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A hydrochemical basis for managing manganese in water supplies from upland basins

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Abstract Manganese (Mn) concentrations exceeding the EC limit (0.05 mg l^{-1}) occur in potable waters supplied from many UK upland basins. Mn removal from raw waters is costly so basin management strategies for Mn control are sought. Streamwater chemistry and discharge were monitored in two basins (HS4 and HS7) within a UK upland water-gathering ground. Cluster analysis, factor analysis and chemical mixing model techniques enabled the timing, sources and hydrological pathways of Mn to be deduced. Elevated Mn concentrations (>0.350 mg l^{-1}) occur at HS4 in summer low flows arising from baseflow sources. At HS7, autumn storms contain maximum Mn, associated with flushing of soil stores. Chemical mixing models show that deep water accounts for 82% of Mn in runoff from HS4 but $<1\%$ at HS7. Contrasting Mn behaviour in HS4 and HS7 demonstrates that basin management requires an extensive knowledge base due to the variability of hydrochemical processes.

INTRODUCTION

The transition metal Mn occurs in two main forms in the environment: soluble Mn(II) and insoluble Mn(IV). Reduction and oxidation reactions govern the behaviour of Mn in soil and water, favouring formation of Mn(II) in groundwater (Jaudon *et al.*, 1989) and also in reducing, acidic soil conditions (Gotoh & Patrick, 1972). The EC Drinking Water Directive (EC, 1980) set the mandatory maximum admissible concentration (MAC) for Mn in drinking water at 0.05 mg l^{-1}. Mn concentrations in excess of the MAC can cause aesthetic and structural difficulties, e.g. deposition on pipeline surfaces (Sly *et al.*, 1990), and have also been associated with adverse neurological effects (Kondakis *et al.*, 1989).

Undesirable Mn levels are a particular problem in the UK in surface drinking water supplies obtained from upland basins where soil conditions favour Mn mobilization. In Scotland, where over 97% of water supply is obtained from surface runoff, Mn concentrations exceed the MAC (0.05 mg l^{-1}) in 8.84% of water supply zones (Scottish Office, 1993).

Removal of undesirable Mn from drinking water by conventional chemical and physical treatment processes is costly because powerful oxidants, such as potassium permanganate or ozone, are required (AWWA, 1993). Biological water treatment plants appear to be more effective in removing Mn but are not widespread (Mouchet, 1992). Source control measures within upland water supply basins have the potential to provide a long-term solution.

Two basin management strategies may be adopted:

(1) Exclusion of raw waters with undesirable Mn concentrations from the water supply system, using intake regulation structures. This requires predictions of where and when Mn levels above 0.05 mg l^{-1} will occur in runoff in the absence of underlying water treatment capacity. McDonald *et al.* (1989) assessed the impacts on water quality and yield of operating a similar policy to lower the colour of raw waters and their work could be applied to Mn concentrations.

(2) Implementation of land uses and land management practices which minimize the movement of Mn into runoff, necessitating an understanding of mobilization processes. Kay & Stoner (1988) examined relationships between land use and Mn in runoff in 13 upland basins in Wales but did not conduct process studies.

Mn has been neglected in hydrological studies of upland drainage basins yet information on the timing and processes of Mn mobilization underpins effective basin management for water quality control. A hydrochemical basis for managing Mn is investigated in this paper for a UK upland water supply basin.

METHODOLOGY

The How Stean drainage basin is an important upland water-gathering ground in northern England, supplying drinking water for the West Yorkshire conurbation and the city of Bradford. Runoff from the How Stean and In Moor basins is diverted by intake structures into an aqueduct which feeds Scar House Reservoir (Fig. 1). From here, water is transferred by tunnel and gravity flows to a number of water treatment works, including Chellow Heights treatment works, Bradford. Mn concentrations in the raw waters received at this works exceeded the MAC in 50% of measurements in the 12 year period, 1979-1992 (Heal, 1996).

Two sub-basins of the How Stean basin, HS4 and HS7, were monitored from September 1993 to December 1994. HS4 has an area of 0.402 km^2 , is drained by a second order stream and 1.3% of the basin is underlain by peat. A third order stream drains the HS7 basin, and 91.1% of the 1.493 km^2 area consists of peat. Both sub-basins are used as rough pasture and about 1.5 km length of ditches have been dug in each to improve drainage (Martin, 1992). Discharge was measured with 90° V-notch weirs and stage recorders. About 2000 streamwater samples were analysed for pH, Eh, specific conductance, colour, Mn, Fe, Al, Ca, Mg, fluoride, chloride, nitrate, sulphate and phosphate. Mn sources and mobilization processes were identified from hydrochemical analysis of streamwater data.

