

The Chemical Composition of the River Aire and Anthropogenic Impacts on the River from its Source to Leeds.

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Abstract

Water samples were collected from the Aire River (flowed from its source at Malham towards Leeds) and its tributaries (Earby Beck, Glusburn, and Eller Beck), in the summer of 2013. Chemical analysis was carried out on the samples to assess the natural and anthropogenic control and impact on the river's composition. The major cations were analysed by ICP-AES and anions by IC and HCl titration. The chemistry of the water for all samples were dominated by calcium and bicarbonate. The results indicated that calcium ions accounted for 89% of the total cation charge budget of the Aire at its source at Malham, but decreased whilst the contribution of sodium, potassium and magnesium ions to the cation budget increased as the flow of the river approached Leeds from source. Sodium ion recorded the highest cation concentration of 61 mgL^{-1} at Calverly Lane Bridge and 39% contribution to the cation charge budget. The anions were dominated by alkalinity for all the samples, however alkalinity decreased in anion charge budget component of 92% from Malham to 37% at Calverly Lane Bridge. The anion budget had increased percentages for chloride, nitrates and sulphate ions as the river approached Leeds. Contributing to 34%, 7% and 22% respectively to the anion budget. The increased concentrations of sodium, potassium, chloride, nitrate and sulphate changed the chemical composition of the river considerably. The reason for the chemical change was attributed to the effects of heavy point source discharges of communal sewage, industrial effluent and agricultural fertilizers input on the improved grasslands of the catchment into the river. The conclusion was that, anthropogenic activity has a considerable effect on the River Aire as it flowed through the urban areas of Bradford and Leeds.

Keywords: Concentration, charge budget, anthropogenic, effluent, fertilisers, point source discharge, River Aire

1. Introduction

Rivers are known to have played an important role in human development. Historically, settlements along rivers have occurred because the rivers provided both water supply and transportation. As a result of human proximity, rivers have been considerably affected by activities ranging from agriculture and flood control to the input of human and industrial wastes (Berner & Berner,1987). Several studies have been undertaken to study the effects of man on riverine systems because of the debilitating effects of man's actions on rivers and the threatening effects of climate change on water bodies. This work seeks to assess the effects of nature and the effects of man on the composition of the River Aire, as it flows from its source (Malham Tarn) to Leeds.

2. Background of Study Area

The River Aire catchment is 1004 km^2 in size. The principal towns and cities it drains are Skipton, Keighley, Bingley, Bradford, Leeds and Castleford with a total population of 1,110,000, with more than half of the population in the Bradford and Leeds areas. (GREAT-ER). The river has its source in the limestone moorlands around Malham, flowing 148km to its confluence with the Ouse near Goole, with the last 26km been tidal.

The geologic map of the catchment is as shown in Figure 1. At the source of the Aire, the Carboniferous Limestone produces the characteristic limestone scenery of the Malham Tarn area. From Skipton to Bradford, the geology is dominated by Miltstone Grit, particularly characteristic of the higher moorland areas. In both these areas, the River Aire and its tributaries erode through glacial drift deposits. At Leeds, Coal Measures made up of shales, grits and coal seams predominate. Downstream of Castleford, the Coal Measures are overlain by a narrow ridge of Magnesian Limestone, and adjacent to this, a large area of soft Sherwood Sandstone which underlies the lower reaches (NRA, 1993).

The Aire catchment exhibits very steep topography from Malham to Gargrave, with quite a flat topography between Gargrave and Keighley. Between Keighley and Leeds, its valley floor steepens again. Downstream of Leeds, the topography is notably lower and flatter (EA, 2005).

