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Boron in the major UK rivers entering the North Sea

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Abstract

Boron in the major UK rivers entering the North Sea is predominantly in dissolved form and concentrations show large variations in time and space. The time-dependent feature relates to seasonal patterns linked to flow. Boron concentrations are well described by a power relationship of the type $[B] = a * \text{flow}^b$, where a and b are constants. In this equation, the a term varies from river to river in relation to the boron concentration at baseflow while the b term is of similar value for all the rivers (around -0.5 to -0.6). The spatial variations are directly linked to the degree of sewage discharge and the dilution associated with (i) rainfall events and (ii) the length of river reach from the pollutant source. Boron concentrations exhibit simple chemically conserved water mixing behaviour. However, deviations between chloride and boron indicate secondary chloride supplies from storm runoff, increased boron contamination for part of the sampling period on one river (the Nidd) and possibly significant atmospheric inputs for the less polluted rivers. Preliminary estimates of riverine fluxes to the North Sea are of the order of 1.6 Gg-B/year and the calculations indicate a relatively low rainfall component (about 25% for the cleaner rivers and much lower values for the more polluted rivers). These preliminary estimates also indicate that about 92% of the riverine fluxes comes from the Humber rivers compared to the more northerly rivers. For the Humber, preliminary estimates indicate that about 60% of the flux is associated with detergent-related sources: historical mining activity may also provide an important source (e.g. mine drainage and land contaminated with fly ash and associated material disposal). This illustrates the usefulness of boron as a tracer for non-biodegradable compounds from anthropogenic sources. © 1998 Elsevier Science B.V.

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1. Introduction

Boron concentrations vary considerably across the northeastern UK rivers entering the North Sea, from a few to up to almost 1000 μg-B/l (Neal et al., 1996, 1997a; Jahiruddin et al., 1998). Such concentrations are not abnormally high across the full spectrum of aquatic freshwater environments as boron can be supplied from weathering of igneous rocks, from volcanism and leaching of salt deposits; concentrations of sev-

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eral thousand μg-B/l can occur when such sources are significant (Christ and Harder, 1978). However, the hydrogeological setting of the UK river drainage area to the North Sea, with a predominant Carboniferous to Cretaceous sedimentary bedrock geology (shales/grits/limestones) and limited sources of saline groundwater aquifers (Jarvie et al., 1997a), means that the rivers of the area have low background boron concentrations (Neal et al., 1996, 1997a) comparable with unpolluted areas of other parts of the world with similar geology unperturbed by activities such as mining, urbanisation and industry (typically about 10 μg-B/l; Christ and Harder, 1978).

Within the northeast of England there are major industrial and urban centres (Jarvie et al., 1997a; Neal et al., 1997b) which generate effluents enriched in boron, in part due to the presence of soluble boron-containing materials used in washing powders. Boron in river water primarily exists as a chemically unreactive form (borate; Bassett, 1980) and since there are low background concentrations from geological sources, boron can be used, as elsewhere (Dyer and Caprara, 1997) as a chemically conservative tracer for anthropogenic influences to these rivers. Boron concentrations are not at environmentally harmful levels within the rivers as maximum concentrations observed (937 μg-B/l) are less than water quality standards set for the protection of sensitive aquatic life (less than 5% exceedence of 2000 μg-B/l for the European Community, WRc, 1991: see also review by TCDE, 1994). Nonetheless, studies of boron distributions can, when coupled to dynamic or even steady-state water quality models (Cooper and Naden, 1998; Eatherall et al., 1998a,b; Kowe et al., 1998; Whitehead et al., 1998a,b), provide an important indicator of the dispersion, diffusion and fate of non-biodegradable pollutants within river systems. Provision of such an indicator is an important step towards the development of much needed environmental management strategies and risk assessment (cf Dyer and Caprara, 1997).

As part of a major water quality initiative of UK rivers entering the North Sea (the Land Ocean Interaction Study; LOIS; Wilkinson et al., 1997; Neal et al., 1997b, 1998a,b; Leeks and Jarvie, 1998), a major database on high-quality determinations of a wide range of chemicals, including boron, has been collected for river basins varying from the Tweed, a near pristine river, to highly industrially polluted south Yorkshire rivers such as the Aire and Calder (Neal et al., 1997b).

In this paper, the distribution of boron is examined for the LOIS rivers in relation to the flow regime and water quality variations across the region. This is undertaken to gain an insight on the dynamics of boron distributions within the area. The results provide new information on the hydrogeochemistry of boron from a clean landscape of the borders of south eastern Scotland and north eastern England to an urban/industrial landscape of south Yorkshire and the central and eastern parts of the midlands of England. The presentation substantially extends the broad preliminary analysis undertaken within the LOIS rivers programme (RACS(R)) to date. Further, it provides (i) a base for chemical flux studies for pollutants to several important UK rivers that act as a major conduit for pollutant transport to the North Sea and (ii) a major study to set beside broad-based associated studies in other parts of the world (Dyer and Caprara, 1997).

2. Experimental

Samples of river water have been collected weekly by grab sampling at 15 key sites across the LOIS region. Two areas have been focused upon, the Tweed basin (three sites with sampling being initiated in the spring of 1994) and the major rivers and tributaries entering the Humber Estuary (12 sites, sampling beginning in the summer of 1993). Details of the locations and the spectrum of agricultural, urban and industrial environments are given in Leeks et al. (1997) and Jarvie et al. (1997a,b).