RESULTS AND DISCUSSION

Timing of Mn concentrations in runoff

Clusters of streamwater observations with similar chemistries are formed from partitioning cluster analysis of the HS4 and HS7 1994 datasets (after Duysings *et al.*, 1983). Each cluster is associated with specific hydrochemical conditions, and mean

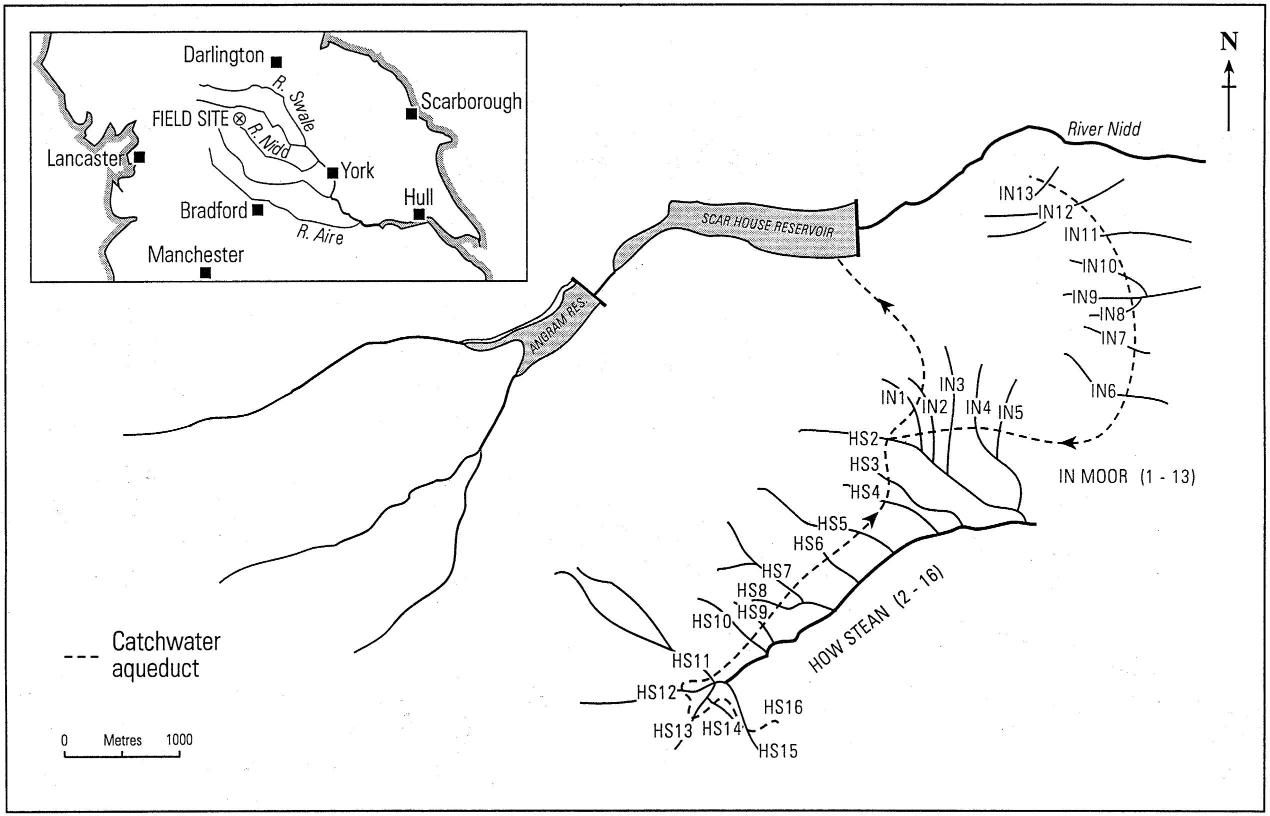

Fig. 1 Map of the How Stean drainage basin and intake system, Yorkshire, UK.

Table 1 Results and interpretation of clusters formed from partitioning cluster analysis of HS4 and HS7 1994 streamwater chemistry data.