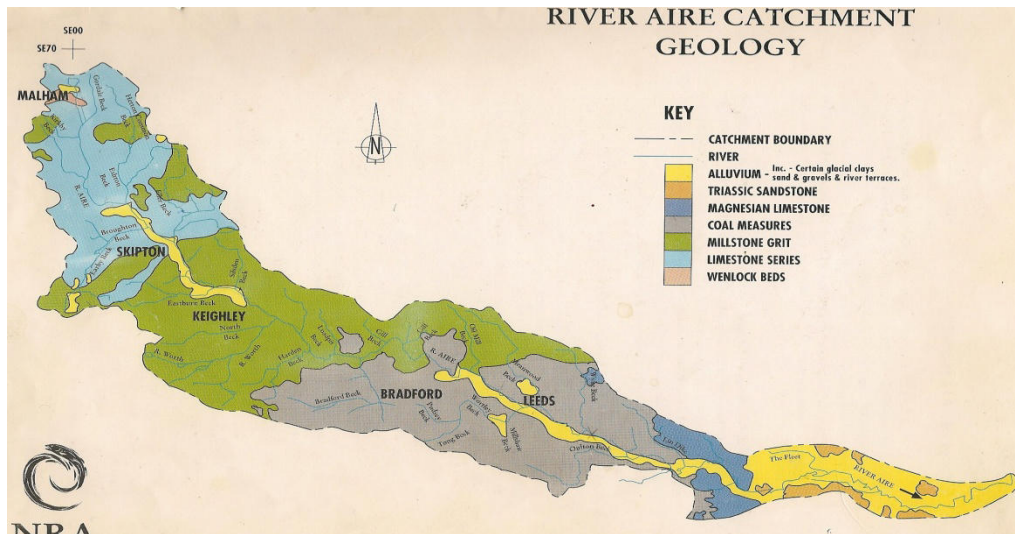


Figure 1. Geological map of the River Aire Catchment (from NRA, (1993))

Figure 2 presents the land use characteristics of the catchment. Dairy cattle and sheep farming are practised on the unimproved grasslands near the source, the practise increasing in intensity towards Keighley on improved and fertilised grasslands. From Keighley towards Leeds, the land use is highly urbanised and industrialised. Below Leeds, the catchment use is predominantly arable and horticultural (EA, 2005).

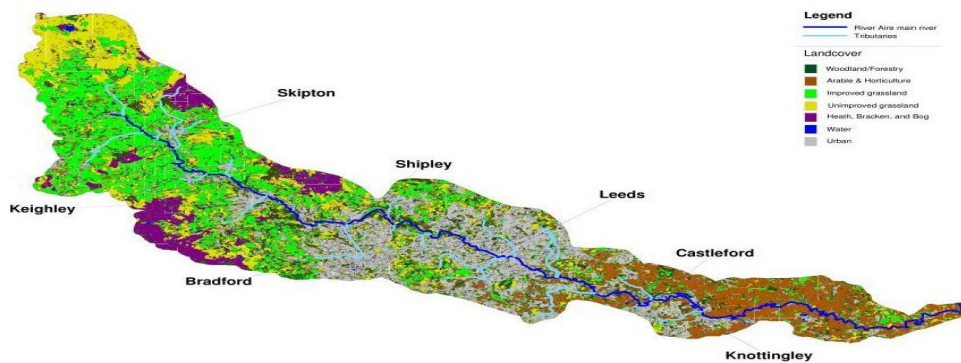


Figure. 2. Land use characteristics map of the River Aire catchment. Legends: Deep Green: Woodland Forestry; Brown: Arable and Horticultural; Green: Improved Grassland; Yellow: Unimproved Grassland; Violet: Peat and Bog; Blue: River; Ash: Urban (from EA Scoping Report, 2005)

The large concentration of population and industries are served by 40 sewage treatment works (STWs), majority of which are trickling filter types which discharge into the Aire catchment (NRA, 1993). A map of the STWs in the catchment is as presented on Figure 3.

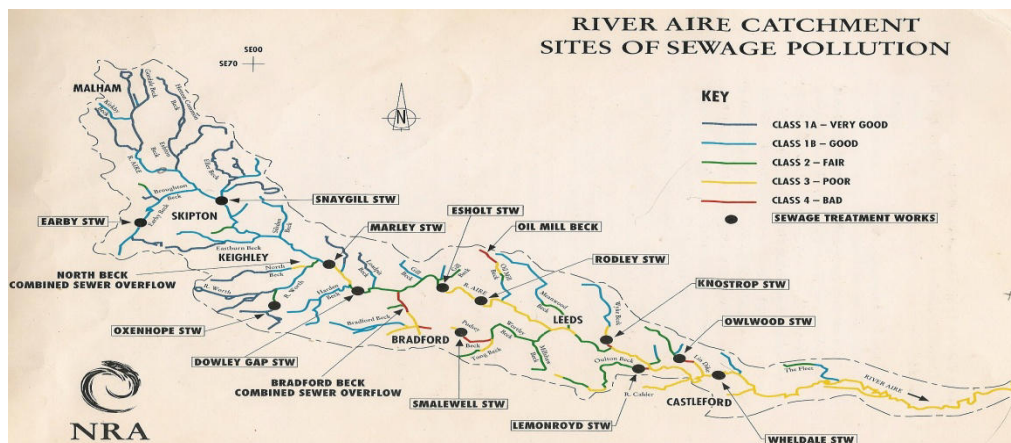


Figure 3. Map of sewage treatment works in the River Aire catchment (from NRA, 1993)

