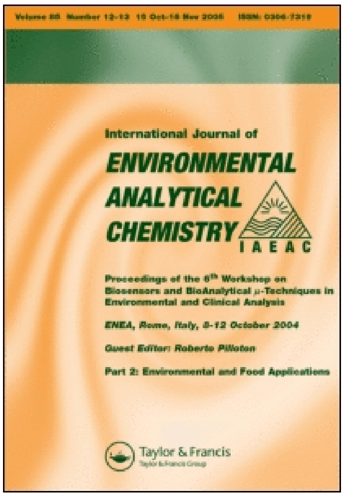

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A BASELINE STUDY OF METAL ION CONTENT OF IRISH CANALS BY ICP-MS

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The first systematic study of the metal ion content of the four main Irish Canal Systems is presented. Samples were collected seasonally over a twelve month period and analysed for 16 trace elements and metals by ICP-MS. The results show that three of the four canals (Royal, Grand, Shannon–Erne) have distinctly different elemental profiles, while the fourth (Barrow) is similar to the Grand Canal, which is to be expected, as they are broadly part of the same system, with a common main feeder. Spatial plots reveal local variations in certain elements, which are related to the nature of feeders in those localities. Simple tests based solely on the 16 elements measured showed that it may be possible to broadly define 'normal' compositions for each canal system, which can be then used to identify 'abnormal' data, and hence provide indicators for environmental change.

Keywords: ICP-MS; Canal water; Ireland; Pattern recognition; Elemental analysis; Elemental profiles

INTRODUCTION

Canals are man-made linear networks of navigable waterway, which cut across watersheds, linking rivers, which would otherwise remain isolated, and act as corridors along which wildlife can travel, on land and in the water [1,2]. The canal systems of Ireland were once an important means of communication and trading from their opening in the late eighteenth century, until cessation of activity in the 1950s [3]. In 1986, the canals were transferred to the Office of Public Works (OPW) and since that date, major restoration and development work has taken place, financed by the Irish State and the European Union. Today the canals are used as important public amenities. They are enjoyed by many people for recreational pursuits such as boating, walking and fishing, and by those interested in nature, architecture and engineering.

The four major canal systems sampled[†] in this work were the Grand Canal, the Royal Canal, the Barrow Canal and the Shannon–Erne waterway (Fig. 1). The main line of

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[†] Each canal sampling site was given a number preceded by an identifier code, G = Grand, R = Royal, B = barrow, S = Shannon. Full details are available from the authors on request.

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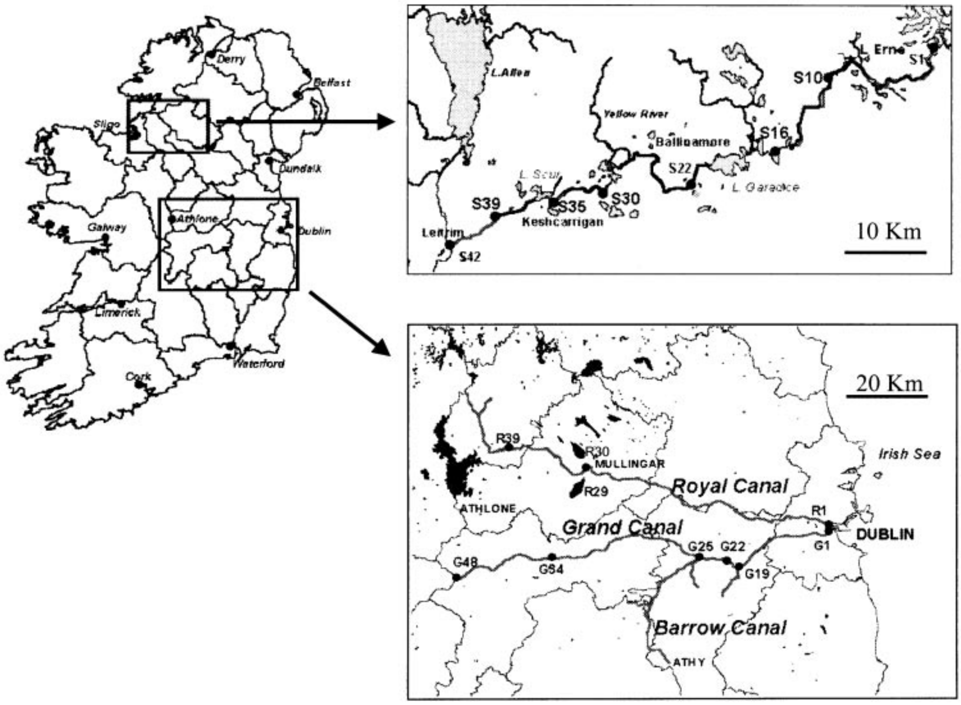