Hydrological interpretation	Mean Mn concentration (mg l^{-1})	Mean discharge ($l\ s^{-1}$)	*n*
HS4			
Winter storms (peak flow)	0.127	22.184	88
Winter storms (basin soils saturated)	0.122	17.276	4
Winter and spring storms (rising limb)	0.123	13.600	110
Spring and autumn storms	0.139	12.350	293
Autumn flush	0.245	13.374	124
Flush of salts from soil surface	0.281	7.140	6
Summer baseflow	0.268	0.408	124
Extreme summer baseflow	0.438	0.143	29
Anomaly	0.415	0.154	1
HS7			
Winter storms (basin soils saturated)	0.061	115.822	113
Winter storms (basin soils unsaturated)	0.068	71.613	152
Autumn and winter storms (recession limb)	0.102	35.428	112
Spring storms (recession limb)	0.070	40.892	41
Summer storm (basin soils unsaturated)	0.033	3.114	2
Autumn flush	0.128	41.482	104
Summer baseflow	0.073	7.152	76
Extreme summer baseflow	0.075	2.251	101
Anomaly	0.051	4.945	2
Anomaly	0.309	62.698	2

Mn concentrations and discharges of all the clusters identified for HS4 and HS7 are shown in Table 1. At HS4, maximum annual Mn concentrations occur in the cluster interpreted as extreme summer baseflow, whilst at HS7 elevated Mn levels were measured in the autumn flush cluster.

Sources of Mn in runoff

Sources of Mn in runoff were identified from factor analysis of the 1994 streamwater chemical datasets for HS4 and HS7, using a Varimax rotation. Five factors with eigenvalues greater than one were extracted for each dataset, and factor loadings are shown in Tables 2 and 3. At HS4 the highest Mn loading is in Factor 1, interpreted as baseflow inputs due to the high loadings on calcium, magnesium and pH. Elevated Mn concentrations probably arise from soil profile weathering in this basin. High Mn loadings occur in Factors 2 and 5 at HS7 which appear to represent flushing of colour, iron, aluminium and nitrate, probably from stores accumulated in surface soil horizons (Mitchell & McDonald, 1992). Plots of scores for factors with high Mn loadings in 1994 (Fig. 2) indicate that HS4 Factor 1 is most important in the summer months, whilst HS7 Factors 2 and 5 have maximum scores in autumn. Maximum HS7 Factor 5 scores are negative because of the negative loadings on Mn and nitrate (Table 3). Thus, Mn in runoff originates from different sources in the two basins: summer baseflow at HS4 and autumnal flushing of surface soil horizons at HS7.

Table 2 Results of factor analysis of HS4 1994 streamwater chemistry data.

Variable	Factor 1	Factor 2	Factor 3	Factor 4	Factor 5	Variance (%)
pH	**0.873**	0.178	-0.113	0.233	-0.211	90.6
Eh	**-0.748**	-0.169	0.350	-0.116	0.100	73.4
S. Cond.	0.099	**-0.923**	0.100	-0.058	0.084	88.2
Colour	**0.899**	0.085	0.230	-0.132	0.059	88.9
Manganese	**0.670**	-0.331	0.348	0.426	-0.160	88.7
Iron	**0.940**	0.036	0.205	0.127	-0.094	95.2
Aluminium	0.138	-0.213	**0.905**	0.078	-0.156	91.3
Calcium	**0.933**	-0.116	0.035	0.197	-0.072	93.0
Magnesium	**0.912**	-0.141	0.172	0.242	-0.123	95.4
Chloride	0.264	0.000	0.053	**0.921**	0.103	93.1
Nitrate	-0.192	-0.012	-0.142	0.084	**0.952**	97.0
Sulphate	-0.169	**-0.917**	0.146	0.092	-0.074	90.4
						Totals
Eigenvalues	5.329	1.949	1.255	1.254	1.065	10.853
Variance (%)	44.4	16.2	10.5	10.4	8.9	90.4

S. Cond. = specific conductance. Factor loadings <-0.5 and >0.5 are emboldened.

Table 3 Results of factor analysis of HS7 1994 streamwater chemistry data.