3. Methods

Samples from the River Aire and its tributaries (Earby Beck, Glusburn, and Eller Beck) were collected on a 2 day fieldtrip on Thursday 5th and Friday 6th September 2013. The sample locations are as shown on Figure 4.

Samples were collected using bucket and line at accessible sites of the river and its tributaries. At each sample location, samples were filtered through a 0.45um filter paper, into 2 50ml vials. Stored samples for metal analyses were acidified with 5ml of 10% HNO₃. The samples were then labelled and sent to the University of Leeds for storage and analyses. The cations were measured on filtered and acidified samples by inductively coupled plasma atomic emission spectrometer (ICP-AES) and Silica by spectrophotometry. The anions (SO₄²⁻, Cl⁻, NO₃⁻) were measured by ion chromatography, and alkalinity (HCO₃⁻) by titration with hydrochloric acid (HCl).

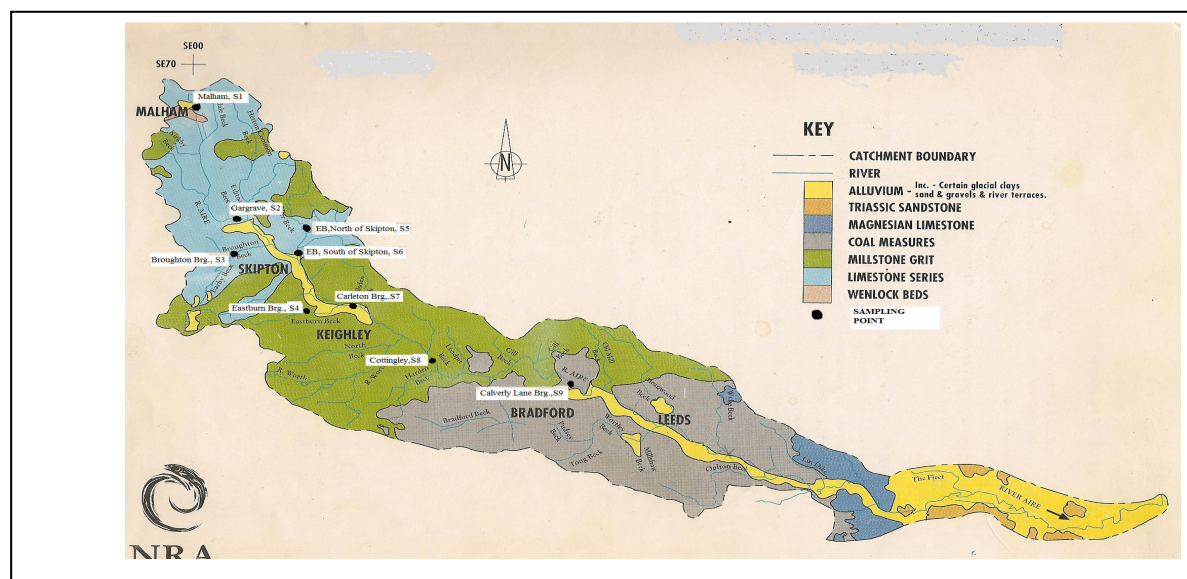


Figure 4. Map of the sampling points of the Aire River and its tributaries superimposed on geological map (from NRA, 1993)

4. Results and Discussions

The data for sample location and codes, the major ions, silica and total dissolved solids (TDS) and the Eq% contributions of the ions to cation and anion components for the Aire and its tributaries are as shown in Tables 1,

2 and 3 respectively.

