Bromine geochemistry of British groundwaters

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Abstract

The concentrations of Br in potable groundwaters in the United Kingdom range from 60 to 340 μg l^{-1}. The occurrence of Br is described in terms of the Br/Cl weight ratio which enables small changes in bromide concentrations to be assessed in terms of salinity. Median values of Br/Cl in groundwaters range from 2.60 to 5.15×10^{-3} compared with a sea water ratio of 3.47×10^{-3}. In recent shallow groundwaters the Br/Cl ratio is rather variable in response to a range of natural and anthropogenic inputs (marine and industrial aerosols, industrial and agricultural chemicals including road salt). Some slight enrichment in Br/Cl also occurs naturally during infiltration as a result of biogeochemical processes.

Evolution of Br/Cl along groundwater flow lines reflects the sources of increasing salinity; either the influence of marine sedimentary formations or evaporites. The groundwaters in the Triassic sandstones of the English Midlands show significant Br depletion due to the evaporite source, in contrast to groundwaters in Cumbria. Br/Cl ratios in the Sherwood Sandstone of the East Midlands mainly reflect the natural input sources and can be used to help understand the palaeohydrology.

KEYWORDS: bromine, groundwaters, sandstones, United Kingdom.

Introduction

HYDROGEOCHEMICAL interest in bromine has centred principally on saline formation waters and brines where it may become enriched in solution during the precipitation of halite (Braitsch and Herrman, 1963; Collins, 1975). In saline formation waters, depletion or enrichment in bromide has been used to indicate respectively an association either with evaporites or with organic rich sediments in which bromine is typically enriched (Rittenhouse, 1967; Rittenhouse *et al.*, 1969). There has been relatively little work carried out on bromine in dilute natural waters partly due to the difficulty of obtaining reliable data at low concentrations. A nationwide study of surface waters in Sweden (Lundström and Olin, 1986) showed that the Br/Cl ratio (2.21×10^{-3}) was slightly depleted in Br compared to marine water. Bromine is released during the burning of fossil fuels and some interest has focused on atmospheric concentrations (Cawse, 1975, 1987). Under the field conditions of most natural waters, bromine occurs almost exclusively as the unassociated bromide ion (Br^-) and only under hypersaline conditions does it form significant complex ions. The geochemistry of bromine is intimately tied to the behaviour of chlorine and its hydrogeochemical behaviour is probably controlled more by physical than by chemical fractionations. Bromide (^{82}Br half life 1.5 days) has also been widely used as a tracer in groundwater studies on account of its mobility.

In dilute natural waters the main controls on the geochemistry of bromine are likely to relate to the source of salinity — atmospheric inputs, contact with or mixing with saline environments during groundwater flow, and the impact of pollution. Recently, interest in the occurrence of bromide has increased because of the conversion of bromide to bromoform (tribromomethane), a possible carcinogen, during ozonation as part of the water treatment process (Cooper *et al.*, 1986; Bourgine *et al.*, 1993). Chlorination can oxidise Br^- to Br_2 or HOBr with the possible production of tribromomethane (Flury and Papritz, 1993). On its own in natural waters Br poses no health problem.

In the present paper data are presented on the occurrence of bromide in the main UK aquifers in relation to possible natural and contaminant sources. As well as providing a review of the occurrence of

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bromide *per se*, these results are used to show how bromine can assist in understanding the origins of chloride within the hydrological cycle. In view of the similarity of the geochemical behaviour of Br and Cl it is important to use the Br/Cl ratio (expressed in this paper in weight rather than molar units) to identify significant anomalies in the natural environment.

Analytical methods and data sources

Most of the results have been obtained during studies by the author of the main British aquifers, either for water resources investigations or as part of work aimed at understanding the origins of saline formation waters. The occurrence of bromide in British aquifers was included in a survey of a wide range of trace elements (Edmunds *et al.*, 1989) which forms the principal data base used in this study. Published data for rainfall are also used in the study. For saline waters both published and unpublished sources are used.

Low level bromide was analysed mainly by automated colorimetry (Moxon and Dixon, 1980), although a few samples including saline waters and brines were analysed by neutron activation at AERE (Harwell). Chloride was analysed by automated colorimetry using mercuric thiocyanate.

