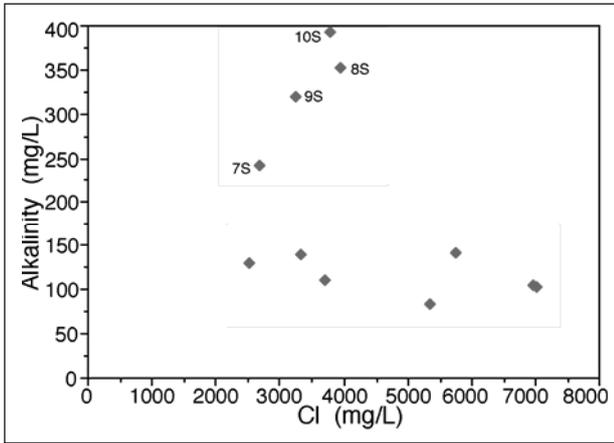


FIGURE 7 lot of alkalinity against Cl for groundwater sampled from the new monitor bores on dykes in the southern section of the RSA (Figure 1).

Data in Figure 8 indicate that in groundwater from monitor bores 7S, 8S, 9S and 10S on the eastern dyke of the RSA both alkalinity and concentrations of 'excess' cations are higher than in groundwater from monitor bores on the western and southern

dykes of the RSA (Figure 1). Data, however, show no clear relationships between 'excess' Br, alkalinity and concentrations of 'excess' cations in groundwater, expected for effects of process fluids on groundwater.

'Excess' concentrations of cations could reflect a non-marine composition of the saline groundwater. Concentrations of Cl in the regional superficial groundwater at the study site are commonly well below 2000 mg/L and no negative 'excess' concentrations of Na are observed, whereas concentrations of Cl in groundwater at the RSA (Figure 6) are well above 2000 mg/L. Data in Figures 6 and 8 suggest the possibility of a source of Cl, dominated by Mg and Ca as counter ions rather than Na. If this were the case, 'excess' concentrations of Br as plotted in Figure 8 (and calculated from data in Figure 6) could be wrong as the assumption of a marine Br/Cl ratio might then not apply.

Positive 'excess' concentrations of Br measured in groundwater samples from the superficial aquifer can also be affected by accumulation of Br relative to Cl through ion-exclusion or salt-sieving processes in clays above an aquitard between the superficial aquifer and underlying confined lower aquifer (see Section 2.2).

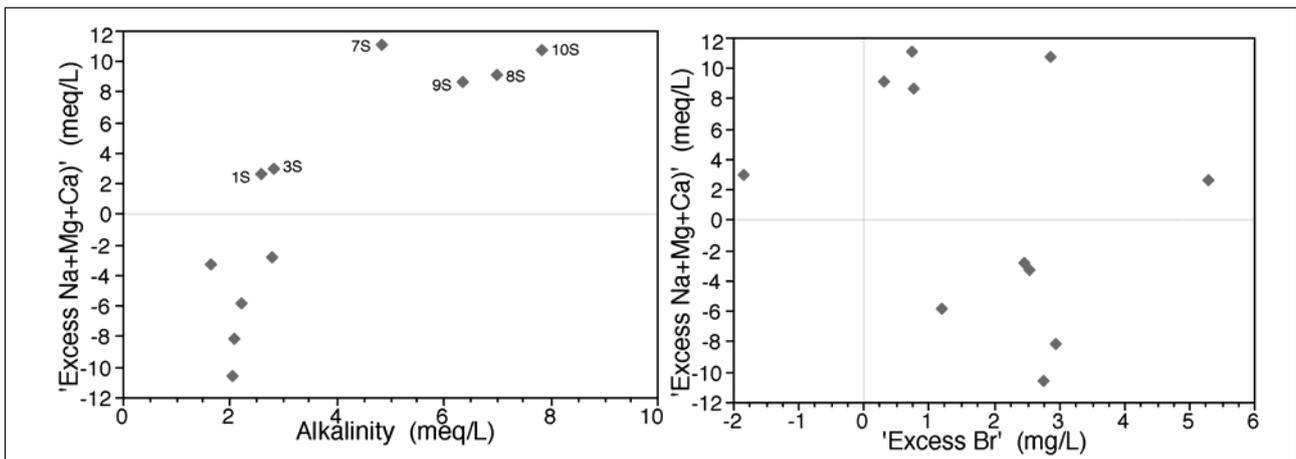


FIGURE 8 Plots of sum of 'excess' equivalent concentrations of 'Na+Mg+Ca' against alkalinity and 'excess' Br for groundwater sampled from the new monitor bores in the southern section of the RSA (Figure 1).