FIGURE 1 Map of Ireland showing locations of the canal systems studied.

the Grand Canal is 131 km long with 43 locks [1], and in this study, samples were retrieved from 47 locations along its length numbered sequentially from the Grand Canal Basin in Dublin Docks (G1) to the River Shannon at Shannon Harbour (G47). The Barrow Canal runs south 45 km from the summit level and intersection with the Grand Canal at Lowtown, Co. Kildare to join the River Barrow at Athy [1]. Samples were taken at 18 locations on this waterway. The main line of the Royal Canal is 145.7 km long with 46 locks and it was sampled at locations ranging from the River Liffey in Dublin (R1) to Ballybrannigan Harbour (R44) [2] (this canal has not yet been fully restored to the River Shannon). The Shannon–Erne Waterway is 62.5 km long [4], and it was sampled at 44 locations from the River Erne in Fermanagh (S1) to the River Shannon at Leitrim (S44).

Despite the fact that the canals cut through a variety of habitats – raised bogs, fens, eskers and solid limestone rock – they each receive water from one main feeder system, as well as several minor feeders. The Grand Canal and Barrow Canal are fed from the Milltown Feeder (G23). This feeder originates in the Pollardstown Fen, an area abundant in springs of lime-rich alkaline waters. The Royal Canal is fed directly from Lough Owel (R30), a lake of unique quality situated in a small carboniferous limestone catchment [5]. The Shannon–Erne system receives water from Lough Scur (S35), a highly coloured peat-stained lake.

A report by the Environmental Protection Agency in 1999 [6] discussed the water quality of Irish canals and referred to work by Caffrey and Allison [7]. The EPA report stated that this information had not previously been presented in national reports. However, the work by Caffrey and Allison concentrated mainly on nutrients and physico-chemical tests and thus before this study began, no detailed information was available on the trace element composition of the canal systems.

Because of the unique feeder systems, it was hoped that the water chemistry would be fairly consistent along the entire length of each canal, enabling a unique ‘elemental fingerprint’ to be established for each water system. The aim of this study was therefore to establish whether each individual canal system possessed unique inorganic chemistry, and whether this chemistry was spatially and temporally consistent.

FIELD SAMPLING

Sampling was carried out on each canal on a seasonal basis by Central Fisheries Board staff (i.e. spring, summer and autumn/winter). Sample sites were spread along the entire length of each system. The samples were sent to the Central Fisheries Board (CFB) laboratory in Dublin, where they were analysed for 16 mineral elements and metals.

Sample Collection

Samples were taken from the canal bank using clean, previously unused 150 mL polypropylene sample bottles. In all cases the bottles were rinsed several times with the sample before filling. At some sites on the Shannon–Erne lakes, samples were taken from a boat mid-lake. Sampling sites were chosen to represent sections of the canal system, i.e. at least one site in each lock system, and additional sites where the lock was particularly long or at a feeder inflow (see Fig. 1).

Sample Storage and Transport

Upon collection, samples were stored in large “cool-boxes” surrounded by ice-packs. Samples from the Royal, Grand and Barrow were returned to the ICP-MS Lab on the evening of collection and stored in a fridge overnight. Samples from the Shannon–Erne system generally arrived in Dublin on the day following collection. All samples were brought to room temperature before sample preparation and analysis.

EXPERIMENTAL

Instrumentation

A Varian Ultramass 700 ICP-Mass Spectrometer fitted with a Varian SPS-5 Autosampler was used for analysis. Sample introduction was via a concentric glass nebulizer (K style) coupled to a Sturman-Masters Spraychamber.

Sample Preparation

Solids in the sample were allowed to settle before the liquid portion was removed by pipetting. Solids cannot be introduced to the fine bore of the ICP-MS nebuliser, and filtering and centrifuging introduces contamination at low levels. The liquid portion was diluted by a factor of 10 with Milli-Q water (18 Mega-Ohm) and acidified to 1% (v/v) with HNO_3 (Aristar Grade). The samples were allowed to stand for a minimum of 16 h before analysis as recommended in US-EPA Method 200.8 [8].