General details of the chemical methodologies are provided by Leeks et al. (1997), although details of analytical methodologies for boron are provided here for completeness.

Both dissolved and acid-available boron fractions were determined. The acid-available fraction represents the dissolved fraction plus that part of the particulate phase which can easily be dissolved or desorbed from the solid phase under acidic conditions. The dissolved fraction was measured as follows. For the dissolved fraction, on the day of collection, the samples were first filtered and the filtrates were then acidified. The acidification, to 1% v/v concentrated Aristar grade nitric acid, ensured that precipitation/adsorption of the boron did not occur to a significant degree during storage. The acid-available fraction was determined after acidification of an unfiltered sample with concentrated Aristar grade nitric acid (1% v/v) and agitating for 24 h, at room temperature, prior to filtration. Samples were then analyzed for boron by inductively coupled plasma optical emission spectrometry (ICP-OES): the lowest quotable values were taken as five times the detection level. In the initial phases of the work, filtration and storage of blank samples were included to test for contamination. For the chemical determinations, mixed quality-control standards were included in the routine analyses. These standards were checked weekly against international quality control references prepared by the United States Geological Survey National Water Quality Laboratory (SRM 1643c). Each new batch of calibration standards was cross-checked with the previous batch to ensure continuity of calibration and to ensure the elimination of a potential error.

Detailed cross comparisons of the boron data for dissolved and acid-available fractions revealed almost identical numbers: cross comparison of results showed excellent reproducibility with over 95% of paired values lying within 5% of each other at concentrations above the lowest quotable value. This illustrates not only the high analytical accuracy, but also the lack of a significant particulate boron component (< 2% of the dissolved component and within the analytical noise of the measurement). For the remaining part of the study, only data for the dissolved fraction data are used.

The results presented here cover the full sampling period from the start dates given above to the end of December 1996.

3. Results and preliminary interpretation

Boron concentrations vary significantly across the region (Table 1). For example, boron concentrations show large fluctuations for each river

Table 1
Boron and chloride concentration statistics for the LOIS rivers: units μg-B/l for boron and mg-Cl/l for chloride; bracketed terms are for chloride

River	Minimum value	Maximum value	Arithmetic mean	Flow-weighted mean	Baseflow	Stormflow
Tweed (Ormiston)	0 (8)	61 (73)	24 (20)	14 (20)	45 (26)	11 (19)
Tweed (Boleside)	0 (7)	38 (25)	15 (13)	11 (11)	24 (13)	7 (12)
Tweed (Norham)	1 (8)	53 (38)	21 (18)	15 (14)	34 (20)	11 (13)
Swale (Catterick)	0 (7)	95 (57)	29 (17)	15 (14)	53 (18)	8 (13)
Swale (Thornton)	1 (7)	113 (98)	46 (31)	26 (26)	85 (36)	15 (22)
Ure	0 (7)	129 (160)	25 (24)	14 (18)	47 (33)	7 (16)
Nidd	11 (14)	269 (245)	96 (37)	49 (33)	188 (35)	28 (34)
Ouse (Clifton)	0 (10)	183 (110)	51 (31)	26 (27)	103 (38)	11 (25)
Ouse (Acaster)	10 (11)	212 (81)	73 (33)	36 (30)	171 (42)	18 (26)
Wharf	0 (6)	132 (92)	44 (25)	22 (19)	82 (30)	11 (21)
Derwent	22 (39)	332 (190)	54 (59)	43 (40)	76 (41)	29 (41)
Aire	47 (13)	770 (300)	339 (129)	185 (82)	573 (173)	82 (66)
Calder	6 (17)	635 (340)	307 (117)	181 (77)	513 (149)	98 (61)
Don	46 (38)	937 (330)	464 (131)	298 (108)	694 (146)	123 (77)
Trent	117 (28)	872 (200)	451 (112)	311 (87)	705 (164)	166 (58)

The values given for baseflow and stormflow correspond, respectively, to the average values for the 10 lowest and 10 highest flow values for which concentration data are available.

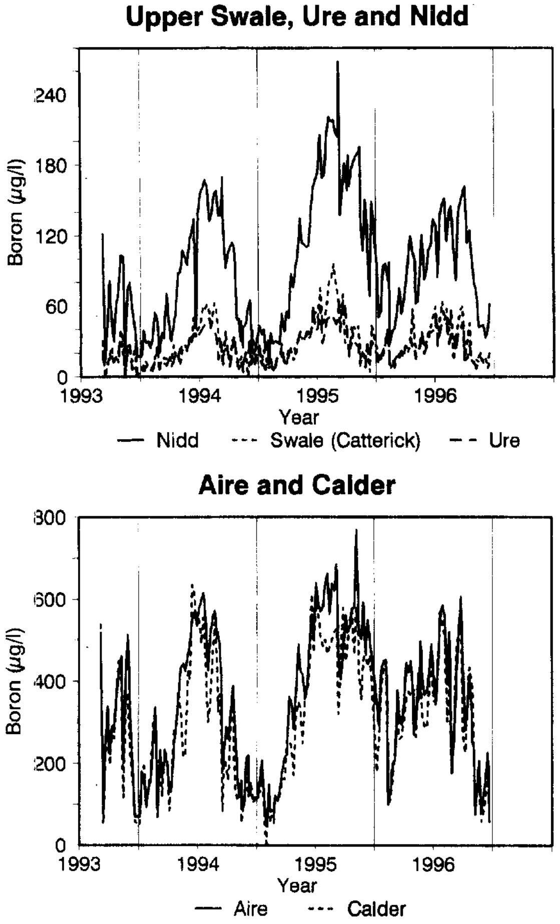

Fig. 1. Illustrations of the relationship between boron concentration and time for the LOIS rivers: upper Swale, Ure, Nidd, Aire and Calder.

over time: ranges for individual rivers span 38–891 μg-B/l. Further, concentrations vary from river to river with average values varying between 15 and 464 μg-B/l.