## 2.4 Findings

The above investigations indicated that groundwater sampled from the lower superficial formation in the drill holes showed no detectable effect from alkaline process fluids; and groundwaters from the newly installed monitor bores in the upper superficial formation had not been noticeably affected by alkaline process fluids. Uncertainties associated with soil water extract data for clayey soil samples, especially from the upper superficial formation, could not afford a definite conclusion about the presence of process fluids using soil water extracts and Na, Cl and Br data.

## 3. Residue Storage Area - Case 2

### 3.1 Description

Fourteen soil cores (T7 – T20) were drilled in an area up to about 300 m north of another RSA into the superficial formation at an Alcoa refinery in Western Australia. Locations of the drill holes in relation to the RSA and perimeter monitor bores are shown in Figure 9. Groundwater and soil materials were sampled in the field during drilling at intervals of between about 1 and 3 metres in order to obtain about 10 samples per drill hole. Soils were analysed for moisture content and extracted with demineralized water in a 1:3 moist soil:water weight ratio. Water extracts and groundwater were analysed for alkalinity, pH, EC, Na, Cl and Br. Groundwater sampled during the drilling was also monitored in the field for temperature, pH and EC.

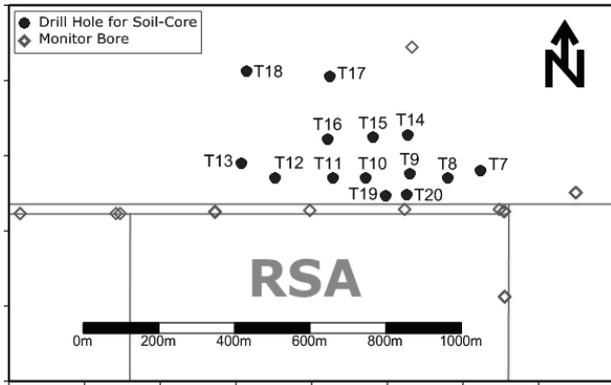


FIGURE 9 Locations of drill holes for soil cores and of surrounding monitor bores in the vicinity of the RSA at an Alcoa refinery in Western Australia.

### 3.2 Results

Concentrations of Na and Br in pore waters, calculated from water extracts of samples of soil cores (Equation 2) and samples of groundwater from the drilling, are plotted against Cl in Figure 10.

Significant excess concentrations of Br, however, mainly apply to groundwater samples only, whereas negative excess Br concentrations commonly apply to pore water. This is further illustrated in Figure 11, where Na/Cl and Cl/Br ratios and excess concentrations of Na and Br are plotted against depth of sampling in soil cores. Significant excess concentrations of both Na and Br in groundwater as well as pore water from water extracts are observed for samples from soil cores T19 and T20 at depths of between 6 and 8 m AHD (or about 8-10 m bgl), suggesting an effect of alkaline process fluids on groundwater at these locations and depths.