The charge balance for the samples fall within the $\pm 5\%$ criteria for acceptance for most laboratories (Schwartz and Zhang, 2003). The River Aire and its tributaries are mildly alkaline in nature with pH values ranging between 7.77 – 8.29. The Aire River exhibited a low TDS (the concentration of $\text{Na}^+ + \text{K}^+ + \text{Ca}^{2+} + \text{Mg}^{2+} + \text{HCO}_3^- + \text{Cl}^- + \text{NO}_3^- + \text{SO}_4^{2-} + \text{SiO}_2$ in mgL^{-1}) of 325.67 mgL^{-1} at Malham, with its highest of 518.34 mgL^{-1} at Calverly Lane Bridge.

The cation budget for the Aire is dominated by Ca^{2+} (contributing 89 Eq% to TZ^+ at Malham), decreasing in concentration (contributing 45 Eq% TZ^+ at Calverly Lane Bridge) as the Aire flows away from its source. The concentration of the cations (Na^+ , K^+) increases as the Aire flows towards Leeds, exhibiting extremely high values particularly for Na^+ at Calverly Lane Bridge. The cation contributions for Na^+ and K^+ are 39 and 5 Eq% respectively to TZ^+ at the Calverly Lane Bridge, as compared to 3 and 0.26 Eq% respectively at the Aire source. K^+ which is usually known to have the least concentration amongst cations in natural waters (Berner & Berner,1987), however exceeded the concentration of Mg^{2+} at Calverly Lane Bridge, with records of 12.77 mgL^{-1} and 9.10 mgL^{-1} for K^+ and Mg^{2+} respectively.

Table 1. Sample code labelling and location of sampling

Sample Code	River Name	Sample Location	Sample Code	River Name	Sample Location
<i>Mainstream Aire River</i>			<i>Tributaries of the Aire</i>		
S1		Malham (Source)	S3	Earby Beck	Broughton Bridge
S2		Gargrave	S4	Glusburn	Eastburn Bridge
S7		Carleton Bridge	S5	Eller Beck	North of Skipton
S8		Cottingley	S6	Eller Beck	South of Skipton
S9		Calverly Lane Bridge			

Table 2. Chemical composition of the River Aire and four (4) of its tributaries

Sample Code	pH	TDS (mg/l)	Cations					Anions				TZ ⁺ meq/l	TZ ⁻ meq/l	CB (%)
			Na ⁺ (mg/l)	K ⁺ (mg/l)	Ca ²⁺ (mg/l)	Mg ²⁺ (mg/l)	SiO ₂ (mg/l)	Cl ⁻ (mg/l)	NO ₃ ⁻ (mg/l)	SO ₄ ²⁻ (mg/l)	HCO ₃ ⁻ (mg/l)			
<i>Mainstream Aire River</i>														
S1	8.14	325.67	3.26	0.44	75.90	4.07	3.00	7.2	3.9	2.4	225.5	4.28	4.01	3.18
S2	7.77	365.39	5.60	0.99	77.80	5.30	1.70	11.6	3.5	11.3	247.6	4.59	4.68	-0.97
S7	8.14	401.77	9.23	1.80	77.94	6.48	0.62	18.9	4.2	19.8	262.8	4.87	5.32	-4.42
S8	8.13	344.41	16.21	3.20	58.80	6.95	1.55	30.3	16.9	27.5	183	4.29	4.70	-4.52
S9	8.17	518.34	61.10	13.50	62.04	9.10	1.30	91.8	31	78.8	169.7	6.85	7.51	-4.62
<i>Tributaries of the Aire</i>														
S3	8.29	373.39	13.96	2.63	65.70	5.30	10.50	19.8	9.6	22.6	223.3	4.39	4.84	-4.92
S4	8.24	255.58	10.06	2.02	49.80	6.40	12.60	20.5	7	20.6	126.6	3.50	3.20	4.57
S5	8.13	160.20	5.97	1.13	22.40	5.30	16.10	13.1	2.7	14.7	78.8	1.84	2.01	-4.36
S6	8.01	254.84	9.46	1.51	46.35	6.14	1.98	19.5	4.6	21.9	143.4	3.27	3.43	-2.42

Table 3. Relative contribution of major ions to TZ⁺ and TZ⁻ at various sampling points of the Aire River

