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Linking groundwaters of high CO_2 to aluminium levels in rivers: the case for the upper Severn in mid-Wales

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Abstract

Al is a critical ecotoxicant in surface waters impacted by acidic deposition. Apart from the most acidic surface waters, Al concentrations are often considered to be controlled by $Al(OH)_3$ or aluminosilicate (clay) solubility for modelling studies. For many UK rivers there is no clear evidence for such solubility controls even though there is the potential under moderately acidic/alkaline conditions. Here, Al solubility in ground and river water is compared for acid sensitive catchments in mid-Wales. The results reveal that there may be a solubility control within the groundwater but a more complex state of affairs within the river. The groundwater is of high CO_2 content and once in the river it degasses to raise pH. However, there is limited change in Al concentration and hence the solubility relationship is lost. The results flag the potential importance of groundwater solubility controls for Al and the potential for the groundwater zone to act as an Al filter. For positive alkalinity groundwaters, the high CO_2 levels depress the pH to near the value for minimum Al solubility. However, there is no simple groundwater end-member.

Examining Al solubility controls solely within the rivers provides cryptic and misleading clues to the hydrogeological controls for Al within catchments. Assessing the within-catchment processes requires direct measurement with full consideration of both inorganic and organic attenuation.

Introduction

Inorganic Al levels in rivers draining acidic and acid sensitive catchments are of concern with regards to acidic deposition as its mobilisation can be detrimental to river ecology [1,2]. Research in this area has been longstanding in relation to issues such as inorganic and organic controls on aluminium solubility, aquatic speciation and within catchment processes [3-20]. The acidification impacts of both H^+ and inorganic Al directly relate acidic and Al bearing soils and the inability of the underlying bedrock to weather sufficiently to release base cations, consume H^+ and inorganic Al while generating HCO_3^-. This is the fundamental issue with regards to catchment susceptibility and impacts. Within the acidification research, much credence has been given to the importance of Al solubility controls within the soils and rivers linked to $Al(OH)_3$ and aluminosilicate (clay) phases although detailed catchment research indicates the significance of factors linked to organic matter and colloid formation.

Our recent studies of UK rivers reveal that such simple solubility controls could not be identified using objective methodologies of examining saturation levels as a function of pH [3]. For these rivers, a curvilinear relationship was observed between mineral saturation and pH, with a maximum around circumneutral pH and undersaturation at both low and high pH. A key property of Al in natural waters is its amphoteric nature with the dominance of Al^{3+} at low pH, and $Al(OH)_4^-$ at high pH [5,6]. Under more acidic conditions, Al undersaturation links to biogeochemical processes occurring within the soil where Al saturation is not reached. Correspondingly, at pH > 9 there may be a lack of available Al to dissolve as pH rises as a consequence of photosynthetic removal of dissolved CO_2 [3]. While pH rise in the river may result from biological removal of CO_2 within the river, there is another mechanism to consider: groundwaters which are high in CO_2 can degas within the river to raise pH.

In this paper, this latter mechanism is considered to draw to a close, with our retirement, our research in this area [3,4,21]. While it is tempting to consider the river water in terms of soil and groundwater/bedrock inputs that mix within the river channel, both can be transported to the river as groundwater associated with fracture flow movement. Indeed, there are no simple soil and groundwater end-members at all. For our and associated studies in mid-Wales, groundwater has been found for catchments with Palaeozoic slate and shale geology at any location where boreholes were introduced [22-27]. Further, the general importance of such groundwater pathways is indicated by the high dampening and “fractal processing” of atmospheric inputs of Na and Cl within the catchment. Such dampening occurs even for areas of “hard rocks” where groundwater inputs might normally, but wrongly, considered as an irrelevance [28-31]. For this paper, the role of CO_2 in helping regulate Al levels in groundwater is explored for key acid impacted catchments in mid-Wales where lack of Al solubility (equilibrium) controls in the river has been previously noted [3,32]. To do this, groundwater is examined for sites within the upper River Seven catchments in mid Wales [24,25]. Such work complements the staggering array of studies of the hydrogeochemistry of Al within catchments. It puts emphasis on one particular aspect: ground-stream water interactions.