Sample Analysis

A quick and reliable method of analysis was required in this study, given the large number of measurements made (*ca.* 30 000 in total). To avoid the need for multiple analysis of each sample, and different sample preparation procedures, only those elements that could be run easily using standard ICP-MS operating conditions were considered. While we were motivated to profile those elements that are important in terms of defining water quality, elements such as Hg, Se, and As, that require more complex analytical procedures unfortunately had to be omitted. The high concentrations of the mineral elements (Ca, Mg, K and Na) in the canal waters made their analysis by ICP-MS difficult. However, due to their low ionisation potentials, it is possible to use cool plasma conditions to measure these elements. These operating conditions have been shown to be suitable for such elements where low detection limits are required, but it also proved useful for analysis at high concentrations in this study because it reduces the mass spectrometer detector sensitivity [9]. Iron was also analysed using cool plasma conditions due to interference from ArO under normal conditions. Typical standard and cool plasma operating conditions used in this study are summarised in Table I.

Calibration was carried out using working standards prepared from pre-mixed Merck multi-element standard IV for ICP. Standards were in the range 10–500 ppb for normal conditions and 50–1000 ppb for cool plasma conditions. The ICP-MS software used linear calibration curves to calculate individual element concentrations. The software automatically flagged any result above the calibration range. For the purposes of this study these high results were considered acceptable because of the extremely linear nature of this method of analysis. However, it must be noted that this was only necessary for elements present in unusually high concentrations such as calcium and sodium.

A composite internal standard representing the range of element masses was "teed-in" to the sample introduction line. Each element was assigned the internal standard closest to its atomic mass. The instrument software measured the internal standard signals with each sample and automatically calculated and corrected for any drift that may have occurred during analysis from the original internal standard signal.

A preparation blank (Milli-Q water/1% v/v Aristar Grade HNO_3) and two different quality control standards representing low and high level concentrations of trace

TABLE I ICP-MS normal and cool operating conditions

	Normal conditions	*Cool plasma conditions (Fe, Ca, Mg, K and Na)*
RF Power	1.28 kW	0.7 kW
Plasma flow	17.0 L/min	18.0 L/min
Auxiliary flow	1.05 L/min	1.00 L/min
Nebuliser flow	0.95 L/min	1.22 L/min
Sample uptake	1 mL/min	0.8 mL/min

elements were also analysed with each set of samples. The quality control standards (named SPSW-1 and SPSW-2) were purchased from Promochem UK and a 10% dilution with Milli-Q water was carried out of each standard before analysis. The certified values were entered into the analytical method and any result outside ±10% was automatically flagged.

On analysis, 5 replicate determinations were made of each sample and a mean concentration was reported by the ICP-MS software. Calculation of element concentrations based on prior calibration equations and correction for internal standard and dilutions was carried out automatically by the instrument software. The results file was then exported to Microsoft® Excel and Minitab® for further processing.

DATA ANALYSIS

Initial data exploration was carried out with Microsoft® Excel using simple graphical displays of the linearity and spatial distribution. Following this, more detailed multivariate analysis using Minitab® software (Minitab Inc., 3081 Enterprise Drive, State College, PA 16801-3008, USA) was carried out. The techniques used were Principal Component Analysis (PCA) and Discriminant Function Analysis (DFA) [10,11]. There has been a rapid increase in the number of papers employing these chemometric techniques for aiding the analysis and interpretation of environmental data since the early 1990s. For example, PCA has been successfully applied to the analysis of sediments and sea waters [12–14] and to the temporal evolution of groundwater composition [15], while Alberto *et al.* [16] used the technique to study the spatial and temporal variations in water quality in a river basin.

DFA has been applied to the identification of origin of Atlantic salmon [17], the interpretation of geochemical development in Managed Retreat sites in the UK [18] and grouping of locations in Hong Kong to select environmental and toxicity data [19]. Classification techniques, such as DFA, are used to predict group memberships using *a priori* information. Environmental problems, however, tend to be orientated towards identifying factors responsible for the state of a given system, and so techniques such as PCA are more popular in comparison.