Bromide in UK saline formation waters

The concentrations of bromide in saline groundwaters (having >1000 mg l^{-1} Cl) are summarised in Fig. 1*a* for waters from formations of U.Palaeozoic (Carboniferous) age. The bulk of these samples are from the Coal Measures strata of NE England (Edmunds, 1975) and were collected from now mainly abandoned working collieries. A few analyses are for samples of interstitial waters extracted from core material from exploration boreholes drilled into the Coal Measures of the English Midlands.

The brines in the NE England coalfield show considerable enrichment in Br/Cl ratios compared to sea water. These brines owe their enrichment in Br to prolonged interaction with the organic-rich Coal Measures strata including coals. In contrast to this main Br-enriched group a smaller group of depleted brines is found associated with the Permian sediments. This group has evolved most probably by reaction with halite which is Br-depleted. Brines in Permian strata which have drained into the Coal Measures strata during mine working can be clearly recognised as a mixing series in Fig. 1*a*.

Extensive studies of the geochemistry of formation waters and brines were carried out during the exploration for geothermal energy (Downing and Gray, 1986) during which bromide was used as a diagnostic element especially in aquifers of Mesozoic age. In the Wessex Basin, brines from the Sherwood Sandstone are strongly depleted in Br indicating that halite dissolution may have occurred. This dissolution could have taken place by various routes, two of which are illustrated in Fig. 1*b*. It is possible that freshwater entering the basin could become strongly enriched in Cl relative to Br. The data suggest however that an evolved seawater at some time in the past, probably during the Miocene, entered or was expelled into the aquifer and subsequently dissolved halite. Groundwaters from the Jurassic Sands in the Wessex basin have salinities about twice that of sea water. Some of this increase where the Br/Cl ratios exceed 1×10^{-3} must also be associated with waters that have dissolved halite. Other waters are relatively enriched in Br/Cl which suggests that marine connate water has evolved in situ, losing water on compaction and gaining bromine from the diagenesis of sedimentary organic matter.

Bromide in the principal aquifers of the UK

Rainfall inputs

The concentrations of bromide and chloride in rainfall and in total deposition have been monitored over a 9-year period at three rural sites in England and Wales (Cawse, 1987) and at Plynlimon Wales over a 5-year period (Neal *et al.*, 1990). These results are summarised in Table 1 together with values for sea water. All sites show an enrichment in Br/Cl above sea water with a value of 3.47×10^{-3}. An enrichment in bromine relative to chlorine is widely observed in marine aerosols probably as a result of lipid containing organic matter which is enriched at the sea surface (Duce and Hoffman, 1976). The rural sites in upland Wales and Cumbria have values of 4.19×10^{-3} and 5.23×10^{-3} respectively. An additional enrichment in Br/Cl is also found as a result of industrial pollution where coal burning produces bromine which is then deposited with rainfall. Thus the highest value of Br/Cl (6.30×10^{-3}) occurs at Styrrup, Notts which lies in the Trent valley close to the Sheffield industrial complex and near to a concentration of fossil-fuel-burning power stations.

Soils and the unsaturated zone

Several studies have noted that bromide is fractionated relative to chloride by vegetation. In the upper River Severn catchment (Wales) Br in streamflow shows no correlation with chloride (as compared with rainfall) and this is interpreted to mean that seasonal cycling is taking place in the subsuface environment (Neal *et al.*, 1990). Field and experimental results for groundwater from Western Australia also indicate