Study area and approach

The water quality data come from the Plynlimon experimental catchments of the Centre for Ecology and Hydrology of the upper River Severn region of mid-Wales based on our research from 1983 to 2010 [24,25,31,33,34]. Within this region, the upper part comprises acid peat moorland while for the lower part there is the Hafren plantation forest mainly comprised of Sitka Spruce on podzol and gley soils. The trees were clear-felled in the mid 1980s for some parts of the catchment and thinned progressively in other parts, followed by natural-reseeding and replanting. The underlying geology comprises mud, grit and slates/shales of Palaeozoic age.

The rivers considered are the three main tributaries of the upper Severn, the Afon Hafren, the Afon Hore and the Nant Tanllwyth. In the case of the Afon Hafren, two sites were monitored for the upper half (acid moorland and peat drainage) and the lower half (spruce forest with podzolic soil). The same monitoring regime applied to the Afon Hore except that for the upper half there is approximately a half each of moorland drainage and forest runoff from podzolic soils. The Tanllwyth (spruce forest with gley soils) was monitored near to its join with the Hafren. Each of these rivers were monitored weekly.

The groundwater data come from five boreholes within the forested part of the catchments: three (HA4, southeast 1 and southeast 3) within the Hafren sub-catchment [24] and two within the Tanllwyth sub-catchment (Tan N and Tan S) [25]. The groundwater monitoring varied from weekly to monthly, depending upon site.

Details of the monitoring programme including location map with monitoring points displayed have been described in detail previously [24,25,33,34]. The salient features of water quality variation have been described previously [23-25,34] and recently summarised with analytical methodologies and data [34]. Further, associated studies on soil water indicate a general undersaturation with respect for $Al(OH)_3$ within the upper soil horizons, approaching saturation towards the base of the soil profile within the C-horizon [35].

The levels of CO_2 saturation are assessed [36] and the results described in terms of an excess partial pressure ($EpCO_2$). $EpCO_2$ represents the level of saturation with respect to water in equilibrium with air. In the case of the river waters of low pH and negative Gran Alkalinity, the errors associated with the methodology mean that the $EpCO_2$ cannot be accurately assessed across the pH range. However, more accurate approaches have previously indicated values close to saturation [37]. For the groundwaters, similar problems are not encountered. Hence, the change in pH with CO_2 degassing to atmospheric saturation is estimated based on the approximate and simple relationship between pH, Gran Alkalinity and $EpCO_2$.
$[H^+]*(\text{Gran Alk} + [H^+]) \approx k*EpCO_2$
where k is a scaling constant linked to Henrys constant and the partial pressure of CO_2 in the atmosphere. For the calculation of pH change with degassing, $EpCO_2$ is set to a value of 1 with degassing and $[H^+]$ is calculated for a given Gran alkalinity concentration. In our case, the Gran Alkalinity is generally measured in the pH range 4.5 to 4.0 (slightly lower for the more acidic waters) and this largely represents titration of the inorganic CO_2 system rather than the stronger organic acids.

Al solubility is assessed based on thermodynamic analysis and only considers the simplest of cases, $Al(OH)_3$ and clay solubility: an analysis of interactions of Al with organic matter surfaces is beyond the scope of the present work. For the assessment, allowance has been made for hydroxyl, fluoride and organic complexation, as well as for temperature [3,38,39]. The method used allows analysis of a large number of waters relatively quickly. There are more elaborate thermodynamic methods now in use[17], but the method was validated using river water data for the acid waters monitoring programme for the Afon Hafren[3,40,41]. For this, the river waters had the Al fractionated into total dissolved, labile and non-labile forms. Inorganic Al was calculated from the total dissolved Al, and this compared well with the measured labile Al: regression analysis revealed a strong linear correlation ($r^2 = 0.81$, $N = 226$), a statistically insignificant intercept and a gradient very close to 1. For our studies, the Al was determined on a 0.45 µm filter, no speciation was undertaken and the measurement will include colloidal as well as inorganic and organic forms[3].

For the analysis, the saturation index is plotted against pH in order to undertake a more objective assessment of mineral saturation [3]. For $Al(OH)_3$, data for crystalline and amorphous forms are plotted to show the range of potential saturations. For Al-silicate (clay) the corresponding range is plotted for kaolinite and halloysite.