RESULTS

The composition of each system, in terms of 16 selected elements is summarised in Table II. A total of 153 sampling locations were involved, and each location was visited on average three times. The names of all sampling sites and the number of individual samples taken can be obtained from the authors on request. The total number of measurements of each element in each canal system varies according to the number of sampling sites on the canal and the number of samples taken at each site (total samples taken were 46, 93, 108, and 116 for the Barrow, Grand, Royal and Shannon–Erne, respectively). Five replicate measurements of each sample were made for the 16 elements monitored to give a total of over 29 000 measurements. In order to identify broad patterns within the data, an average arithmetic mean and standard deviation of each element was calculated for each canal system (Table II). These environmental standard

TABLE II Summary data for each canal system

Elements	*Barrow $n=46$*		*Grand $n=93$*		*Royal $n=108$*		*Shannon–Erne $n=116$*		*EU MAC**
	Mean	*%RSD*	*Mean*	*%RSD*	*Mean*	*%RSD*	*Mean*	*%RSD*	
Ca (mg/L)	109	25	98.1	28.1	118	28.1	31.7	39.6	200
K (mg/L)	2.39	68.3	2.12	43.0	2.79	42.6	1.96	47.9	12
Mg (mg/L)	14.5	13.7	12.2	20.2	8.27	20.6	3.76	57.1	50
Na (mg/L)	9.28	22.3	10.3	25.0	10.1	27.1	8.39	16.0	150
Al (μg/L)	6.72	37.2	10.8	93.2	12.2	314	99.4	186	200
Ba (μg/L)	53.9	23.4	57.3	33.5	37.1	62.3	17.5	38.5	500
Cd (μg/L)	0.33	73.7	0.09	130	0.17	120	0.17	95.6	5
Co (μg/L)	0.42	73.6	0.25	63.0	0.36	46.8	0.17	55.6	N/A
Cr (μg/L)	2.71	99.0	1.38	63.7	2.14	67.0	1.22	92.8	50
Cu (μg/L)	0.79	58.3	1.10	57.6	1.47	88.5	2.80	86.6	500
Fe (μg/L)	24.7	89.9	43.6	91.8	27.9	117	317	93.5	200
Mn (μg/L)	1.14	51.9	8.01	431	5.40	197.5	13.7	59.7	50
Ni (μg/L)	4.75	42.9	2.77	54.8	5.24	42.0	4.25	42.4	50
Pb (μg/L)	0.11	197	0.07	114	0.09	88.7	0.45	85.7	50
Sr (μg/L)	200	17.8	214	18.6	379	28.9	130.5	51.6	N/A
Zn (μg/L)	3.86	158	2.33	267	1.45	188	5.00	159	1000

Mean values and %RSD for 16 elements in the 4 major canal systems. *EU Maximum Admissible Concentrations (MAC) for drinking water. The number of samples (n) given above is a combination of the number of sampling sites on each canal and the number of times each site was sampled. This was usually 3 times, with a minority being sampled twice or four times.

deviations provide initial information on the relative spatial and temporal variation in the data and will be discussed later.

Some broad conclusions can be drawn from the data in Table II.

- In general, the canal water is unpolluted in terms of heavy and transition metal content (Pb, Zn, Cr, Co, Cd, Mn, Cu, Ni) as the levels found are all below the EU-maximum admissible concentrations.
- The mean concentrations of periodic table Group II elements are lower in the Shannon–Erne than in the other three systems.
- Al, Fe and Mn mean concentrations are relatively high in the Shannon–Erne system. Fe in particular is very high – values up to 1165 μg/L were found, which is approximately an order of magnitude higher than the other systems.
- The mean concentrations of periodic table Group I elements K and Na are relatively constant across all four systems at around 2–3 and 8.5–9.5 mg/L, respectively.
- There is always a strong similarity between the mean concentrations of elements in the Barrow and Grand Canals. The correlation coefficient between the two data sets is high ($R=0.9975$), although when Group II elements and Iron are omitted, this drops to $R=0.7473$, suggesting there are some differences that might serve as a basis for discriminating the two water bodies.
- The relative standard deviations indicate how variable each element is within each canal system data set. There are two main contributors to this variability – the spatial or geographic variability and the temporal variability. For example, the mean concentration of Al is highest in the Shannon–Erne system (80.78 μg/L), but the variance is much higher in the Royal (%RSD = 323.9 compared to 60.4), which establishes that there are places in the Royal Canal where the Al concentration strays quite an amount from the mean.

Chemometric Analysis of Data

Principal Component Analysis was carried out on the arithmetic mean concentrations for each sampling location on the four canal systems. As expected from the high correlation between the Barrow and Grand Canals, a plot of PC1 *vs* PC2 shows quite an overlap of the points relating to these two systems (Fig. 2). The Shannon–Erne is separated well in the first principal component, and the Royal Canal is separated from the others in the second principal component.

