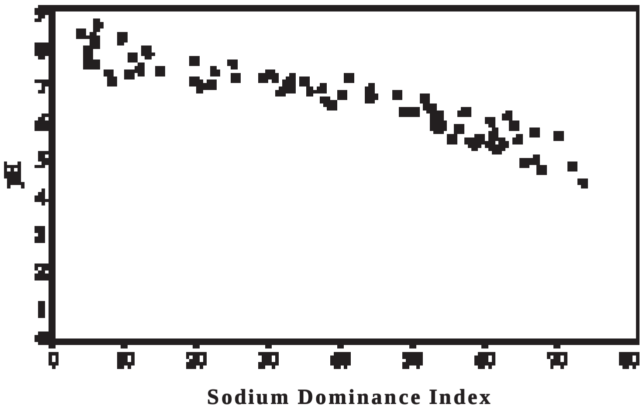
Relationship between the Index and pH and alkalinity

The relation with pH was linear (Figure 3). Figure 4 illustrates the linear relationship between Sodium Dominance and alkalinity for sites considered to be acid sensitive (i.e. alkalinity <200 meq l^{-1}). These sites all have Sodium Dominance Index values in excess of 40%.

Research Conclusions

The results are encouraging and provide strong support for the application of the Sodium Dominance Index as a measure of acid sensitivity in Irish rivers. Those water bodies which have been traditionally classified as sensitive, on the basis of low pH and alkalinity, had Sodium Dominance values consistently greater than 40% regardless of whether the sample was taken at base flow or during high discharge conditions.

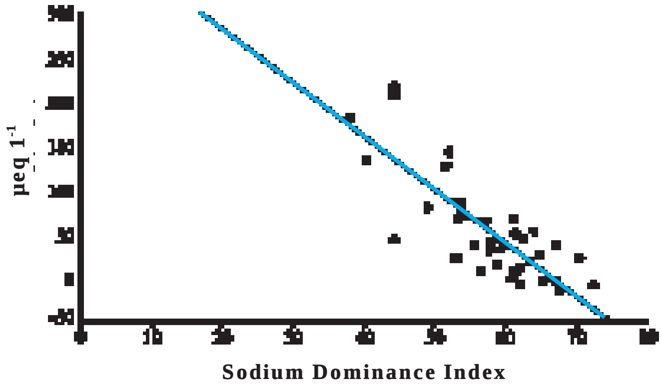


Equation of the regression:
$y = 7.89 - 0.01x - 0.0004x^2$, n = 82, $r^2 = 0.89$

Figure 3. Relationship between Sodium Dominance Index and pH

A single water sample appears to be sufficient to determine sensitivity, but potential longitudinal variation within a single river system must be taken into account and may demand more intensive sampling, particularly where geology/soils, gradient and other conditions are likely to change along the length of the river.

The minor variation (<10%) in the Index within low alkalinity sites is encouraging. The findings suggest that neither time of year nor stream condition need to be considered in sampling. However, pending further testing of the Index, alkalinity should be retained as a back-up measure of acid-sensitivity.



Equation of the regression: $y = 402.8 - 6.0x$, n = 40, $r^2 = 0.65$

Figure 4. Relationship between Sodium Dominance Index and alkalinity for low alkalinity sites.

Finally, a further challenge exists in relation to the classification of acid sensitive waters. The sensitive category as currently defined using alkalinity and hardness, is very broad and encompasses waters which vary greatly in their susceptibility to acid inputs.

It is, therefore, critical that the concept of sensitivity be further advanced to permit classes of sensitive waters to be defined. This would be a valuable guide for land use planning and would help mitigate potential negative impacts on the aquatic environment. The Sodium Dominance Index may provide a means for developing sensitivity grades. Clearly, sites with index values in excess of 60% are more sensitive than those circa 40%. The derivation of sensitivity classes must also take cognisance of the biological community. It is intended to investigate the relationship between the index value and the nature of the biological community.

Sodium Dominance Index
as a measure of acid-sensitivity in Irish rivers.