A comparison is made between the saturation levels for the rivers and the degassed groundwaters. For this, a curve is fitted between pH and the saturation index for the degassed groundwater. This curve is then plotted as a pH versus Saturation Index diagram with the river data. The curve is generated after a statistical fit between the saturation index and a simple polynomial in pH ($SI = a*pH^3 + b*pH^2 + c*pH + d/pH + e$, where a, b, c, d, e represent regression constants). Initial analysis reveals that this relationship fits the data well ($r^2 = 0.794$, N = 522).

Results

River water chemistry

The river water quality varies markedly as a function of flow in response to the relative inputs what might be termed “ground” and “soil” water.

Groundwater. Its chemistry is determined by reactions in the lower soils and bedrock where mineral weathering ensures positive Gran Alkalinity and low Al solubility. Groundwater dominates the river water under baseflow conditions: Gran Alkalinity for individual sites ranges between 49 and 152 µEq/l, while the corresponding range is 6.6 to 7.0 for pH and 65 to 135 µg/l for Al (Table 1).

Soil water. Its chemistry is largely determined by acidic and dissolved organic carbon (DOC) bearing soils. Soil water inputs dominate at high flows when the rivers become both acidic and Al bearing: the Gran Alkalinity for individual sites range between -20 and -48 µEq/l, 4.4 to 4.8 for pH and 200 to 570 µg/l for Al (Table 1).

The relationships of pH with Gran Alkalinity and Al concentration are curvilinear (Figures 1 and 2). In the case of Gran Alkalinity, concentrations increase with increasing pH and for low pH, Gran Alkalinity is negative. Correspondingly, Al concentrations increase with increasing pH and level off at higher pH.

The river waters are generally undersaturated with regards to amorphous $Al(OH)_3$. For more crystalline forms, the waters are undersaturated at low pH with decreasing undersaturation to saturation and then to increasing oversaturation as pH rises to around 7.0 after which oversaturation declines (Figure 3). The curves for kaolinite and halloysite are similar except that at intermediate to higher pH, the waters remain oversaturated for both forms. For $Al(OH)_3$, kaolinite and halloysite, at no point is there a clear trend of a constant saturation across any pH band and the crossover point from increase to decrease is marked by a curve rather than a plateau.

Borehole Chemistry

As with the river waters, the boreholes exhibit a wide range in Gran Alkalinity (Table 2) and it seems that borehole water comprises a mix of soil and reacted (weathered) groundwater. Thus, for the top 10% of Gran Alkalinity at each site, the averages vary between 37 and 2029 µEq/l: the corresponding averages are 5.0 and 6.5 for pH and 4 to 100 µg/l for Al. At low Gran Alkalinity, the average Gran alkalinity varies between -9 and 49 µEq/l: the corresponding values are 4.7 to 5.3 for pH and 56 to 320 µg/l for Al. The borehole water is generally greatly oversaturated with respect to CO_2 (average $EpCO_2$ varies across the sites of 27 to 85 times atmospheric pressure). There is a curvilinear relationship for pH with Gran Alkalinity and Al concentration (Figure 1, 2). However, there is high scatter in Al concentration for lower pH and the higher Al concentrations (for a given pH) occur for the Tan South borehole.

The borehole waters are approximately saturated with respect to crystalline $Al(OH)_3$ and undersaturated with respect to less crystalline forms (Figure 4). Thus, for crystalline $Al(OH)_3$ the saturation index is close to zero (average = -0.30, 2 std = 1.10), while for amorphous $Al(OH)_3$ the saturation is three orders of magnitude lower (-3 on a logarithmic scale). Correspondingly, the waters have saturation levels between kaolinite and halloysite (Figure 4).

With degassing, pH increases due to a redistribution of the inorganic CO_2 system. The shift is greatest towards higher pH as Gran Alkalinity is higher. The range in pH for the degassed borehole waters is 4.72 to 8.58. There is a curvilinear relationship between pH and Gran Alkalinity (Figure 1) while Al concentrations decline and level off with increasing pH (Figure 2).