Examination of the loading coefficients reveals that the PC1 coefficient is being dominated by elements such as Ni and the Group II elements, particularly Ba and Mg. The PC2 coefficient is dominated by Fe, Al, Cu, Pb (which are all relatively high in Shannon–Erne) and the Group II elements (which are all relatively low in Shannon–Erne). The Royal Canal has the highest mean concentration of Sr (389 µg/L) and the concentrations across this system were relatively consistent (%RSD = 28.9). It is therefore likely that this element must be a major contributor to the differentiation of the Royal from the other water bodies as seen in Fig. 2.

When periodic table Group II elements are removed from the data set, and the same data exploration carried out, the discrimination between the Royal, the Barrow and the Grand is lost and the Shannon–Erne points start to diagonalise (not shown). Diagonalisation is an indication of loss of information, so it can be concluded that these elements play a particularly important role in discriminating between the four water bodies.

Identification of 'Unknowns'

Linear Discriminant Function Analysis (LDFA) was carried out on the data and the results are displayed in Table III. Cross-validation was then carried out using a variation of the "leave-one-out" method, where one sample was removed and the

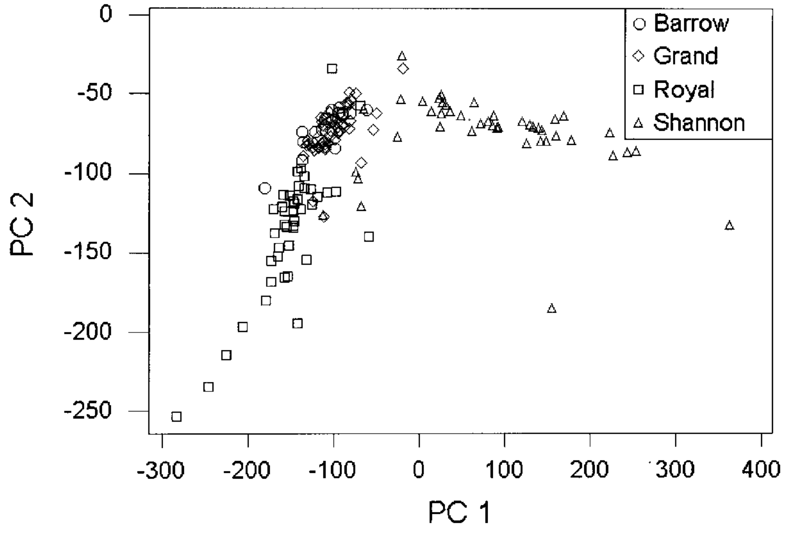

FIGURE 2 Plot of first two principal components.

TABLE III Summary of classification (with cross-validation in parenthesis)

	Royal		*Grand*		*Barrow*		*Shannon–Erne*	
Royal	42	(39)	1	(1)	0	(0)	0	(2)
Grand	2	(3)	45	(42)	2	(3)	0	(0)
Barrow	0	(0)	1	(3)	16	(14)	0	(0)
Shannon–Erne	0	(2)	0	(1)	0	(1)	44	(42)
Total *N*	44		47		18		44	
N Correct	42	(39)	45	(42)	16	(14)	44	(42)
Proportion	0.96	(0.89)	0.96	(0.90)	0.89	(0.78)	1.0	(0.93)

remaining data used to generate a new classification rule. The new rule was then applied to the entire data set, and those omitted were examined for membership of the predetermined groups. These results are given in parenthesis and reflect the accuracy of the discrimination rules derived. It was found that the Shannon–Erne canal was almost perfectly discriminated – (95.5% of results were correctly classified) – whilst the Grand displayed certain levels of overlap with both the Barrow and Royal, due to similarities in their elemental composition (Table II). This suggests that a 'normal' profile for each can be defined, which could be used to detect 'abnormal' or polluted conditions.

GEOGRAPHICAL DISTRIBUTION OF ELEMENTS

Although the discriminant analysis suggests that each water body is relatively distinct from the others, the relative standard deviations in Table II reveal that certain elements must vary considerably along the length of a particular canal system. Geographic (spatial) distributions of elements were therefore explored, and some that display interesting features are presented.