Despite the large variations in boron concentration, the data are described well in relation to seasonal variability and source contributions as is shown below.

3.1. Seasonal variations

All the rivers exhibit a strong seasonal pattern with maximum boron concentrations occurring during the summer months (Fig. 1). The fluctuations occurring in each river are similar although the amplitudes of change vary from river to river.

The reason for this variation becomes clear when the relationship between boron concentration and flow is explored (Fig. 2). Thus, the characteristic pattern observed for all the rivers is an inversely proportional relationship between boron concentration and flow. This relationship is well described by an equation of the form

$$B = a * \text{flow}^{b}$$

where a and b are constants (Table 2). For this relationship, the a term varies from river to river approximately in proportion to the boron concentration at baseflow condition while the b term is much less variable from river to river with values typically around -0.5 to -0.6.

The seasonal pattern of boron, therefore, simply relates to the seasonal pattern for flow and the contrasting chemistries of baseflow and stormflow waters.

3.2. Regional variations

There is a very marked change in boron concentration across the LOIS region with baseflow, average and stormflow concentrations all increasing together from north to south (Table 1, Fig. 3). This is in line with declining water quality and increasing urban and industrial contamination (cf Neal et al., 1997b; Jarvie et al., 1997b).

The regional variations of average boron concentration are analyzed here by comparison with averages for chloride and soluble reactive phosphate (SRP). These determinands are used to separate out two potentially important boron supplies to the rivers; atmospheric and sewage sources. In the case of chloride there are both significant atmospheric and pollutant sources. For the less polluted rivers, the atmospheric chloride component becomes proportionately more important although absolute concentrations are, of course, much lower. Correspondingly, SRP concentrations reflect primarily a sewage contribution (House et al., 1997; Jarvie et al., 1997b): SRP concentrations in rainfall are low.

Table 2
Linear regression information for the logarithm of flow (independent variable) and the logarithm of boron concentration (dependent variable) with the LOIS rivers: the terms in brackets for the constant and gradient columns are standard errors, N is the number of data points for the regression and the bracketed term in the R^2 column represents regression based on unlogged values

River	a	b	R^2	N
Tweed (Ormiston)	1.73 (0.10)	−0.490 (0.094)	0.341 (0.141)	54
Tweed (Boleside)	1.59 (0.10)	−0.387 (0.068)	0.374 (0.025)	54
Tweed (Norham)	1.88 (0.14)	−0.461 (0.080)	0.336 (0.091)	55
Swale (Catterick)	1.84 (0.03)	−0.569 (0.028)	0.716 (0.107)	158
Swale (Thornton)	2.14 (0.03)	−0.508 (0.022)	0.744 (0.352)	180
Ure	1.84 (0.03)	−0.467 (0.027)	0.653 (0.223)	176
Nidd	2.24 (0.02)	−0.537 (0.024)	0.731 (0.201)	179
Ouse (Clifton)	2.50 (0.05)	−0.605 (0.029)	0.708 (0.401)	167
Ouse (Acaster)	2.57 (0.03)	−0.555 (0.022)	0.834 (0.392)	126
Wharf	2.08 (0.03)	−0.574 (0.030)	0.673 (0.301)	178
Derwent	2.08 (0.03)	−0.378 (0.023)	0.609 (0.160)	171
Aire	3.29 (0.03)	−0.589 (0.020)	0.818 (0.479)	191
Calder	3.19 (0.04)	−0.673 (0.032)	0.708 (0.316)	175
Don	3.19 (0.03)	−0.565 (0.026)	0.724 (0.357)	179
Trent	3.71 (0.04)	−0.618 (0.022)	0.837 (0.552)	130

a represents the constant term and b the gradient for the regression.

There are also potential geological weathering sources. For example, the shales in the area, being of marine origin, will be moderately enriched in boron. Comment on this aspect is made in connection to the flux estimation.

3.3. Estimates of atmospheric boron inputs

The atmospheric levels of boron have not been measured for the region. Before proceeding further with the interrogation of the LOIS data it is necessary to provide an estimate of what this input should be. Little information on boron in rainfall is available for the UK. Here, information from a study of the hydrochemistry of an upland area of mid-Wales is utilized (the Plynlimon catchments: Neal et al., 1992; Neal, 1997). An analysis of boron and chloride in rainfall in mid-Wales gives a boron to chloride ratio of about 0.75 on a μg-B/l to mg-Cl/l basis; this compares with a value of about 0.25 for sea-water (Rosler and Lange, 1972). Furthermore, there is an additional atmospheric input at Plynlimon from mist and dry deposition (B:Cl ratio of 1.73) giving a net atmospheric B:Cl ratio of 0.92 (Neal, 1997). This illustrates that anthropogenic sources of boron can be significant in rainfall even well away from industrial areas: atmospheric pollutant components such as fly ash are highly enriched in boron and they have high B:Cl ratios of the order of 1000 (Adriano et al., 1980). On transfer from the atmosphere to the river, boron, being a nutrient, is utilized by the vegetation. Thus, about 30% of the boron input from the atmosphere can be retained within the catchment; for Plynlimon, the net B:Cl export ratio to the river from the atmosphere is 0.75 (Neal, 1997): see also Jahiruddin et al. (1998) for data on the Scottish Dee basin where similar results occur.