Mary Kelly-Quinn and Miriam Ryan

Introduction

Acidification is one of the major pressures on freshwater upland rivers and lakes in many parts of the world. However, all waters are not equally vulnerable to acidification. The acid buffering capacity of aquatic systems is determined by the alkalinity associated with the cationic (e.g. calcium, magnesium) contribution from catchment bedrock and soils. Waters draining catchments with easily weathered, carbonate-rich materials such as limestone, are better buffered from acidification. In contrast, those draining resistant rocks, such as granite and quartzite, with low base cation content (soft-waters), are considered to be the most susceptible to acidification, particularly where the soils are peaty and mineral biogeochemical weathering is negligible.

Acid-sensitive rivers in Ireland are usually soft waters and most are located in upland regions. Many of these rivers are ecologically important as spawning and nursery areas for both salmon and trout, contributing young fish to many of the key salmonid fisheries in the country. They are also important habitats for macroinvertebrates and birds. These waters are naturally characteristised by high variability in pH due to episodic acidity. (The scale ranges from 1 to 14 i.e. pH 7 is neutral, but with increasing acidity the pH value decreases). The pH values are typically above 7.0 at low flow but fall to circa 4.5 as water levels rise. Organic acids derived from peaty soils are often the major cause of the acidity. When acidifying pollutants such as sulphate and NOx are superimposed on the natural background acidity, adverse changes in water chemistry and ultimately, the ecology

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occur. Increases in acidity are often accompanied by elevated concentrations of inorganic aluminium which exceed the threshold (40 µg L^{-1}) considered to be harmful to salmonids. Young fish are particularly sensitive to aluminium toxicity.
Various land-use activities can potentially contribute to freshwater acidification. In the U.K., coniferous forests have been shown to exacerbate the acidification processes in soft-waters draining areas which receive heavy loads of atmospheric pollutants. Interception and scavenging of the pollutants by the forest canopy is considered to be the principle process involved. In Ireland studies undertaken in a national project called AQUAFOR identified some sites with increased acidity associated with poorly-buffered waters in the east (Wicklow), west (Galway/Mayo) and parts of the south-west region of the country. Drainage operations in peat-dominated catchments may also exacerbate acidification processes by increasing the release of organic anions into drainage water and/or by enhancing mineralisation of organic N and S. Furthermore, surface drains lead to a rapid loss of water, which may reduce time for buffering reactions with rocks and soils.

In view of the ecological importance of soft waters it is important that measures are taken to avoid increased rates of acidification. This necessitates the identification of acid-sensitive waters. The most commonly adopted indicators are pH and alkalinity. Low pH (<5.0) and low alkalinity (<10 mg L^{-1} $CaCO_3$) are clearly indicative of low buffering capacity. However, as outlined above, both parameters are extremely variable within any one catchment depending on flow conditions and geology. Clearly, what is needed is a parameter that is both relatively stable and independent of season and flow.

The contribution of sodium (Na^+) to the sum of the major cations (**Sodium Dominance or Weathering Index**) in river waters has been proposed as an indicator of the acid sensitivity of rivers of upland Scotland, particularly where sea salt inputs, particularly sodium, dominate the base cation composition of the river water. The extent of sodium dominance provides a quantitative indication of catchment weathering rate, incorporating the effects of diverse geological composition. A value >c. 40% has been proposed for the more sensitive catchments whereas much lower levels are indicative of well buffered catchments. Furthermore, a single base-flow sample may be all that is required to accurately classify the acid sensitivity of a water body.

Study Objectives

The potential application of the Sodium Dominance Index to classify/identify acid-sensitive Irish rivers was assessed. Four key areas were addressed:

- Variation in the Sodium Dominance Index across geological types;
- Variation in the Sodium Dominance Index during typical acid episodes in Wicklow and Galway; Differences between high and base-flow values for the Index;
- Variation in the Index within sites;
- Relationship between the Index and traditional measures of acid status/sensitivity such as pH and alkalinity.