Variable	Factor 1	Factor 2	Factor 3	Factor 4	Factor 5	Variance (%)
pH	**0.913**	-0.132	-0.054	-0.235	-0.123	92.4
Eh	**-0.725**	0.276	0.100	0.361	0.162	76.9
S. Cond.	**0.829**	-0.010	0.321	0.026	0.348	91.1
Colour	-0.292	**0.854**	-0.027	0.223	0.024	86.6
Manganese	0.150	**0.589**	0.208	-0.012	**-0.663**	85.3
Iron	0.066	**0.942**	0.065	-0.080	-0.040	90.3
Aluminium	-0.085	**0.846**	0.118	0.151	-0.051	76.2
Calcium	**0.964**	-0.042	0.107	-0.112	0.099	96.5
Magnesium	**0.967**	0.011	0.123	-0.098	0.092	96.9
Chloride	0.289	-0.163	0.171	**-0.899**	0.066	95.2
Nitrate	**-0.591**	-0.117	-0.128	0.116	**-0.655**	82.1
Sulphate	0.133	0.145	**0.947**	-0.137	-0.023	95.5
						Totals
Eigenvalues	4.480	2.836	1.147	1.128	1.059	10.651
Variance (%)	37.3	23.6	9.6	9.4	8.8	88.8

S. Cond. = specific conductance. Factor loadings <-0.5 and >0.5 are emboldened.

Hydrological pathways of Mn

Discharge measured at HS4 and HS7 in 1994 was separated into soil water and deep water components using a two-component chemical mixing model (Pinder & Jones, 1969; Robson & Neal, 1990). Soil water and deep water compositions were determined indirectly from stormflow and baseflow streamwater chemistries. Double mass plots of discharge and chemical load (Smit *et al.*, 1995) enabled selection of magnesium and sulphate as conservative solutes for HS4 and HS7, respectively (Heal, 1996).

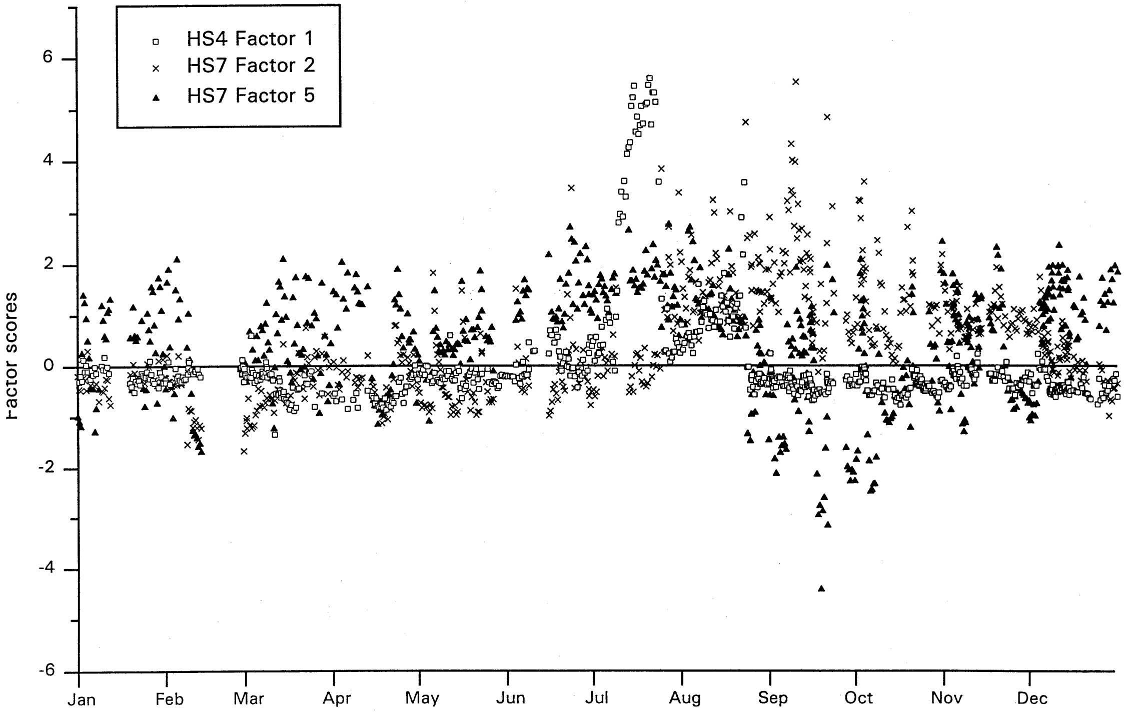

Fig. 2 Factor score plots for HS4 Factor 1, HS7 Factor 2, and HS7 Factor 5, 1994.