This net export ratio is used with the LOIS river water data to give a qualitative guide to the significance of the atmospheric inputs to riverine boron fluxes in the LOIS rivers (see discussions later in this paper in Section 3.5). Thus, using this value with the estimates of chloride fluxes to the LOIS catchments provided by Smith et al. (1997) gives a background value for atmospheric inputs of boron corresponding to around 5 μg-B/l in runoff.

3.4. Boron relationships with chloride and soluble reactive phosphorus (SRP) for the LOIS rivers

For the averaged data for the individual rivers

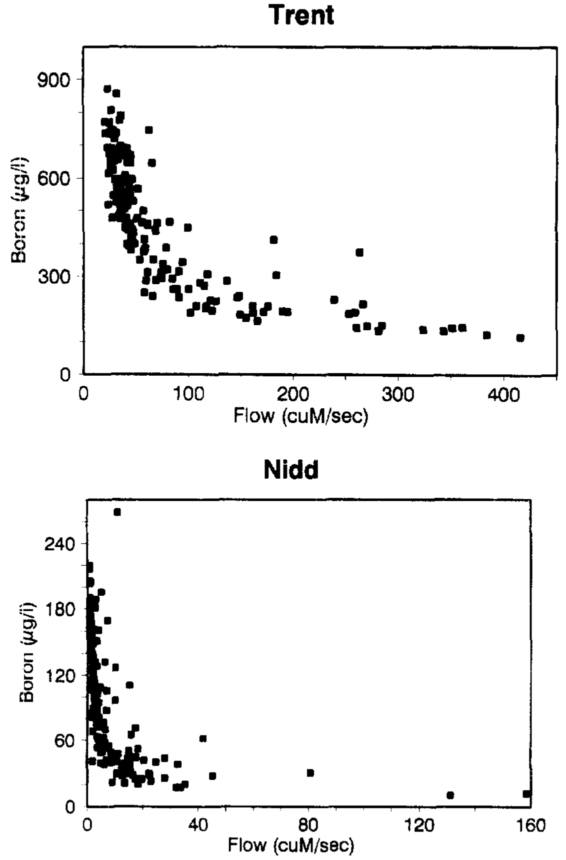

Fig. 2. Illustrations of the relationship between boron concentration and flow for the LOIS rivers: the Nidd and Trent.

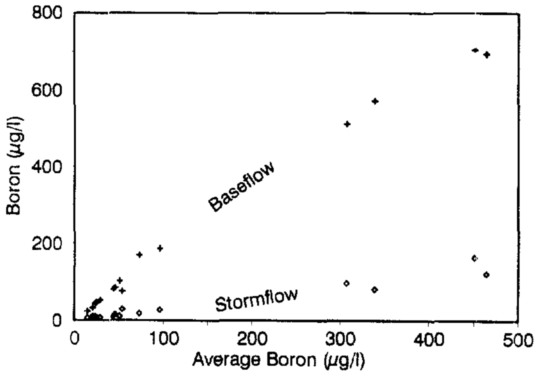

Fig. 3. The relationship between average boron concentration at baseflow and stormflow with the average boron concentration for the LOIS rivers.

across the region, there are strong linear relationships between boron and both chloride and SRP (Fig. 4). Thus,

$$[\text{Boron}, \mu g/l] = (0.2 \pm 20.8) + (1.00 \pm 0.04).\ [\text{Cl}, mg/l]$$

$$R^2 = 0.996,\ N = 15$$

$$[\text{Boron}, \mu g/l] = (7.3 \pm 66.0) + (0.276 \pm 0.015).\ [\text{SRP}, \mu g/l]$$

$$R^2 = 0.963,\ N = 15$$

where the ± term represents twice the standard error.

There are three important inferences from these results. Firstly, the marked linear relationship between average concentrations of boron and SRP for each river indicates a strong regional pattern for boron associated with sewage sources given that this provides the primary source of SRP. Secondly, the strong linear relationship between boron and chloride also implies a major sewage component across the region although the relative importance of atmospheric sources may be much higher for some rivers across the range of flows or at certain flow levels. For example, the boron to chloride ratio for all the rivers approaches that of rainfall under high flow conditions when boron concentrations are at their lowest (Tables 1 and 3); this is the condition where rainfall inputs would be expected to be at their highest. Furthermore, the closest match occurs for the cleaner rivers where chloride and boron are at their lowest concentrations for the LOIS region (Table 3). Thirdly, the patterns observed are broadly consistent with a two component boron-chloride mixing model involving sewage sources and rainfall.