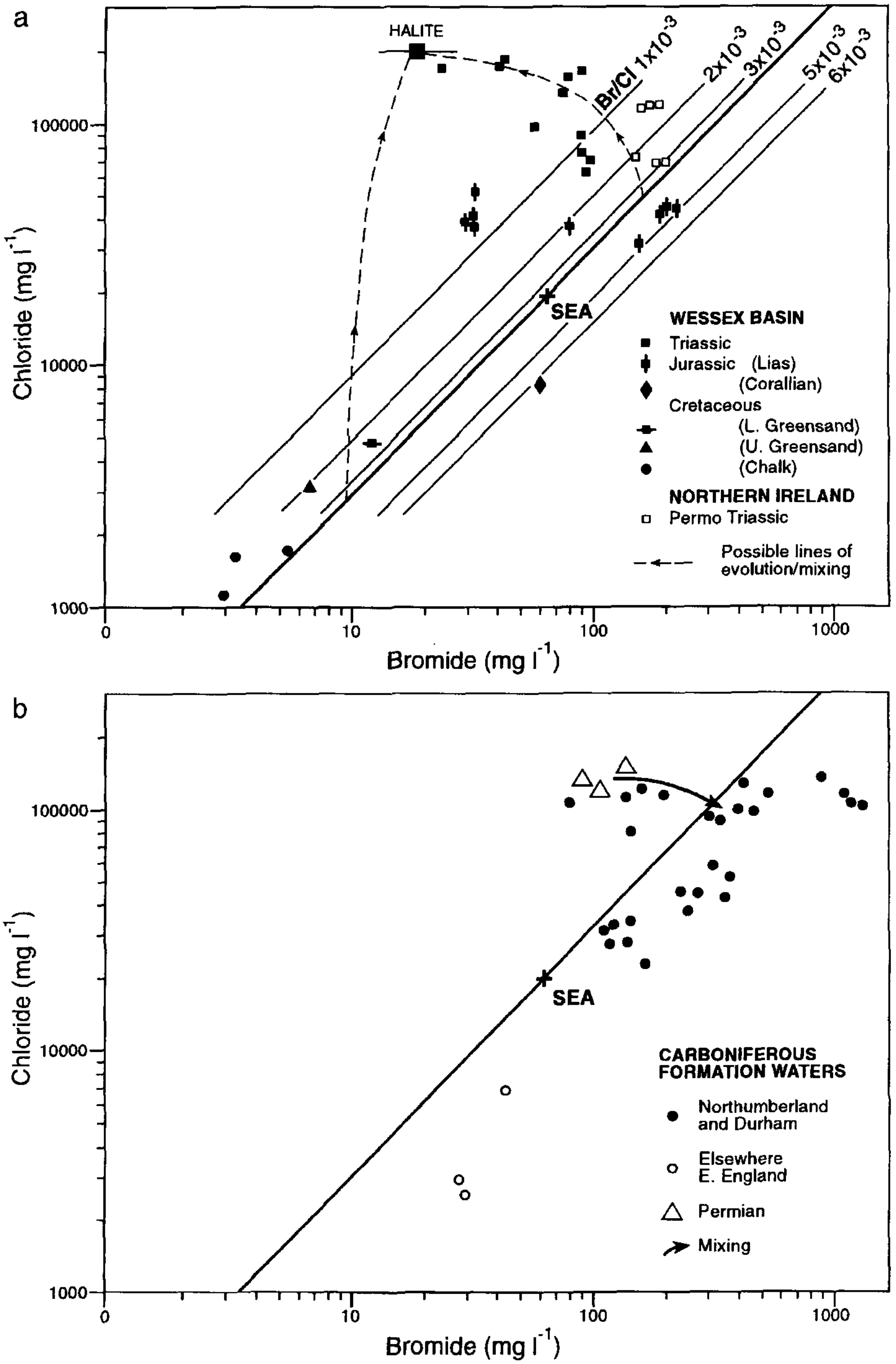

FIG. 1. Bromide *vs.*chloride in formation waters of the UK in relation to sea water: (*a*) Mesozoic basins — lines of equal Br/Cl (weight) ratio are shown, also mixing lines for possible evolution of Br-depleted brines from either brackish water or saline water (*b*) Carboniferous basins — brines from Permian strata in the Northumberland – Durham area are shown with probable lines of mixing with formation waters in underlying Carboniferous strata.

TABLE 1. Weighted mean bromide in UK rainfall and sea water. [1] denotes data from Cawse (1987) and [2] data from Neal *et al.* (1990)

Station	Br	Cl	Br/Cl
Styrrup (Notts)[1] 1972–1981	0.0500	7.93	6.30×10^{-3}
Chilton (Oxon)[1] 1972–1981	0.0298	6.27	4.75×10^{-3}
Wraymires (Cumbria) [1] 1972–1981	0.0215	4.11	5.23×10^{-3}
Plynlimon (Wales)[2]	0.0194	4.63	4.19×10^{-3}
Sea water	67	19300	3.47×10^{-3}

that bromide is enriched in organic horizons and is subsequently released on breakdown (Gerritse and George, 1988). In the UK the only data available are from the unsaturated zone of the Chalk at Black Wood (Hampshire) beneath deciduous forest where the Br is significantly enriched with respect to Cl (Br/Cl = 7.56×10^{-3}), (Kinniburgh, pers. comm.).