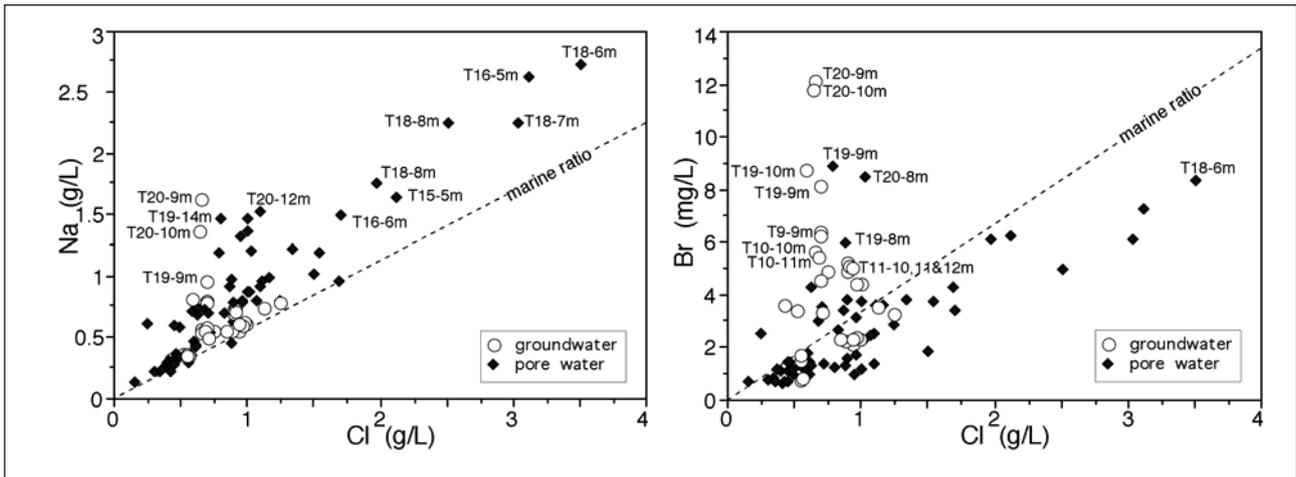


FIGURE 10 Plots of concentrations of Na and Br against Cl in pore waters (from water extracts) and in groundwater from drill holes in an area north of the RSA (Figure 9). Data are compared with marine Na/Cl and Br/Cl ratios, indicated by dashed lines. Suffixes indicate depth below ground level (m bgl).

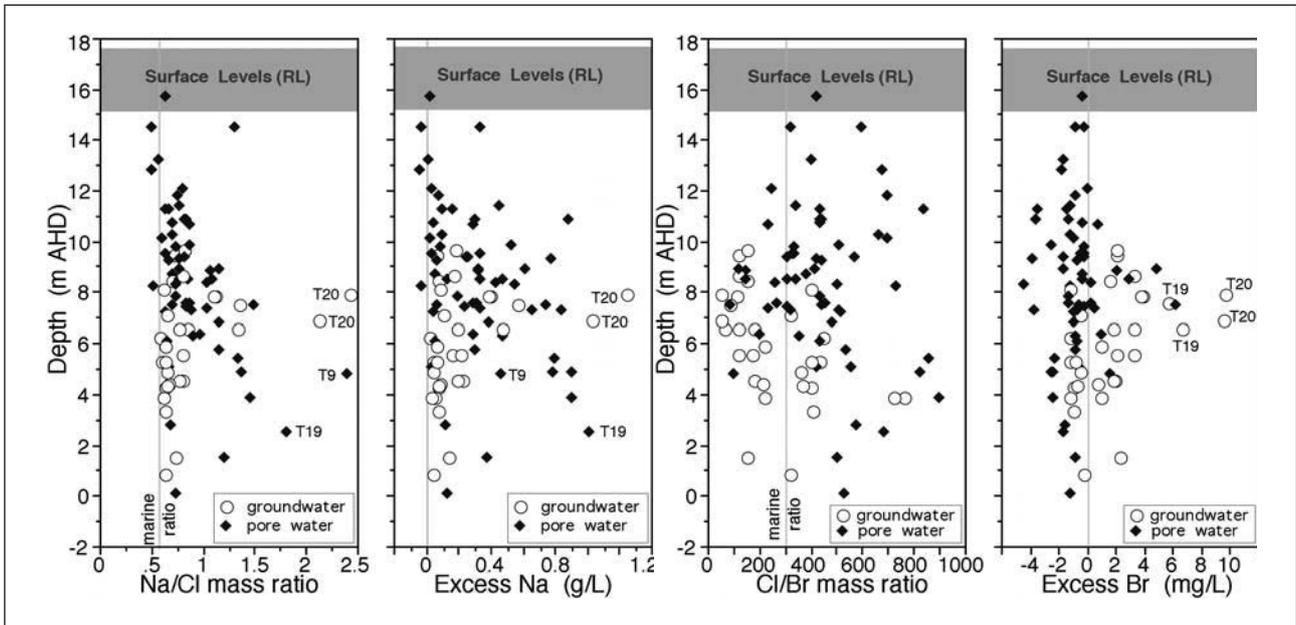


FIGURE 11 Plots against depth of Na/Cl and Cl/Br mass ratios and associated excess concentrations of Na and Br in pore waters (from water extracts) and in groundwater from drill holes in an area north of the RSA (Figure 9). Mass ratios are compared with marine ratios. Shaded area shows range of ground surface levels of the drill holes.