The separated HS4 1994 hydrograph (Fig. 3) indicates that the deep water component is most significant in summer, with soil water an increasing contributor to runoff during winter. Linear regression of Mn concentration in runoff against proportion of deep water resulted in r^2 values of 82.4% for HS4 and 0.6% for HS7, further demonstrating that Mn in HS4 runoff is closely related to deep water contributions.

Management implications

The different timing and sources of undesirable Mn concentrations in runoff from HS4 and HS7 require varied management strategies to improve raw water quality. Intake regulation structures in the How Stean basin should open during summer baseflow at HS4 and in autumn at HS7 so runoff with elevated Mn concentrations does not enter the drinking water system. Land-use management is most appropriate for the HS7 basin where Mn is washed out from surface soil stores in the autumn. Practices which exacerbate the drying out of soils in summer, such as drainage ditch construction, could be discouraged in order to reduce the accumulation of a Mn soil store.

This study demonstrates how hydrochemical investigations are of applied interest for basin water quality management. Although only two basins are examined here,

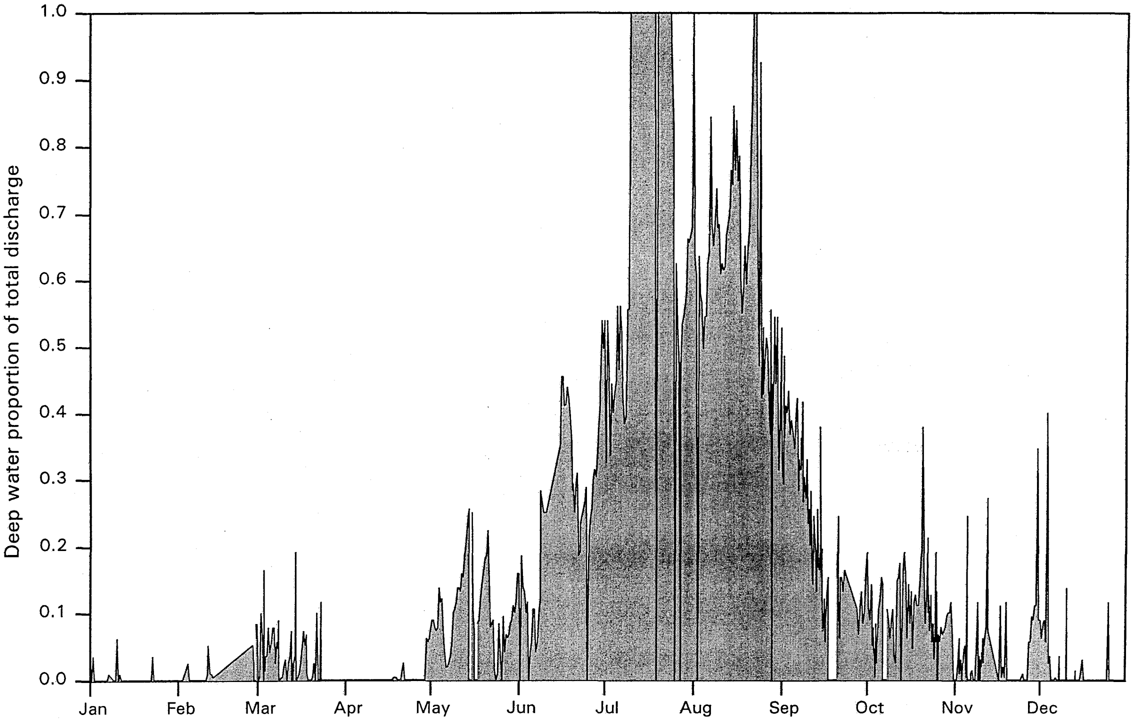

Fig. 3 Proportion of deep water in total discharge from HS4 during 1994.

the results suggest that water quality management strategies may be not effective when applied uniformly over a whole drainage basin. Further investigations of Mn behaviour in a number of upland basins, with differing land uses, are necessary to provide more detailed information for management strategies. Geographic Information Systems (GIS) are suitable tools for water quality decision-making and the application of hydrochemical research results to water supply basins. Development of GIS for basin water quality hazard mapping is ongoing (A. McDonald & A. Smith, personal communication) but more field data are required to construct and validate these systems.

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