With regard to sewage inputs to the individual LOIS rivers, the relationships between boron and chloride concentration can be used to assess patterns in more detail. In general, chloride and boron concentrations are related, with higher concentrations occurring at baseflow compared with stormflow (Table 1). For many of the LOIS rivers there is a linear relationship between the two components and this is most clearly observed for the more polluted rivers such as the Trent

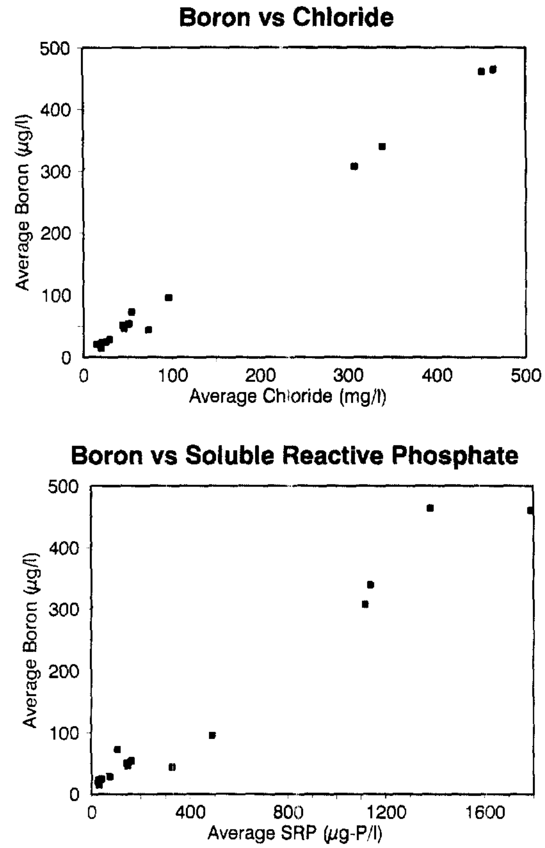

Fig. 4. The relationship between average boron concentration with average chloride and with average soluble reactive phosphate (SRP) concentration for the LOIS rivers.

Table 3
Boron to chloride ratios (µg-B/l:mg-Cl/l) for the LOIS rivers: the ratios are calculated from mean concentration values

River	Baseflow	Stormflow	Arithmetic mean	Flow weighted mean
Tweed (Ormiston)	1.73	0.54	1.21	0.67
Tweed (Boleside)	1.83	0.61	1.18	1.06
Tweed (Norham)	1.72	0.82	1.17	1.08
Swale (Catterick)	2.89	0.61	1.67	1.10
Swale (Thornton)	2.33	0.67	1.48	0.99
Ure	1.40	0.45	1.05	0.76
Nidd	5.30	0.81	2.60	1.47
Ouse (Clifton)	2.75	0.45	1.65	0.99
Ouse (Acaster)	4.04	0.70	2.20	1.20
Wharf	2.74	0.54	1.78	1.15
Derwent	1.84	0.71	0.91	1.07
Aire	3.31	1.24	2.64	2.25
Calder	3.43	1.61	2.62	2.33
Don	4.75	1.60	3.53	2.75
Trent	4.28	2.85	4.02	3.56

The values given for baseflow and stormflow correspond, respectively, to the average values for the 10 lowest and 10 highest flow values for which concentration data are available.

(Fig. 5; Table 4). This pattern reflects the dilution of sewage discharges from rainwater during high flow conditions. Even where the strongest patterns are observed, there is considerable data scatter and it is clear that there is a greater complexity to the various inputs when examined for individual rivers compared with both regional trends and flow relationships. Indeed, for the less polluted rivers, the trends break down completely (Table 4) because the chloride variation does not exhibit the declining concentrations with increasing flow observed for boron (Table 1). The lack of flow dilution for chloride probably represents additional contributions of chloride at high flows from storm runoff and sources of chloride such as road salts, during the winter, and rainfall. However, this is not the sole reason. For example, there is some data structure between boron and chloride for some of the less polluted rivers and this is most clearly marked for the Nidd where two trends are observed (Fig. 4). In the case of the Nidd, the anomalously low values for boron, relative to chloride, occur solely during the first 6 months of 1996 and it seems that there are changing sewage outflow patterns. As the ratio of boron to chloride is higher for the Nidd during baseflow compared even to the industrial rivers (Table 3), it seems that there may have been additional pollutant sources of boron during the earlier years of study.

The contrasting patterns observed between the cleaner and more polluted rivers reflect the domination of point-source inputs of boron and chloride across the flow range: i.e. the magnitude of the sewage inputs for the more polluted rivers masks the much smaller changes at high flow that are observed much more clearly for a cleaner river.