Sample Code	Cations				Anions			
	Na ⁺	K ⁺	Ca ²⁺	Mg ²⁺	Cl ⁻	NO ₃ ⁻	SO ₄ ²⁻	HCO ₃ ⁻
All values are in Eq%								
S1	3.32	0.26	88.59	7.83	5.06	1.57	1.25	92.12
S2	5.31	0.55	84.63	9.51	7.00	1.21	5.03	86.77
S7	8.24	0.95	79.86	10.95	10.02	1.27	7.75	80.96
S8	16.43	1.91	68.35	13.32	18.19	5.80	12.18	63.83
S9	38.81	5.04	45.21	10.94	34.48	6.66	21.84	37.03

The anion budget in all the samples is dominated by alkalinity at all the locations, (HCO₃⁻ contributing 92Eq% to the TZ⁻ at Malham), and decreasing in concentration (contributing 37 Eq% TZ⁻ at Calverly Lane Bridge) as the Aire flowed towards Leeds. The concentrations and contributions of Cl⁻, NO₃⁻ and SO₄²⁻ to the TZ⁻ are very low

(5.06, 1.57 and 1.25 Eq% to TZ⁻ respectively) at the source of the Aire but they exhibit high values of concentration and anion charge balance (34.48, 6.66 and 21.84 Eq% to TZ⁻ respectively) as the Aire approached Leeds, particularly at Carlveley Lane Bridge.

The trends highlighted above are shown Figures 5, 6 and 7 for the major cation and anion contribution to the TZ⁺ and TZ⁻, and the plot of the concentrations of the major ions on the hand plotted Ternary diagram at the various sampling points respectively.

Even though the Aire flows on Miltstone Grit lower down its catchment, the silica concentration decreases.

Among the tributaries of the Aire, Earby Beck records the highest TDS (373.39 mgL⁻¹) with the lowest TDS been recorded by Eller Beck, North of Skipton. The Eller Beck, North of Skipton records the highest silica concentration of 16mgL⁻¹ for the tributaries. The tributaries also recorded higher concentrations in Na⁺, Cl⁻, NO₃⁻ and SO₄²⁻ as compared to the concentrations of the same analytes for the source of the Aire.

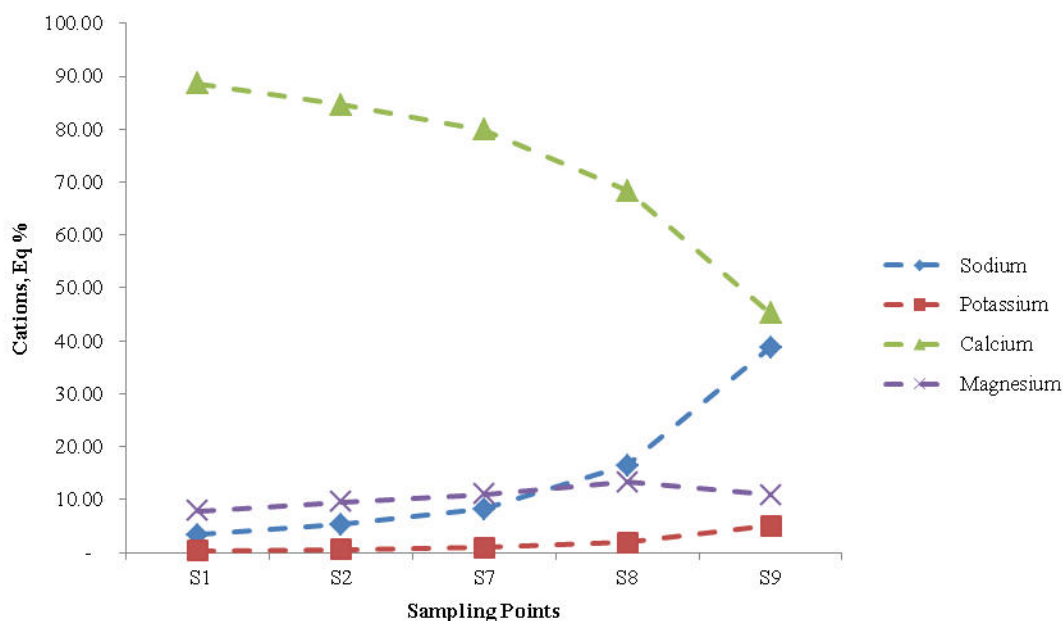


Figure 5. Cation Eq% contribution to the TZ⁺ at the various sampling points as the River Aire flows from its source (Malham, S1, rural) to Leeds (S9, urban)

Chemical weathering of the various lithologies, atmospheric deposition and anthropogenic sources in the Aire Catchment supply the major ions in the Aire River. An attempt will be made to trace sources of the major ions in the River Aire as it flows from its source towards Leeds.