$Al(OH)_3$ saturation index at low pH is similar to that for un-degassed groundwater with values close to crystalline gibbsite saturation as the pH change is relatively small. However, as pH increases with degassing, oversaturation occurs and the degree of oversaturation increases to a maximum around pH 6.7 after which there is a decline as pH increases further. For most of the pH range, the oversaturation lies between saturation levels for crystalline and amorphous $Al(OH)_3$. Kaolinite and halloysite exhibits a similar pattern to that for $Al(OH)_3$ with the exception that there is oversaturation for all but the most acidic waters (Figure 4).

River-borehole water comparisons

Both the river and the (un-degassed) borehole waters exhibit curvilinear relationships of pH with both Gran Alkalinity and Al. However, the curves differ as the higher CO_2 concentrations in the borehole water compact the pattern to lower pH (Figure 1, 2).

The systematic variation in borehole water quality for all sites monitored indicates that there is sub-surface transport of both soil water and true groundwater of positive Gran Alkalinity. However, the river water has the lowest pH and Gran Alkalinity as well as the highest Al concentration. Hence there must be more acidic and Al bearing inputs that are not registered within the groundwater monitoring programme. Such inputs are characteristic of the acidic soil waters but it is unclear if such waters are supplied via the groundwater (i.e. the acid extremes have not been sampled in groundwater), or there is more direct input from the soil to the river water. The groundwater can have even higher Gran Alkalinity compared to the river, but there are large variations across the sites. Hence, there are areas within the catchment of high weathering. However, these areas must have a smaller influence on river (baseflow) chemistry as such high values do not occur within the rivers.

There is approximate saturation with respect to crystalline $Al(OH)_3$ or some form of Al-silicate within the boreholes. However, there is no convincing argument for an Al solubility control within the river. The river results closely mirror that predicted when borehole water degasses. This is shown for example in Figure 3 where the pH versus saturation of microcrystalline $Al(OH)_3$ plots for the river data fit well with the curve for the degassed borehole water. Identical figures would have been observed for crystalline and amorphous forms except that there would have been a vertical shift in the line/curve due to the differences in the equilibrium constant for $Al(OH)_3$ solubility with change in crystallinity. A comparison of the saturation index for the rivers with the corresponding estimates for the degassed borehole water at the same pH as the river reveals a strong statistical relationship with gradient insignificantly different from unity and an intercept insignificantly different from zero ($r^2 = 0.937$, N = 5997). Nonetheless, caution must be taken with this analysis as there is an autocorrelation term (saturation level will have been assessed for each data point via a speciation calculation based on pH). Indeed the criticism posed previously for using pAl^{3+} versus pH for characterising $Al(OH)_3$ controls because of the dependent axes can be equally applied to the method used here for comparing saturation index relationships in a hypothesis testing mode. As a more objective test the analysis has been repeated by comparing Al concentrations in the river with the computed estimates for the degassed groundwater. In this case the two datasets are independent. A plot of pH versus the logarithm of the Al concentration reveals an approximate straight line and the regression relationship is used here to estimate the Al concentration in the river using pH values for the river. The regression of the calculated versus observed Al concentration in the river exhibits a strong correlation with an intercept insignificantly different from zero ($r^2 = 0.592$, N = 5997). Nonetheless, the gradient is not unity and the Al concentration in the river is overestimated by around 59±2%. However, if the anomalous Tan South borehole data is excluded from the analysis a strong correlation remains ($r^2 = 0.528$, N = 5997) and the relationship becomes almost 1:1 with a change to an overestimate of only 1±1%. This represents the most compelling case for Al concentrations in the river being determined by Al concentrations in the groundwater.

Discussion

Many studies point to the importance of Al solubility controls across a wide range of aquatic environments. The publication list is vast [4-20]. There are a wide range of inorganic and organic solubility controls and interactions between the soil solution and the mineral/organic surfaces that come into play. However, whatever the details of the mechanisms operative, it is from within the soils that the Al within the rivers originates.

Here, focus is on the groundwater fracture flow system as it is here where much of the water passes to the river and it is here where true groundwater and soil water mixes before entering the river. Indeed, it is here where there are the potential for “seeding” of Al precipitates and our results match closely those from other studies [5-7,42].