3.5. Flux considerations

In terms of boron fluxes to the North Sea,

Table 4
Linear regression information for chloride (independent variable) and boron (dependent variable) with the LOIS rivers: the terms in brackets are standard errors and N is the number of data points for the regression

River	Constant	Gradient	R^2	N
Tweed (Ormiston)	7.2 (3.4)	0.89 (0.16)	0.232	92
Tweed (Boleside)	8.6 (4.1)	0.53 (0.31)	0.027	92
Tweed (Norham)	11.1 (3.6)	0.57 (0.19)	0.079	92
Swale (Catterick)	16.8 (4.3)	0.73 (0.24)	0.055	157
Swale (Thornton)	24.9 (4.8)	0.71 (0.14)	0.124	166
Ure	10.6 (2.2)	0.63 (0.08)	0.259	167
Nidd	96.5 (7.9)	0.03 (0.18)	0.002	169
Ouse (Clifton)	28.6 (6.2)	0.76 (0.19)	0.088	166
Ouse (Acaster)	13.6 (12.7)	1.88 (0.36)	0.184	104
Wharf	17.7 (4.4)	1.11 (0.16)	0.215	167
Derwent	85.7 (17.6)	−0.84 (0.45)	0.020	157
Aire	77.2 (23.5)	2.14 (0.34)	0.482	155
Calder	51.7 (20.8)	2.22 (0.16)	0.523	156
Don	88.0 (44.9)	2.84 (0.33)	0.312	155
Trent	−57.1 (22.9)	4.52 (0.19)	0.769	148

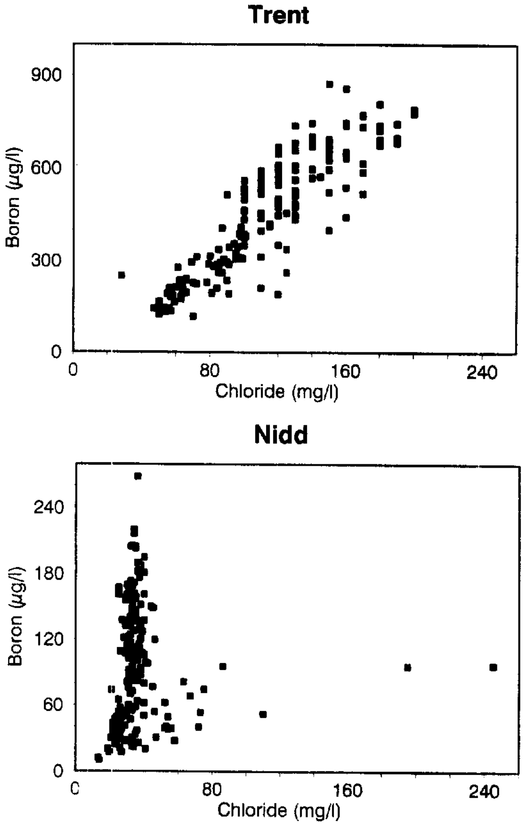

Fig. 5. The relationship between boron concentration and chloride concentration for the LOIS rivers: an illustration of the range of pattern based on data for the Trent and Nidd.

there are major uncertainties associated with the details of atmospheric inputs (e.g. due to the unknown amount of dry deposition) and the difficulties of determining accurate riverine fluxes (Webb et al., 1997). However, the data presented in this paper, when combined with information from earlier publications on atmospheric inputs and riverine runoff for chloride in the region (Smith et al., 1997; Robson and Neal, 1997), can be used to gauge the fluxes involved. Table 5 summarises these calculations based on a separation between the Northern rivers and those entering the Humber estuary. For the calculations, the chloride fluxes are taken from Smith et al. (1997); the boron to chloride ratios in rainfall and in rivers are taken from the Welsh study at Plynlimon and the present study, respectively. The results indicate (1) a total boron flux input to the North Sea from the LOIS rivers of about 1.6 Gg-B/year, (2) about 25% and 3% of the riverine boron fluxes for the northern and Humber rivers, respectively, are derived from rainfall and (3) about 92% of the riverine boron flux comes from the Humber rivers.

Some quantification of the sources of the riverine boron flux in the Humber catchment can be made using data on per capita boron usage derived from detergent-related sources (Holt et al., 1997) and the population of the Humber catchment which is about 11 million people (Edwards et al., 1997; Jarvie et al., 1997a). The per capita boron usage of 80.3 g-B/year leads to a boron load of about 0.9 Gg-B/year, which can be attributed to detergent-related sources. Thus, this anthropogenic source of boron contributes ~ 60% of the riverine output of boron from the heavily-populated Humber catchment.

The pollutant sources for the remaining 40% of the boron-flux contribution to the Humber estuary are not known. However, a major potential contributor is the sedimentary deposits of marine origin such as the carboniferous shales which can be enriched in this component but depleted in

Table 5
Boron flux data for the Northern and Humber rivers

	Units	Northern rivers	Humber rivers	Total rivers
Catchment area	km^2	10 691	17 965	28 656
Atmospheric Cl input	kg/ha/year	41	35	37.2
B:Cl ratio in rainfall	μg-B/l:mg-Cl/l	0.75	0.75	0.75
Atmospheric B input	g/ha/year	30.75	26.25	27.9
Riverine Cl output	kg/ha/year	115	284	220.9
B:Cl ratio in river	μg-B/l:mg-Cl/l	1.07	2.89	2.21
B output to North Sea	g-B/ha/year	123.05	820.76	560.5
Atmospheric input of B	Gg-B/year	0.0329	0.0472	0.080
Riverine output of B	Gg-B/year	0.1316	1.475	1.606
% Riverine flux		8.2	91.8	100

For the tables, catchment areas are taken from Robson and Neal (1997), and chloride fluxes from Smith et al. (1997). Boron to chloride ratios are taken from Table 1 of this paper: for the northern rivers, the ratio based on flow weighted boron and chloride values for the Tweed at Norham have been used, while for the Humber rivers the corresponding values for the Ouse, Aire, Calder, Don and Trent have been used after allowance for the relative catchment sizes.