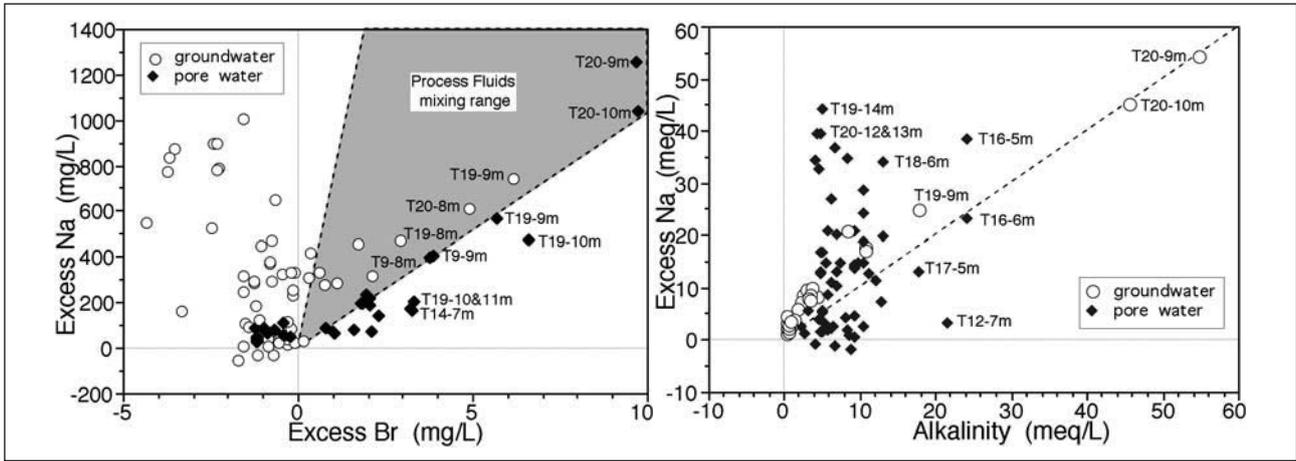


FIGURE 12 Plot of concentrations of 'excess' Br and 'excess' Na and of 'excess' Na and alkalinity in pore waters (from water extracts) and in groundwater from drill holes in an area north of the RSA (Figure 9). Shaded area is what can be expected for mixing with process fluids. Dashed line in alkalinity plot applies if alkalinity is from NaOH only and has not been affected by soil reactions.

A plot of 'excess' Br against 'excess' Na in Figure 12 suggests a link with effects of alkaline process fluids, particularly in groundwater samples from soil cores T9, T19 and T20. Concentrations of 'excess' Na in many pore waters as calculated from water extracts, however, are elevated but not related to any 'excess' Br. Concentrations of 'excess' Na in these pore waters can be considered an artifact of the soil water extraction process, as described in Section 2.2, resulting from a shift in ion-exchange equilibrium on extraction.

If derived from alkaline process fluids, equivalent concentrations of 'excess' Na and alkalinity should be equal. This is tested in a plot in Figure 12. 'Excess' Na is matched both by alkalinity and 'excess' Br most clearly in groundwater from soil cores T19 and T20. In a number of extracts 'excess' Na is affected to a varying extent by ion-exchange and alkalinity is affected by acid generated in core materials on storage from oxidation of pyrite ( $\text{pH} \ll 7$  in Figure 13; Gerritse & Thomas 2005). Acidification is indicated in Figure 13 for samples from soil cores T7, T8, T11, T19 and T20 at depths between 2 and 6 m AHD, suggesting presence of pyrite at these depths.

Groundwater pH measured in the laboratory is commonly higher than measured in the field, reflecting loss of  $\text{CO}_2$  from samples and associated increase in pH (Gerritse & Thomas 2005). The difference is particularly large for groundwater sampled from T20 at 9 m bgl (7.9 m AHD in Figure 13).