Aquifers in the UK

Bromide and chloride were determined in representative areas and/or along flow lines in all the principal British aquifers and the minimum, median and maximum concentrations are summarised by aquifer in Table 2. The median concentrations of Br in UK groundwaters (including all sources judged as potable supplies but excluding saline sources) range from 60 to 183 µg l^{-1}. The overall composition relative to sea water, rainfall and unsaturated zone groundwater can be seen in Fig. 2. At low salinities there is a wide scatter which must be partly a reflection of regional differences in the input Br/Cl values. However, there is a tendency for bromide to become depleted relative to rainfall and also in relation to the sea water line, in groundwaters at low salinities (Cl<30mg l^{-1}). This may indicate that during infiltration bromide has been selectively removed by vegetation, or in some cases that a contaminant source with low Br/Cl ratios (road salt or agricultural fertilisers) has contributed to the chloride pool. Concentrations above 50 mg l^{-1} Cl are likely to reflect processes taking place in the aquifer, rather than effects that have occurred solely as a result of inputs or processes taking place during

TABLE 2. Bromide in UK groundwaters, summarised from Edmunds *et al.*, (1989). r^2 is the linear correlation coefficient squared for a regression of Br *vs.* Cl

Aquifer	Bromide (mg l^{-1}) Min	Median	Max	Chloride (Median)	Br/Cl $\times 10^{-3}$	r^2 (Br/Cl)
Chalk (Berks)	0.020	0.067	1.140	17.7	3.78	0.95
Chalk (London)	0.045	0.183	0.620	42.0	4.35	0.98
Lincolnshire Limestone (W)	0.086	0.132	0.190	31.2	4.23	0.34
Lincolnshire Limestone (E)	0.079	0.183	3.47	72	4.72	0.99
Millstone Grit	0.040	0.070	0.108	13.6	5.15	0.76
Carboniferous Limestone	0.053	0.068	0.134	15.6	4.34	0.79
Lower Greensand	0.030	0.056	0.124	14.0	4.00	0.94
Wealden	0.066	0.100	0.180	28.0	3.57	0.96
Sherwood Sandstone—Shropshire	0.016	0.060	0.330	23.0	2.60	0.56
Sherwood Sandstone—W Midlands	0.037	0.080	0.200	28.0	2.85	0.61
Sherwood Sandstone—Lancs/Cheshire	0.048	0.080	0.190	26.5	3.02	0.92
Sherwood Sandstone—Cumbria	0.046	0.074	0.293	24.2	3.96	0.83
Carboniferous—Shropshire	0.048	0.091	7.30	34.0	2.67	0.84
Old Red Sandstone—Moray	0.052	0.131	2.70	39.2	3.34	0.89