The Shannon–Erne Canal

The Shannon–Erne system has a much higher overall concentration of iron than the other canal systems (Table II). This was investigated in further detail by plotting the geographical distribution of the mean iron concentration from Lough Erne (S1) in the east to Leitrim (S44) at the River Shannon (Fig. 3). Particularly high iron concentrations are evident for the Yellow River (S25) and Aghascashlawn River (S34) tributaries, both of which flow from a mountainous area of shale, sandstone and coal, known locally as the "Iron Mountains" due to high iron deposits in the red/orange coloured soils. In times of flood both of these rivers discharge large brown "plumes" of material into their respective lakes. Interestingly, the average iron concentration in Shannon–Erne canal (317.66 μg/L) is the only example that is higher than the EU-maximum admissible concentration (MAC), which is 200 μg/L for drinking water. In contrast, the Groups I and II elements K, Na, Ca and Mg show the opposite pattern to Fe, with minimum values in the spatial plot corresponding to the Yellow River and Aghascashlawn River (Fig. 3).

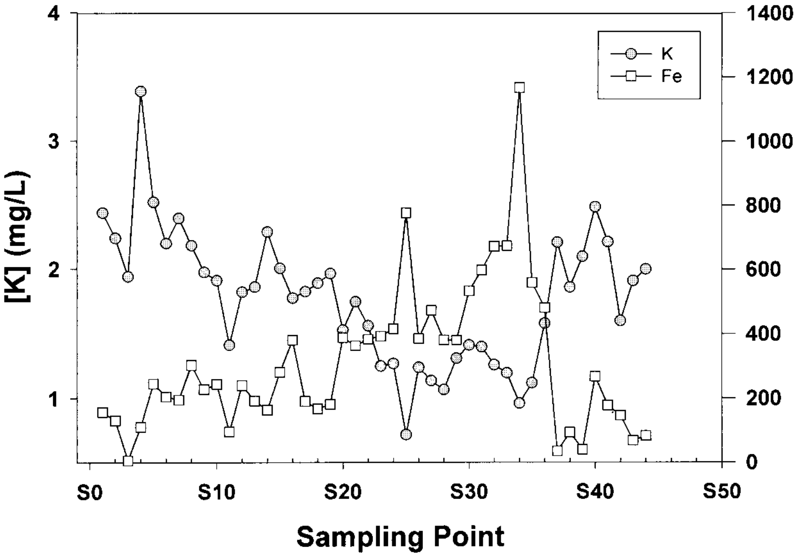

FIGURE 3 Shannon–Erne canal [Fe, K] spatial profile.

Royal Canal

The mean concentrations of each element at each sampling location were plotted spatially from Dublin in the east (R1) to Ballybrannigan Harbour (R44) in the west. Again, some interesting trends were noted, particularly the sudden increase or decrease in some elemental concentrations near the main feeder from Lough Owel at Mullingar (R30). A particularly clear drop in concentration at the Owel feeder is seen for Ca, Mg, Ba, Sr, Cu, Fe, Mn and Ni. The profile for Ni is shown in Fig. 4 to illustrate these metals. This feature is due to water entering the system from Lough Owel, which is generally regarded as being a clean lake.

Whereas most other elements occur in lower concentrations in the Lough Owel Feeder (Fig. 4), sodium, potassium and zinc are present in higher concentrations than in the adjacent regions of the canal (e.g. see potassium in Fig. 4). Another notable feature of the spatial distribution of sodium and potassium is the increase in concentration at the eastern end of the canal (R1–R3) where it links to salt water at Dublin. The geographical distribution of aluminium in this water body was of particular interest, given the very large relative standard deviation (Table II). The levels are generally low, at *ca.* 5.0 μg/L, for the entire water body except in the greater Dublin region (R1–R14). Here the levels reach almost 30 μg/L in two places (R8 and R14), and over 10 μg/L at three nearby locations (R2, R5 and R9). Whilst this about a factor of ten lower than the EU-MAC value in current regulations (200 μg/L [20]), it is interesting to note that R9 and many other higher than average results are found in samples at or near feeders and tributaries to the canals. This may be due to colloidal suspensions, and a more focused local study could confirm this.