The values of TDS within the reaches of study characterises the Aire River as a freshwater body (Davies and DeWeist, 1966). Dominance of Ca²⁺ and HCO₃⁻ from Malham to Gargrave correspond to the Limestone source and the steep slope that enhances dissolution of the limestone bedrock on which the river flows. The very low concentrations of Na⁺, K⁺ and Cl⁻ may be attributable to windblown aerosols which originate from the coast and reach land surface through precipitation. In contrast, the SO₄²⁻ and NO₃⁻ could originate from acid deposition from anthropogenic sources like industrial and vehicle emissions. The high concentration of Na⁺, K⁺, Cl⁻, NO₃⁻ and SO₄²⁻ noted for the Aire tributaries are probably from the effluent from untreated sewage that is discharged directly into the tributaries and leached fertilizer applied on the improved grasslands and livestock droppings that has reached groundwater, that is supplying base flow to the tributaries since, the study was conducted in late summer. The tributaries contribute to the Aire at Carleton Bridge, increasing the concentration of the above named species for the Aire at that location.

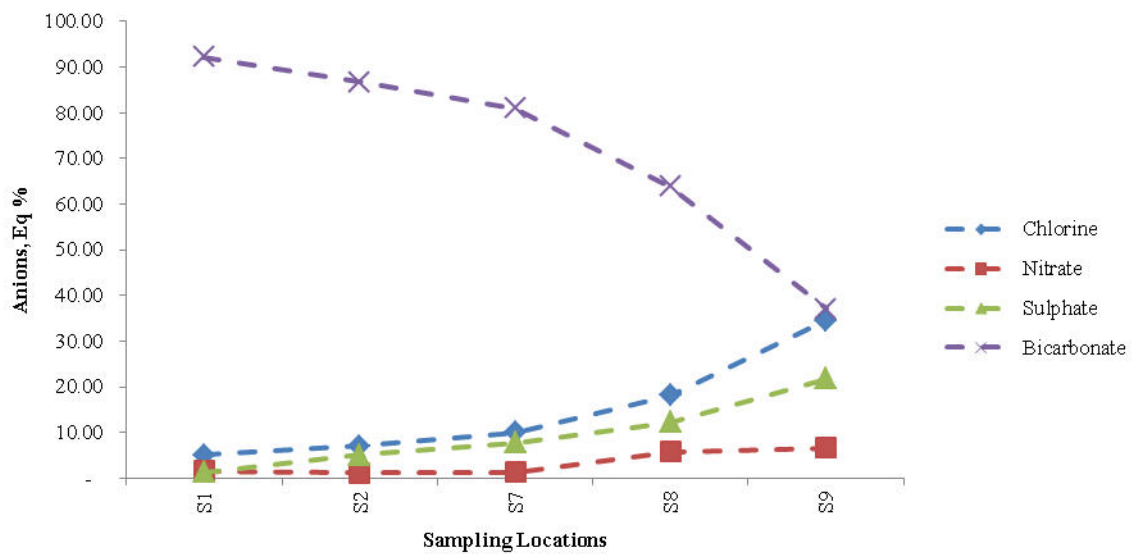


Figure 6. Anion Eq% contribution to the TZ at the various sampling points as the River Aire flows from its source (Malham,S1, rural) to Leeds (S9, urban)