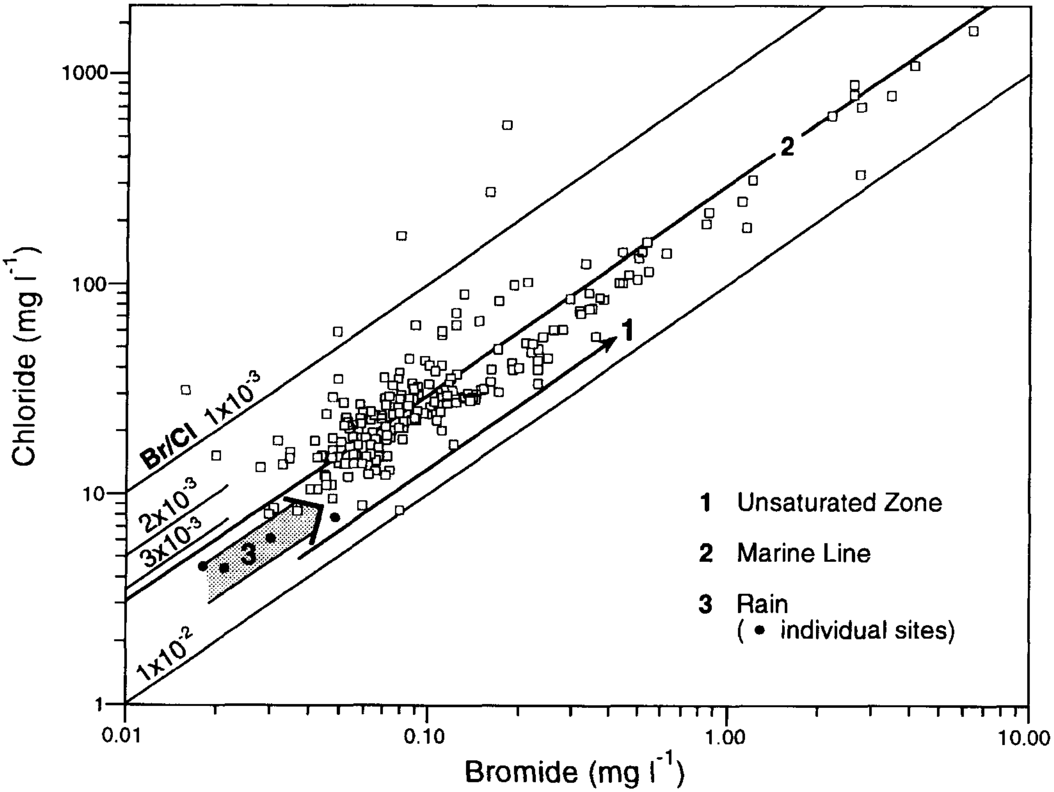

FIG. 2. Bromide/chloride relationships in all U.K. groundwaters relative to Br/Cl ratio in sea water, in rain (data from Table 1) and in the unsaturated zone.

evapotranspiration and recharge. Two distinct trends can therefore be recognised at salinities >50 mg l^{-1} Cl: a) strong bromide depletion to Br/Cl ratios below 1×10^{-3} signifying the dissolution or addition of chloride from an evaporite source and b) an increase of Cl within a narrow range in Br/Cl ratio (3×10^{-3} – 5×10^{-3}) and generally slightly above the marine ratio. This indicates the addition of both Br and Cl from a residual marine source, typically traces of chloride associated with marine formations, the slight Br enrichment above sea water being maintained by the diagenesis of organic matter.

The Br data are shown by aquifer as cumulative frequency diagrams in Fig. 3 and in terms of the Br/Cl ratio in Fig. 4. The Br cumulative frequency diagram emphasizes the net increase in Br in UK aquifers above rainfall input concentrations as a result of evapotranspiration. In most aquifers the total Br concentrations do not exceed 0.1 mg l^{-1} and in others it is only the upper ten percentile in which an overall increase in salinity causes the increase in Br. The increase in Br with increasing salinity is most apparent in the Jurassic (Lincolnshire) limestone in which the bromide is likely to be derived from organic matter.

The Br occurrence is best described in terms of the Br/Cl ratio (Fig. 4). This illustrates that groundwaters in the Triassic sandstones in Shropshire, Worcestershire, Cheshire and Lancashire all have low values for Br/Cl and have gained chloride from interaction with a sedimentary source containing halite. This might be by mixing with small amounts of saline water from overlying formations or by direct contact with evaporites. In contrast, the groundwaters from the Carlisle Basin and adjacent areas show a relative enrichment in Br compared with other formations. This is almost certain to indicate that there is no influence from evaporites on the groundwater sources. The thick evaporites of southern Britain are indeed absent here, although some halite is locally to be found in the Stanwix shales of northern Cumbria. The higher Br/Cl ratios probably indicate that some other regional influence, possibly organic material in the drift deposits, or groundwater recharge from the surrounding, mainly Carboniferous, catchments is dominant.