Given the wide range in borehole water chemistry across the upper Severn catchment [22,24,25], it is unrealistic to expect a direct equivalence of water quality and Al saturations for the river and borehole sites. For example, at the local scale there is a large variation in Al concentration and pH for streamlets where water is supplied from the near-surface soils and from deeper within the groundwater system [43,44]. In previous studies for the upper Severn rivers, the relationship between H^+ and Al concentrations has been linked to soil and groundwater end-member mixing with $Al(OH)_3$ solubility controls for the situation where the waters on mixing become oversaturated [45]. By transferring the precipitation mechanism from the river to the groundwater, this inconsistency is overcome at least for the less acidic waters. However, no simple groundwater end-member exists and fracture flow transport represents a continuum of soil and reacted (weathered) waters from below the soil layer. For the most acidic waters, the river may be supplied from soil drainage to the river (in which case the previous mixing analysis remains operative under the more acidic conditions in the river). Alternatively, the soil waters may transfer to the river via the groundwater. However, the extreme events have been missed for the boreholes. This may be due to a lack of high resolution monitoring. Alternatively, they may have been missed because of waters being transferred from ephemeral fractures at shallower depths (during wet conditions) than our boreholes monitor. In either case, the results would look similar as under the most acidic conditions CO_2 degassing would have very limited effect on pH.

Our study flags the potential significance of Al solubility controls within the groundwater fracture system and the role that CO_2 degassing has in modifying the Al speciation and saturation level within the river. The analysis explains why Al concentrations simply decline with increasing pH rather than exhibiting a minimum concentration around pH 6 to 7 linked to solubility controls. Within the fractures, the pH is below the minimum for Al solubility. Then, with rising pH on degassing in the river, Al(OH) species initially become increasingly dominant and Al saturation increases, but then declines at higher pH when $Al(OH)_4^-$ predominates The variations in saturation index for the river largely matches that for the change in Al speciation as a function of pH. Thus, determining simply Al saturations within the river can only provide cryptic and perhaps misleading clues about what the determinative Al solubility controls actually are.

The data presented here are limited in that only “total dissolved” (0.45 μm filterable) Al and some of this “dissolved” component may well contain colloidal Al. This raises issues such as to whether CO_2 degassing of groundwaters leading to pH rise within the river induces colloid generation. However, colloid generation and transport might also occur within the soil, bedrock and groundwater flow pathways. Further, there is also the potential for the interactions between dissolved Al and organic surfaces as well as with silicates [3,8-16,46-50].

Whatever the details, the work seems to indicate that the fracture flow system is working in such a way that it acts as an “Al filter”. At the heart of this are four key features:

1. The water movement is as shallow fracture flow.
2. There are variable inputs of soil and groundwater within the system.
3. CO_2 is generated by DOC breakdown.
4. Within the fractures, CO_2 degassing does not occur.

Thus, as the, acidic, DOC and Al soil water enters the fracture system, the DOC is partly broken down to generate CO_2 and lower the concentration of the Al-organic complexes. When this water mixes with higher alkalinity groundwater, the pH rises and Al precipitates. Nonetheless, since the CO_2 concentrations are high, the pH does not rise sufficiently to pass the point of minimum Al solubility within the fractures. On transfer to the river, the CO_2 degasses and pH increases. However, since Al supplies are largely confined to within the catchment (and the soils in particular), on degassing, there is not the potential for Al-solution within the river.

Clearly there is a need to consider Al functioning in relation to hydrogeological factors with fracture flow of water and hydrochemical processing.

Conclusion

Al regulation within catchments is a complex affair. Our studies indicate that the fracture flow groundwater component to river flow is of critical importance. While there is data scatter, the borehole observations provide the most convincing evidence for a Al solubility control in the groundwater and the findings match results for other catchments. Indeed, the suggestion of solubility controls in the groundwater and not the river explains the inconsistency between mixing model results (soil and groundwaters mixing within the river to give $Al(OH)_3$ solubility controls when conditions allow) and thermodynamic analysis that indicates no such equilibrium. Nonetheless, what the determinative equilibrium mechanism is cannot be assessed here: more needs to be done than just thermodynamic analysis.