Data Source

This assessment used stream-water chemistry data collected during the AQUAFOR project (1990-1993) together with data from a number of other projects in University College Dublin, University College Cork and Trinity College Dublin. Overall, they represent a wide range of geological types, such as granite, Old Red Sandstone and limestone, from low to high acid-sensitivity. A large number of sites were located on the east coast but data from streams in counties Galway, Cork and Cavan were also included. In total data from 99 sites were made available. The chemical parameters used were pH, conductivity, alkalinity, ionic calcium (Ca^{2+}), magnesium (Mg^{2+}), sodium (Na^{+}) and potassium (K^{+}).

The Sodium Dominance or Weathering Index was calculated as the percentage Na^{+} contribution to the sum of the major cations ($Ca^{2+} + Mg^{2+} + Na^{+} + K^{+}$). The data were converted to meq L^{-1}.

Data analyses

The statistical tests outlined below were carried out using SPSS (Statistical Package for Social Science). Results were considered significant at the $P < 0.05$ level (all 2-tailed). The data were all initially tested for normality (Kolmogorov-Smirnov test). Regression analysis was used to examine the bivariate relationships between the Sodium Dominance Index and pH and the Sodium Dominance Index and alkalinity. Partial correlations (data log transformed to linearise the relationships) were then used to further examine these relationships and to determine which variables were more strongly related to the Sodium Dominance Index. Partial correlations were necessary because the levels of collinearity between these variables were unacceptably high. A paired t-test was used to test for significant differences between the Sodium Dominance Index under base flow and storm flow conditions within the same sampling sites.

Results

Cation Composition

Variability in the Sodium Dominance Index across geological types

As expected the highest total ionic concentration occurred in streams draining limestone areas with conductivity values in excess of 300 µS cm^{-1}. Conductivity measurements provide an indication of the ionic content of the water and where alkalinity values are likely to fall. Granite regions had conductivity values typically less than 100 µS cm^{-1}. Catchments with sandstones, slates and other sedimentary rocks generally constituted the intermediate

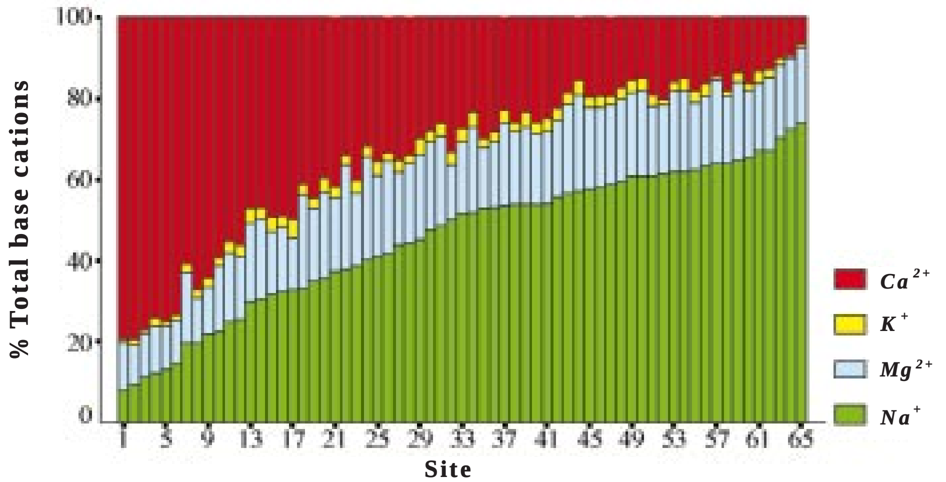

Figure 1. Percentage of total base cations represented by Na^{+}, Ca^{2+}, Mg^{2+} and K^{+} at sites ranging from Limestone (1) to Granite (65).