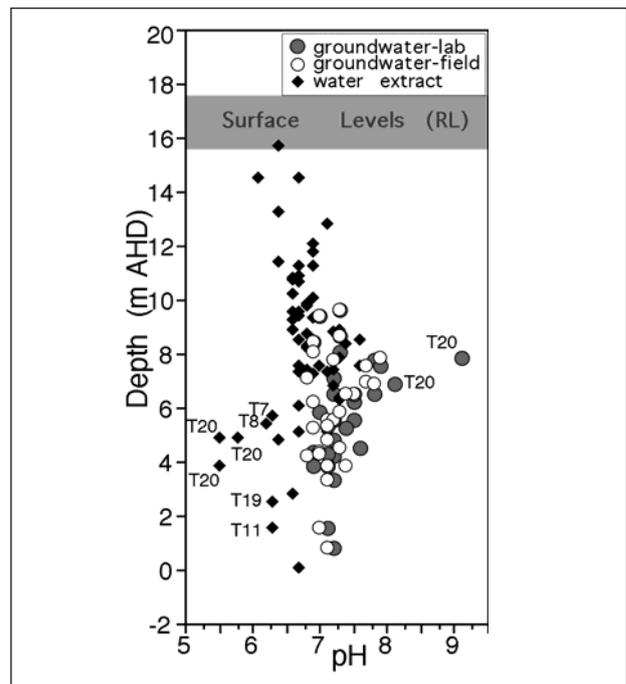


FIGURE 13 Depth profiles for pH, measured in the laboratory and in the field in pore waters (from water extracts) and groundwater sampled from drill holes north of the RSA (Figure 9). Shaded area gives the range of ground surface levels of the drill holes.

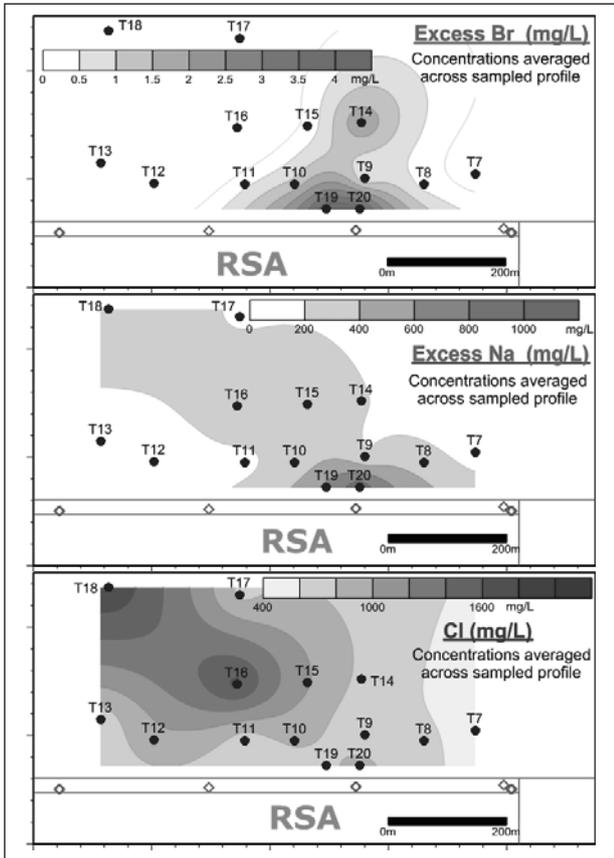


FIGURE 14 Contour plots for 'excess Br', 'excess Na' and Cl in pore waters (from water extracts) and groundwater sampled from drill holes north of the RSA. Concentrations, averaged across the sampled profile of each drill hole were 'kriged' and are shown as contours.

### Findings

Concentrations of 'excess' Br, 'excess' Na and Cl averaged across the sampled sections of the profiles of soil cores at the RSA are plotted as areal contour plots in Figure 14. Assuming 'excess' Br and Na to be proportional to effects of alkaline process fluids, as was concluded before from Figure 12, these areal plots indicate that effects of alkaline process fluids are evident at soil cores T19 and T20 and nearest neighbours. In all other soil cores 'excess' concentrations of Br are not significantly elevated and any 'excess' concentrations of Na in soil extracts, particularly in saline areas, are likely to have resulted from ion-exchange reactions and not from alkaline process fluids. 'Excess' concentrations of Br and Na (Figure 12) as well as pH (Figure 13) in soil cores T19 and T20 and nearest neighbours peak at depths from about 6 to 12 m bgl (10 to 4 m AHD). Elevated concentrations of 'excess' Br are readily seen in the profiles of 'excess' concentrations of Br for pore waters in the soil cores in Figure 15.