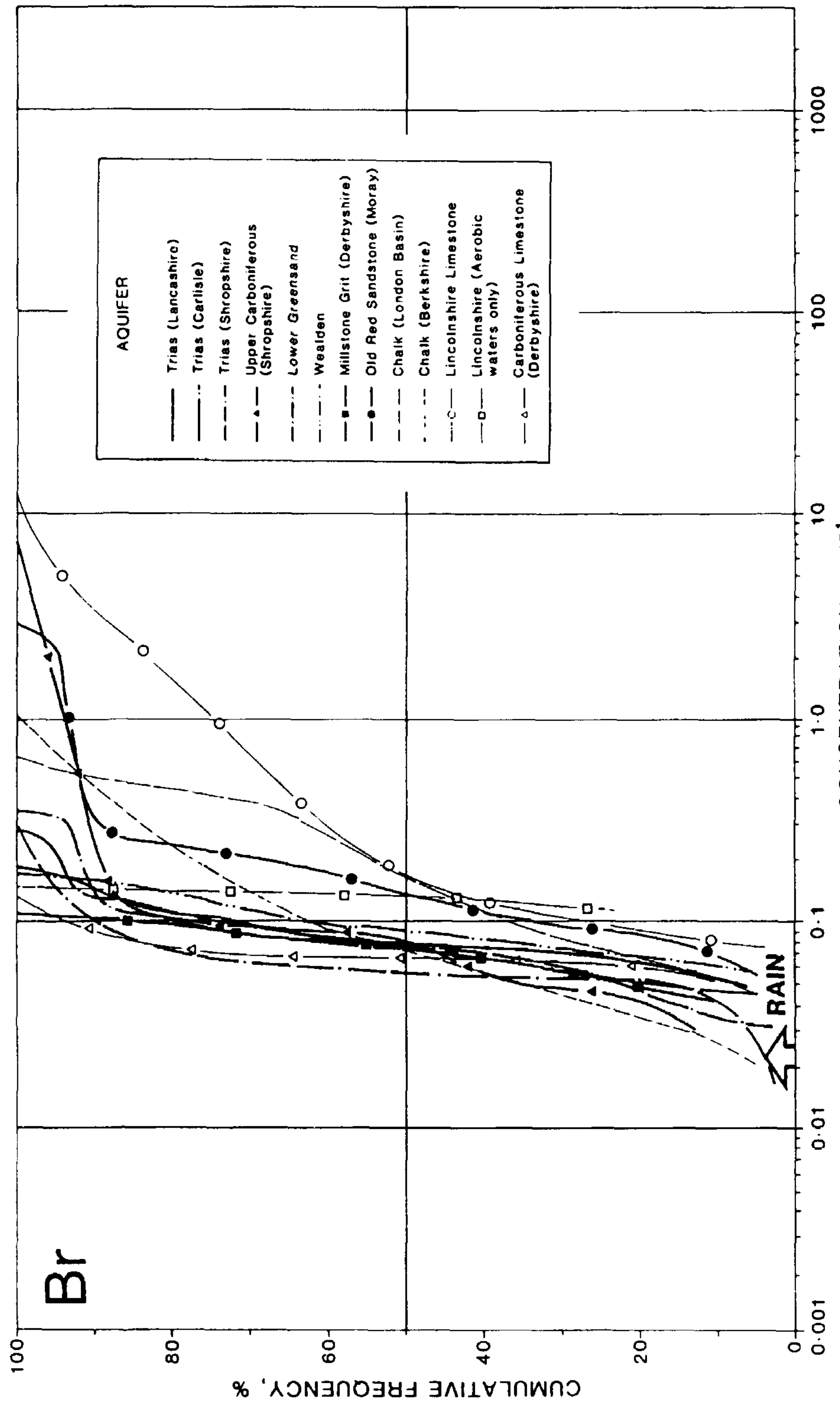

Fig. 3. Cumulative frequency diagram showing the occurrence of bromide in the main UK aquifers.