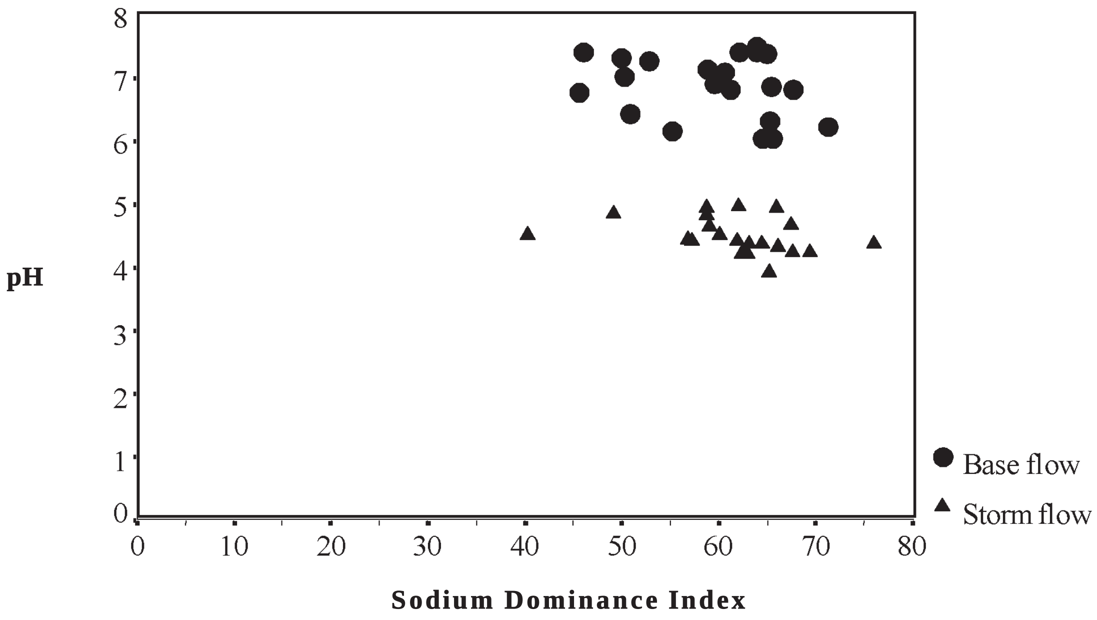

Figure 2. Relationship between Sodium Dominance Index (SDI) and pH at storm and base flow.

group but some had conductivity values as low as 50 µS cm^{-1}. Potassium (K^+) was a minor cation in all waters, generally constituting less that 4% of the total cation concentrations. Calcium and sodium were the most variable ions over the range of sites examined. The lowest sodium concentrations were associated with sites on the Wicklow granites in the eastern region of the country. A number of the Douglas and Araglin sites in Cork had only slightly higher concentrations than the Wicklow sites. The sodium values recorded for the Galway sites were markedly higher due to inputs of marine ions during Atlantic storms. Calcium concentrations were within a similar range in streams draining granite in both Wicklow and Galway but the percentage contribution of calcium was lower in the western sites. A number of the headwater sites in the Douglas catchment, on Old Red Sandstone, had equally low calcium concentrations. The results also highlight how headwater streams in any river system can differ markedly from each other. Sites are ranked in order of increasing sodium contribution in Figure 1 which demonstrate the range of values found. As can be seen sites with low calcium had the highest % sodium contribution, thus the highest Sodium Dominance Index.

Variability of the Sodium Dominance Index during acid episodes

The Sodium Dominance Index showed little variation (max. C.V. = 7.32)[1] during the course of acid episodes in streams from Wicklow and Galway, with all values well above 50%. The Galway values were consistently higher than those for Wicklow. The Index was generally independent of pH change in the Wicklow sites but the index value showed a significant correlation with pH in two of the five acid episodes examined from the Galway sites. However, even on those occasions the coefficient of variation for the Index, over the pH range of two units, was less than 3.0.

Variation within individual sites

The relative stability of the Index was further evident from examination of the variation in the index values within individual sites. Low conductivity waters on granite and the headwater sections of Douglas and Araglin had the lowest variation in the Index, (values above 50%). Some of the other sites in the Kilworth area, however, showed high variation in the Index values. However, at all of these sites the Index was less than 40%. The Index values for sites on the Galway granites (in excess of 70%) were substantially higher (approx 10%) than those on the Wicklow granites. High marine inputs along the west coast probably account for these differences.

High and base-flow values for the Index

Paired storm (pH 5.0) and base flow data (pH > 6.0) were randomly extracted from the dataset and the Sodium Dominance values were compared (Figure 2). Suitable data were only available from the 21 sites. No significant difference existed between the high and baseflow values.

[1] *Footnote: cv =coefficient of variation, which provides a relative measure of data dispersion compared to the mean.*