Grand Canal

A gradual decrease in sodium concentration westward from Dublin is seen in the spatial distribution plot for the Grand Canal (Fig. 5), which is reminiscent of the distribution

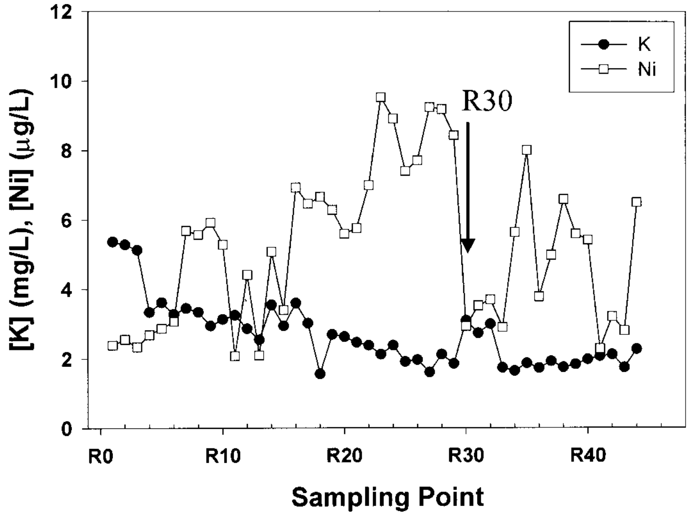

FIGURE 4 Royal canal [K, Ni] spatial profile.

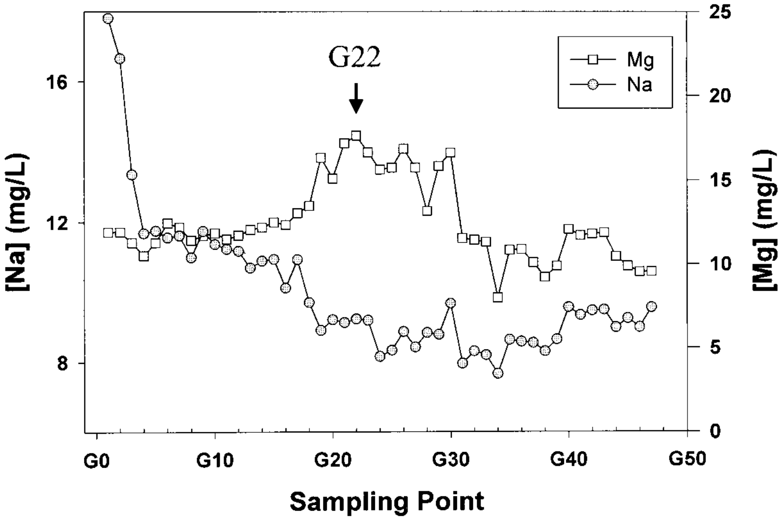

FIGURE 5 Grand canal [Mg, Na] spatial profile.

found for potassium in the Royal canal mentioned previously. There is a marked decrease in the sodium concentration from the site closest to the sea (G1) at the Grand Canal Basin (G1–G7) in Dublin, which would be expected due to intrusions of salt-water into this area. In contrast, the magnesium concentration in this canal shows a peak at Robertstown (G22, *ca.* 14 mg/L), which is near the Milltown Feeder (Lowtown, G23, the summit level of the canal) with concentrations dropping off to east and west. This trend (i.e. a peak in the region of the summit level), is also seen for calcium and to a lesser degree for nickel. Once again, the enhancing effect of feeders due to elevated levels of some elements (e.g. Mg) and a simultaneous dilution effect on other elements (e.g. Na) is clearly evident at sampling sites G20 and G23. In contrast, the

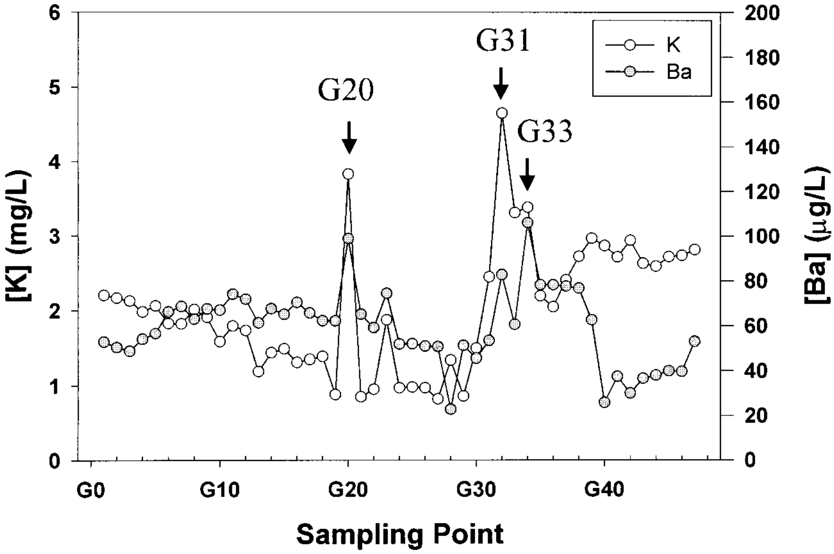

FIGURE 6 Grand canal [K, Ba] spatial profile.

feeders at G20 and G31–G33 are high in potassium and barium, and result in localised elevated levels of these elements (Fig. 6).