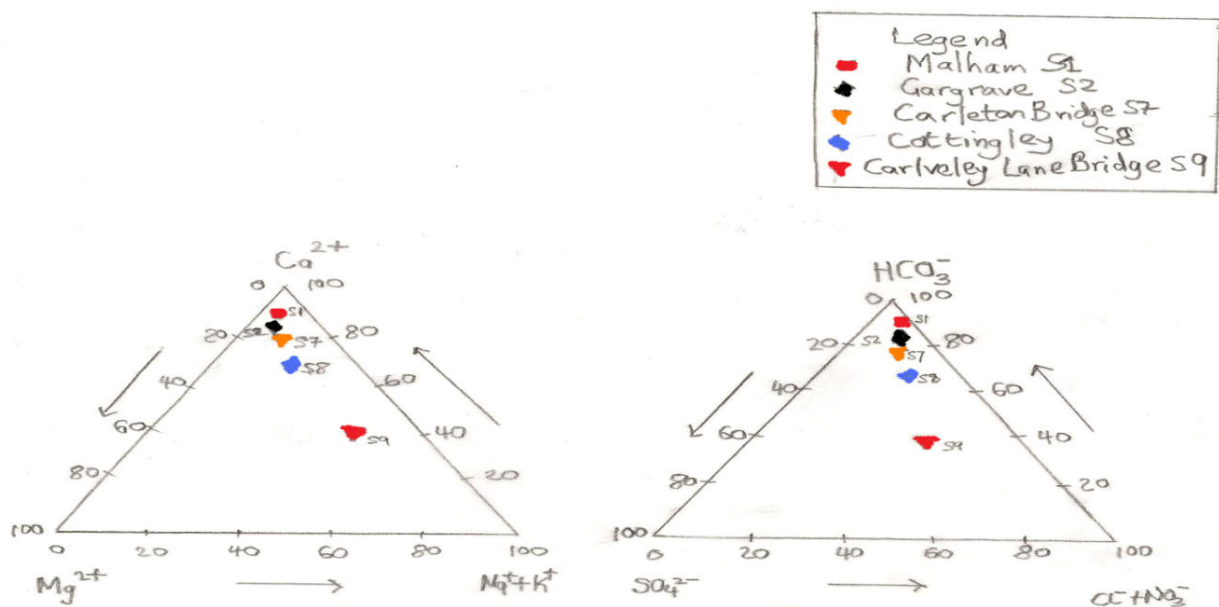


Figure 7. Ternary plots for cations and anions in the Aire River along its course from Malham,S1 towards Leeds,S9

The reduction of silica concentration as the Aire flows downstream on the Miltstone Grit is due to the resistance of quartz to erosion and weathering and to the flattening of the topography which reduces river abrasive action (Berner & Berner, 1987). A comparison of the very high silica concentration values that have been recorded for the tributaries that are on very steep slopes of the Aire catchment illustrates this reasoning.

As the Aire flows from Keighley towards the heavily populated and industrialised cities of Bradford and Leeds, extremely high concentrations of Na^+ , K^+ , Cl^- , NO_3^- and SO_4^{2-} are recorded at Cottingley and Calverly Lane Bridge. These are from point source effluent discharges into the Aire River from communal sewage treatment works and wastes and brines from industries that are concentrated around these urban centres. Previous work by the NRA (1993) and Ward and Robinson (2002) cite the Aire as a catchment in the UK with large inputs of industrial effluent and domestic sewage resulting in very high concentrations of chloride, nitrates, sodium and sulphates.

The high TDS exhibited by the Aire River as it flows downstream can affect Salmonids and their spawning habitats (Weber – Scannel and Duffy, 2007). High nitrate concentrations from domestic sewage can lead to enrichment of the Aire, resulting in excessive algal growth. Eutrophication can lead to severe oxygen depletion leading to the death of fishes and other aquatic life. River enrichment can also lead to problems for water supply abstractions by causing taste, smell and filtration problems.

The concentrations of the major ions satisfied the UK national standard for water supply to taps (Water Supply & Quality Regulations 2000) for the reach under study, implying that the treatment of Aire River under the reach of study for consumption will not be problematic for TDS. However, these values could increase and exceed admissible values because of anthropogenic activity.

5. Conclusion

Limestone dissolution dominates the Aire River at its source, contributing high calcium and bicarbonate ions. As it flows from Gargrave to Keighley, the impact of agriculture and slight urbanisation is noted in the change in the chemistry of the Aire. As the Aire reaches Calverly Lane Bridge, flowing through the highly urbanised cities of Bradford and Leeds, the anthropogenic impacts on the river are noticeable by the high concentrations of sodium, potassium, chloride, nitrate and sulphate ions, which drastically change the chemistry of the river.

In conclusion, it is noted that the chemical composition of the Aire as it flows from its source is highly influenced by natural control of limestone dissolution; however as it flows downstream away from its source through Keighley towards Leeds, the chemical composition is considerably influenced by the activities of man like agriculture, urbanisation and industrialisation.

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