chloride. The boron associated with these sedimentary rocks is susceptible to removal by leaching either within the rock or subsequent to mining extraction. Preliminary work in the South Yorkshire region being undertaken by Unilever and the Environment Agency as part of the GREAT-ER project (Feijtel et al., 1997) is indicating that boron leaching is enhanced in the derelict mining areas and runoff (e.g. in the Rivers Went and Rother) can have boron concentrations as high as those in the main polluted Humber rivers. However, while the B:Cl ratios can also be high (1.4–3.0) compared to the cleaner Humber rivers, an additional source of boron may also be required to explain the total boron flux to the Humber estuary. This additional flux may well be associated with the historic disposal of fly ash and related products, enriched to several hundred parts per million boron which is in a highly soluble form (cf Adriano et al., 1980; Hebblethwaite and Emberson, 1993), from the mining industry to landfill and surface disposal sites.

4. Discussion

This paper shows that the distribution of boron within the major LOIS rivers is related to both hydrological and source contribution factors. Much of the boron input to the river is derived from sewage discharges and the levels of boron are highest during baseflow periods when dilution of sewage inputs are at their lowest. The levels of boron are related to the flux contributions of sewage and land and mine runoff linked to the degree of dilution by rainfall. Most of this boron is accountable as coming from detergent-related sources and historic mining activity. While there are broad patterns between the highly polluted rivers and the more pristine ones, there are also more subtle changes which relate to the nature of the sewage inputs and the atmospheric sources. For example, the Nidd seems to provide an anomalously high boron content for what might be considered to be one of the cleaner of the LOIS rivers. However, the sampling point on the Nidd is less than 20 km from the large towns of Harrogate and Knaresborough which supply a major amount of sewage to the river (Lewis et al., 1997). Thus, a higher boron level would be expected. Correspondingly, there is a factor of 1.5 difference in the concentrations of boron at the two sites on the Swale. The lower concentrations occur at the Clifton site just upstream of the major urban area of York while the higher concentrations occur at the Acaster site just downstream of both York and the main sewage outfall for the city.

In terms of the flux calculations, riverine boron fluxes are dominated by pollutant rather than atmospheric sources (75% and more). Further, the Humber rivers provide the major outputs of boron to the North Sea from the LOIS rivers in the Trent-Tweed area (92%) even though they contribute just over a half (56%) of the flow.

5. Wider comment

The present study indicates that the use of boron as a tracer of sewage outfalls is eminently sensible when there is a lack of other significant sources. However, to take matters further, greater enquiry is required to identify (a) the scale of the inputs for all the major LOIS rivers (the Wear and Tyne have not been sampled for example), (b) the extent of both local and regional variations and (c) the relative importance of atmospheric and other pollutant boron sources for the less polluted rivers.

References

Adriano, D.C., Page, A.L., Elseewi, A.A., Chang, A.C., Straughan, I., 1980. Utilization and disposal of fly ash and other coal residues in Terrestrial Ecosystems, a review. J. Environ. Qual. 9, 333–344.

Bassett, R.L., 1980. A critical evaluation of thermodynamic data for boron ions, ion pairs, complexes and poly anions in aqueous solution at 298.15 K and 1 bar. Geochim. Cosmochim. Acta. 44, 1151–1160.

Christ, C.L., Harder, H., 1978. Boron. In: Wedepohl, K.H. (Ed.), Handbook of Geochemistry, Vol II/1, Elements H(1) to Al(13). Springer Verlag, Berlin, pp. 5-A-1–5-O-10.

Cooper, D.M., Naden, P.S., 1998. Approaches to delivery modelling in LOIS. Sci. Total Environ. 210/211, 483–498.

Dyer, S.D., Caprara, R.J., 1997. A method for evaluating consumer product ingredient contributions to surface and drinking water: boron as a test case. Environ. Toxicol. Chem. 16, 2070–2081.

Eatherall, A., Boorman, D.B., Williams, R.J., Kowe, R., 1998. Modelling in-stream water quality in LOIS. Sci. Total Environ. 210/211, 499–517.

Eatherall, A., Naden, P.S., Cooper, D.M., 1998. Simulating carbon flux to the estuary: the first step. Sci. Total Environ. 210/211, 519–533.

Edwards, A.M.C., Freestone, R.J., Crockett, C.P., 1997. River management in the Humber Catchment. Sci. Total Environ. 194/195, 235–246.

Feijtel, T.C.J., Boeije, G., Mattheis, M., Young, A., Morris, G., Gandolfi, C., Hansen, B., Fox, K.K., Holt, M., Koch, V., Schroder, R., Cassani, G., Schowanek, D., Rosenblom, J., Niessen, H., 1997. Development of a geography-referenced Regional Exposure Assessment Tool for European Rivers — GREAT-ER. Contributions to GREAT-ER 1. Chemosphere 34, 2351–2374.

Hebblethwaite, R.L., Emberson, P., 1993. Rising from the ashes. Landscape Design 10, 31–34.

Holt, M.S., Fox, K.K., Burford, M., Daniel, M., Buckland, H., 1997. GREAT-ER Project, UK monitoring study on the removal of linear alkylbenzene sulphonate in trickling filter type sewage treatment plants. Sci. Total Environ. in press.