Barrow Canal

In general, the mean concentrations of elements in the Barrow Canal are similar to those of the Grand Canal (Table II). The PCA plot (Fig. 2) shows large overlap between these two systems and it was difficult to separate them using this technique. Thus, it is evident that the water chemistry of the Grand Canal and Barrow Canal is very similar, which is not surprising as they arise from the same primary feeder system (the Milltown Feeder) that meets the canals at Lowtown (G23). There were no obvious common trends seen in spatial plots of the Barrow Canal, apart from a rise in the levels of sodium and cobalt at the southern end, near Athy. The mean concentrations of calcium and manganese in the tributaries were found to be generally higher than the main canal channel, while those of iron and aluminium were lower.

Temporal Variations

Temporal variation proved difficult to assess in this study due to the fact that sampling was carried out at just three occasions during the year. These were spring, summer and autumn/winter. Nevertheless, it was interesting to note that concentrations of some elements decreased during summer, whilst others increased. Previous work elsewhere has suggested that differences due to geographical position are more important than seasonal variation. Marengo *et al.* [21] found that seasonally dependent species tended to be those affected by phytoplankton activity. Thus, it was not expected to find much seasonal variation in the low concentration metals and transition elements. Generally, this was found to be the case, with the exception of iron, which seemed to increase in summer, and manganese, which decreased in summer. Most interestingly, two major elements – calcium and potassium (and to a lesser extent also sodium) – showed a decrease in the summer samples. This was seen in all four canal systems and may be related to a loss of mineral elements due to biological uptake and precipitation. Indeed, Caffrey *et al.* have mentioned these two pathways in previous works on the canals where loss of nutrients in summer was observed [3,7,22].

CONCLUSIONS

This investigation has revealed that, for the 16 elements tested, the composition of the Royal, Shannon–Erne and Grand canals is distinctly different, whereas the Barrow is broadly similar to the Grand canal. Results also indicate there are interesting patterns in the spatial distribution of some of these elements across the length of the canals. In general, the principal water source dominates the chemical content throughout each system, with localised influences from secondary feeders. The water quality in terms of these elements monitored is good, with no incidences of pollution. The average concentration of iron in the Shannon–Erne system is the only example that exceeds the EU-MAC level, and this arises from natural sources.

The chemistry of the Shannon–Erne waterway is clearly different from the other canal systems. This canal is well-separated geographically from the others, and the concentrations of some metals (e.g. iron) is strikingly elevated. This causes the Shannon–Erne waterway to cluster separately from the other systems in all subsequent plots. It is separated in the first component in PCA and almost perfectly discriminated using DFA.

A strong correlation exists, particularly for major elements, between the results obtained for the Grand and Barrow canals, both of which receive water from a common source, the Milltown Feeder. In this case, separation was only achieved when the third discriminant factor was reached. This suggests that the major elements are derived from the main water source but minor elements have a more local origin. Some separation was achieved in the second discriminant factor (DF2) when Al, Ba, Mg and Sr were removed from the data set. Removal of these elements clearly promotes the minor "local" elements to higher significance.

It is evident from Table II that element concentrations in the Royal are broadly similar to those in the Grand and Barrow. However, good separation was achieved between these and the Royal in the original DFA plot (not shown). Upon removal of Al, Ba, Mg and Sr separation is lost in the first discriminant factor (DF1), and the Royal completely overlaps with the Barrow in DF2.

This study demonstrates how multivariate analysis can be used to group water samples from canal systems and distinguish them from each other. The cross-validation work illustrates the possibility of defining a 'normal elemental profile' for these water bodies that could be used to identify 'abnormal' profiles in the future. Furthermore, geographical (spatial) plots of certain elements revealed gradual trends in concentration as well as some interesting patterns such as localised peaks and troughs, which are related to the composition of local feeders.

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