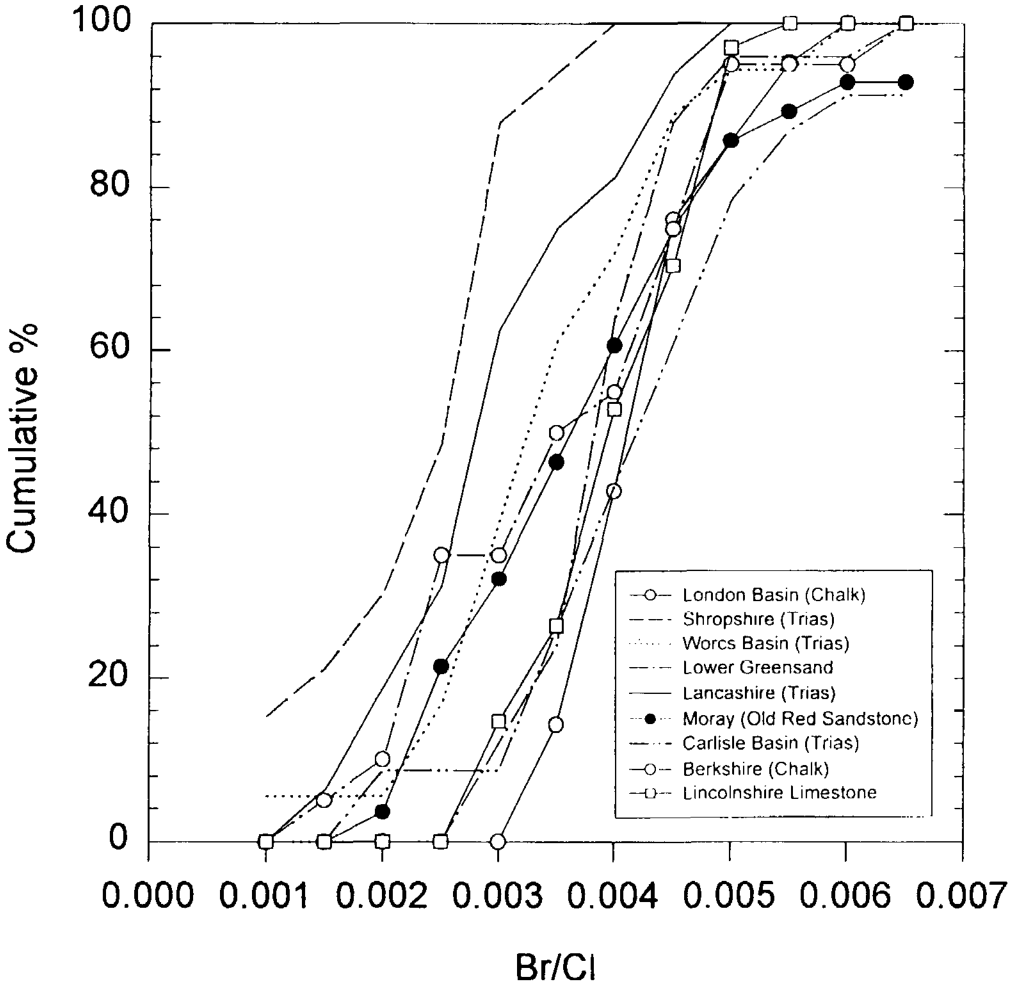

FIG. 4. Cumulative frequency diagram showing the Br/Cl ratios for major U.K. aquifers.

Bromide in the East Midlands Sherwood Sandstone aquifer — a case study

The East Midlands Sherwood Sandstone aquifer is probably the best understood of all UK aquifers having been the subject of intensive hydrogeochemical study (Bath *et al.*, 1979; Edmunds *et al.*, 1982; Andrews *et al.*, 1983, 1994). This background gives an excellent framework against which to follow the geochemistry of bromine. The Sherwood Sandstone aquifer dips uniformly eastwards and it is possible to examine the hydrogeochemical changes over a distance of some 30 km. The earlier studies have shown, using various stable and radioisotope data, that the groundwaters are of remarkably good quality and contain a record of inputs over at least the past 30 000 yr. The results for bromide are shown (Fig. 5) as Br/Cl ratios in comparison with Cl which has been used to indicate the recharge history of the aquifer; the data are plotted against groundwater temperature which serves as a proxy for distance/depth of groundwater circulation.

The extent of migration of modern (post-industrial age) waters is illustrated by Cl where concentrations of 50–300 mg l^{-1} are well above present day rainfall (see Table 1—Styrrup which is within the area) after allowing for evapotranspiration which would concentrate rain by a factor of about 2.5 to give an input Cl of 20 mg l^{-1}. The older groundwaters mainly have Cl concentrations much lower than the modern recharge, some <10 mg l^{-1}. These values almost certainly reflect natural input concentrations from rainfall