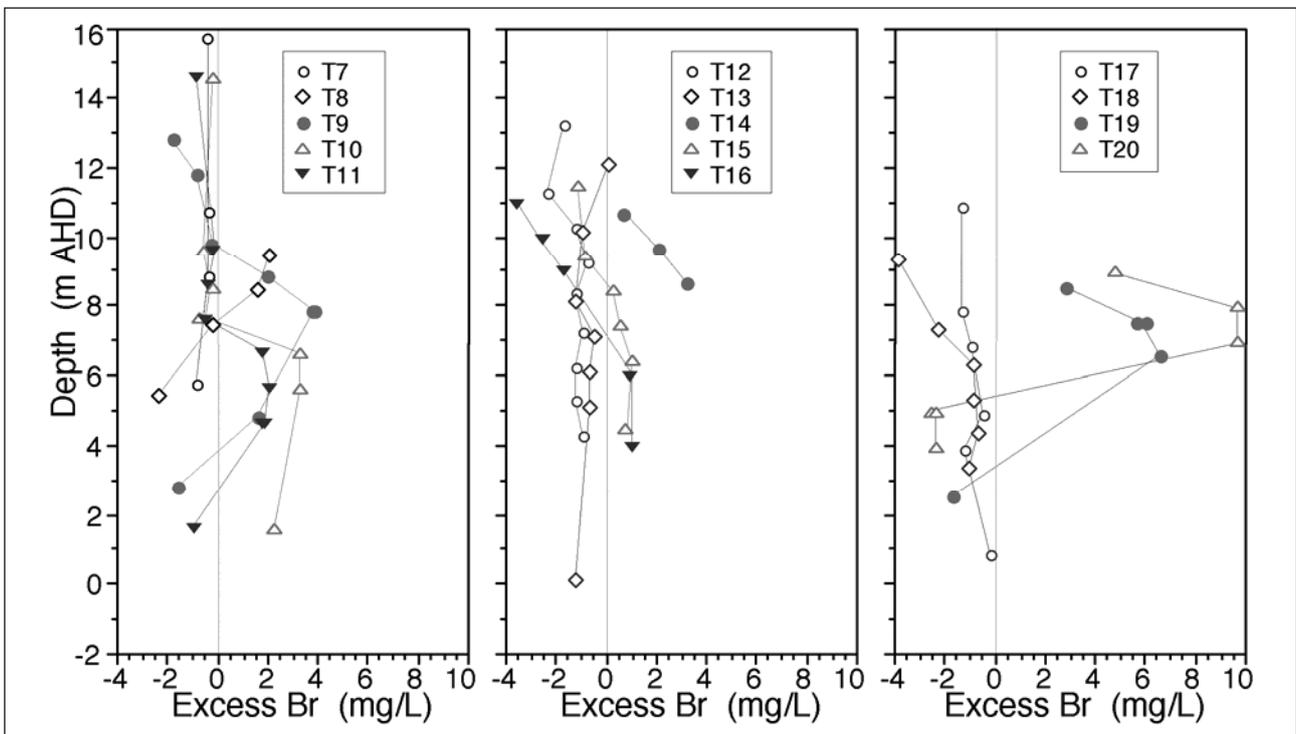


FIGURE 15 Depth profiles for 'excess' Br in pore water (from water extracts) and groundwater sampled from drill holes north of the RSA (Figure 9).

#### 4. Conclusions

Leaks and spills of alkaline process fluids in soils and groundwater increase alkalinity, pH and associated Na/Cl and Br/Cl ratios. Various processes, however, can mask and/or mimic any number of these increases, particularly when extracting pore water from clayey soils. Detection of effects of process fluids on soils and groundwater thus requires an evaluation all these increases. Examples discussed in Sections 2 and 3 illustrate this. Spatial variability of soil processes, particularly ion exchange reactions when extracting pore water, can be such that effects of alkaline process fluids at low levels cannot be unambiguously detected. Results for groundwater are more robust in this respect, but can also be affected by soil processes, such as weathering, ion exchange, 'salt sieving' and acid generated from pyrite oxidation.

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#### References

- Gerritse, RG & George, RJ 1988, 'The role of soil organic matter in the geochemical cycling of chloride and bromide', *Journal of Hydrology* vol. 101, pp. 83-95.
- Gerritse, RG, Barber, C & Adeney, .A 1990, *The Impact of Residential Urban Areas on the Quality of Groundwater in the Swan Coastal Plain of Western Australia*, Water Resources Series no. 3, CSIRO, Division of Water Resources.
- Gerritse, RG & Thomas, GA 2005, *Natural remediation of alkaline contamination of groundwater through buffering: Implications for management*, Proceedings 7th International Alumina Quality Workshop, 16-21 October, Perth, Western Australia.