House, W.A., Leach, D., Warwick, M., Whitton, B.A., Pattinson, S.N., Ryland, G., Pinder, A., Ingram, J., Lishman, J.P., Smith, S.M., Rigg, E., Denison, F.H., 1997. Nutrient transport in the Humber rivers. Sci. Total Environ. 194/195, 303–320.

Jarvie, H.P., Neal, C., Robson, A.J., 1997a. The geography of the Humber catchments. Sci. Total Environ. 194/195, 87–100.

Jarvie, H.P., Ryland, G., Leach, D.V., Neal, C., House, W.A., 1997b. Major element and inorganic carbon chemistry for the Humber Rivers. Sci. Total Environ. 194/195, 285–302.

Jahiruddin, M., Smart, R., Wade, A.J., Neal, C., Cresser, M.S., 1998. Factors regulating the distribution of boron in water in the River Dee catchment in north east Scotland. Sci. Total Environ. 210/211, 53–62.

Kowe, R., Skidmore, R.E., Whitton, B.A., Pinder, A., 1998. Modelling phytoplankton dynamics in the river Swale, an upland river in NE England. Sci. Total Environ. 210/211, 535–546.

Leeks, G.J.L., Jarvie, H.P., 1998. Introduction to the Land Ocean Interaction Study (LOIS): rationale and international context. Sci. Total Environ. 210/211, 5–20.

Leeks, G.J.L., Neal, C., Jarvie, H.P., Casey, H., Leach, D.V., 1997. The LOIS river monitoring network; strategy and implementation. Sci. Total Environ. 194/195, 101–110.

Lewis, D.R., Williams, R.J., Whitehead, P.G., 1997. Quality simulation along rivers (QUASAR): an application to the Yorkshire Ouse. Sci. Total Environ. 194/195, 399–418.

Neal, C., 1997. Boron water quality for the Plynlimon catchments, mid-Wales. Hydrol. Earth Systems Sci. in press.

Neal, C., Smith, C.J., Hill, S., 1992. Forestry Impact on Upland Water Quality. Institute of Hydrology, Report Series. 119. Institute of Hydrology, Wallingford, UK, p. 50.

Neal, C., Smith, C.J., Jeffery, H.A., Jarvie, H.P., Robson, A.J., 1996. Trace element concentrations in the major rivers entering the Humber estuary. NE Engl. J. Hydrol. 182, 37–64.

Neal, C., Robson, A.J., Jeffery, H.A., Harrow, M.L., Neal, M., Smith, C.J., Jarvie, H.P., 1997a. Trace element inter-relationships for the Humber rivers: inferences for hydrological and chemical controls. Sci. Total Environ. 194/195, 321–344.

Neal, C., House, W.A., Jarvie, H.P., Leeks, G.J.L., Marker, A.H., 1997b. Conclusions to the special volume of Science of the Total Environment concerning UK fluxes to the North Sea, Land Ocean Interaction Study: river basins research, the first two years. Sci. Total Environ. 194/195, 467–478.

Neal, C., House, W.A., Whitton, B.A., Leeks, G.J.L., 1998a. Foreword to special issue: water quality and biology of UK rivers entering the North Sea: the Land Ocean Interaction Study (LOIS) and associated work. Sci. Total Environ. 210/211, 1–4.

Neal, C., House, W.A., Whitton, B.A., Leeks, G.J.L., 1998b. Conclusions to special issue: water quality and biology of UK rivers entering the North Sea: the Land Ocean Interaction Study (LOIS) and associated work. Sci. Total Environ. 210/211, 585–594.

Robson, A.J., Neal, C., 1997. A summary of regional water quality for Eastern UK rivers. Sci. Total Environ. 194/195, 15–38.

Rosler, H.J., Lange, H., 1972. Geochemical Tables. Elsevier, Amsterdam, pp. 312–352.

Smith, R.I., Cape, J.N., Binnie, J., Murray, T.D., Young, M., Fowler, D., 1997. Deposition of atmospheric pollutants in the LOIS area. Sci. Total Environ. 194/195, 71–86.

TCDE, 1994. Technical Committee on Detergents and the Environment, Perborate bleach in detergents — an environmental summary. Department of the Environment, London, pp. 43–49.

WRc, 1991. UK Water Quality Standards Arising from EC Directives. Water Research Centre, Research and Development Report P-11. Foundations for Water Research, Marlow, UK, p. 250.

Webb, B.W., Philips, J.M., Walling, D.E., Littlewood, I.G., Watts, C.D., Leeks, G.J.L., 1997. Load estimation for British rivers and their relevance to the LOIS RACS(R) programme. Sci. Total Environ. 194/195, 379–390.

Whitehead, P.G., Wilson, E.J., Butterfield, D., 1998a. A semi-distributed integrated nitrogen model for multiple source assessment in catchments (INCA): part I — model structure and process equations. Sci. Total Environ. 210/211, 547–558.

Whitehead, P.G., Wilson, E.J., Butterfield, D., Seed, K., 1998b. A semi-distributed integrated nitrogen model for multiple source assessment in catchments (INCA): part II — application to large river basins in South Wales and Eastern England. Sci. Total Environ. 210/211, 559–583.

Wilkinson, W.B., Leeks, G.J.L., Morris, A., Walling, D.E., 1997. Rivers and coastal research in the Land Ocean Interaction Study. Sci. Total Environ. 194/195, 5–14.