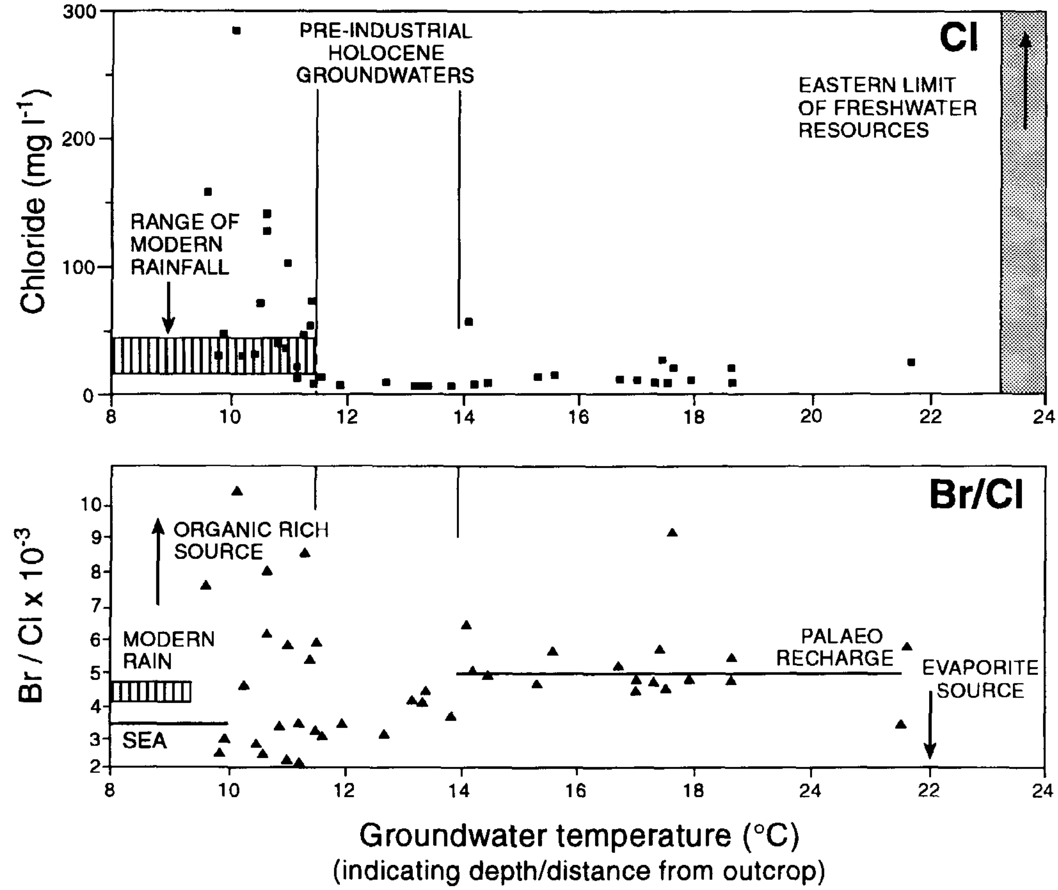

FIG. 5. Cl and Br/Cl in the East Midlands Triassic aquifer. Data plotted against temperature as a proxy for distance from recharge area/depth.

during the late Pleistocene and Holocene. Chloride contributions from water-rock interaction are absent over a flow distance of some 30km until east of the Trent Valley.

The Br/Cl ratios of groundwater at outcrop are highly variable which must reflect a variety of input sources as well as mixing between these. Some of the scatter is due to rainfall which in the past 200 years is likely to have been higher than the baseline value for maritime rain as a result of industrial pollution. Br/Cl values exceed the highest expected for rainfall in several high chloride waters. For these sources the high Br indicates contamination from Coal Measures strata in the form of colliery drainage locally recharging the aquifer via surface waters. Some of the groundwaters with low Br/Cl may have a small contribution of Cl from road salt or from agricultural chemicals. The Br/Cl in the older groundwaters, in contrast, is relatively constant (5×10^{-3}) and, significantly, does not vary with distance or depth along the line of flow. This implies that the input signal is retained. Interpretation of this must be speculative but a higher Br/Cl ratio during late Pleistocene/Early Holocene could correlate with more continental conditions and a less maritime influence in the source of rain since Br/Cl tends to increase with time, altitude and distance as air masses pass over continents (Winchester and Duce, 1967). Alternatively the Br increase could be due to organic enrichment from a denser vegetation cover than at the present day.

Conclusions

The concentrations of Br in UK potable waters range from 16 to 7300 $\mu g\ l^{-1}$ (with median concentrations in individual aquifers ranging from 60–183 μg l^{-1}; this variation is closely related to chloride. The Br/Cl ratio may vary over an order of magnitude and these variations can be used to distinguish the origins of the input chloride as well as the geochemical evolution of groundwater. Some of the largest differences in Br/Cl reflect the inputs either from rainfall or from pollutant sources. It is clear from groundwater in the East Midlands Sherwood Sandstone aquifer that present day concentrations of both Cl and Br in groundwaters are significantly higher than the pre-industrial baseline.

It is also apparent that slight enrichment in Br relative to Cl occurs during infiltration and that this may be due to the decay of organic matter which is selectively enriched in Br. Once in the aquifer system and once the input signals have homogenised by dispersion, the Br/Cl ratios are more uniform. Characteristic Br/Cl ratios can be identified for the main UK aquifers which reflect either the marine origin of the sedimentary rock or the influence of evaporites. The most Br-depleted groundwaters in the UK are found in the Triassic sandstone aquifers of the English Midlands although this depletion is not observed in the same aquifers in Cumbria where recharge has been influenced by contact with Carboniferous strata. Natural concentrations in UK groundwaters do not pose any problems with respect to health.

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