Our work in this area is now completed, but we hope that data is brought together from a wide range of aquatic environments and compared within a consistent and objective analytical (thermodynamic) methodology. Although in some studies groundwater is measured, in many it is not and this needs to change in order to describe more fully and more accurately Al flux transfers and attenuation through catchments of the type studied in this paper. Mixing relationships between soil and groundwater need further examination for Al in relation to organic and Si complexation, colloidal formation and stability as well as the influence of CO_2 levels in modifying pH. The work then must be set within a strong framework of biological measurement and ecotoxicology to examine more fully Al impacts on the aquatic environment.

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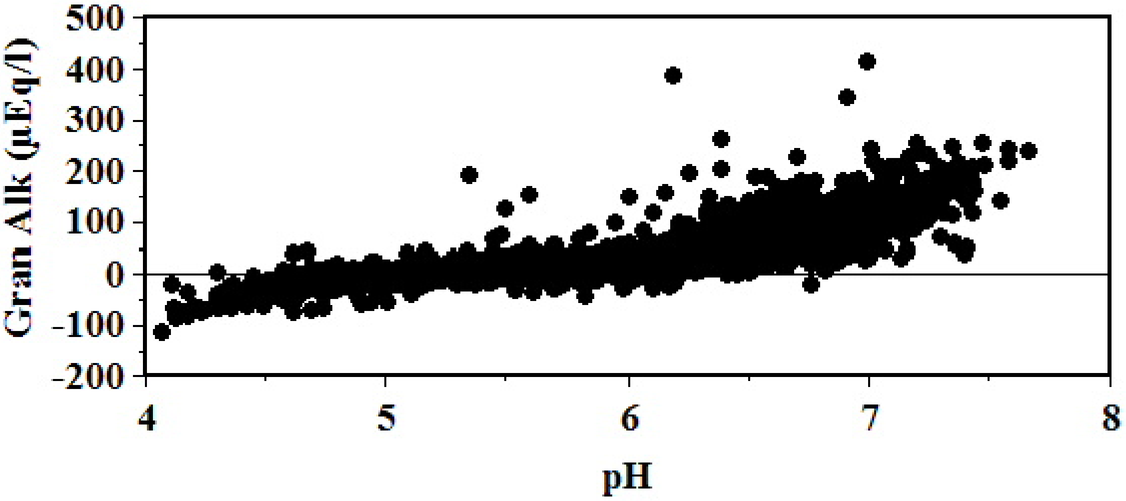
Table 1. A comparison of Al, pH, Gran Alkalinity, Si, DOC and F variations in Upper Severn rivers. Averages for the top 10% (high) and bottom 10% (low) alkalinities are also presented and these represent baseflow and stormflow waters. N.B. $EpCO_2 \approx 1$, but values are not presented owing to high errors in the calculation especially at low pH.

	Al	Si	DOC	F	pH	G Alk
	μg/l	mg/l	mg/l	mg/l		μEq/l
	Upper Hafren					
Average	106	1.6	1.6	0.03	5.7	13
High Gran Alk	65	1.8	1.0	0.03	6.5	49
Low Gran Alk	200	1.0	2.5	0.03	4.8	-20
Minimum	10	0.0	0.0	0.00	4.4	-59
Maximum	662	2.5	9.7	0.40	7.2	194
	Lower Hafren					
Average	190	1.6	1.8	0.04	5.4	1
High Gran Alk	82	1.8	1.5	0.04	6.3	43
Low Gran Alk	396	1.1	2.7	0.05	4.5	-35
Minimum	24	0.5	0.0	0.00	4.1	-80
Maximum	748	4.6	11.9	0.20	7.0	415
	Upper Hore					
Average	225	1.3	1.9	0.05	5.9	38
High Gran Alk	110	1.8	1.4	0.05	7.0	152
Low Gran Alk	452	0.9	2.8	0.05	4.6	-28
Minimum	4	0.0	0.0	0.00	4.2	-72
Maximum	3030	3.4	21.3	0.20	7.7	257
	Lower Hore					
Average	211	1.5	1.8	0.05	5.9	35
High Gran Alk	97	1.9	1.5	0.04	7.0	148
Low Gran Alk	475	1.0	2.3	0.06	4.6	-29
Minimum	8	0.0	0.0	0.00	3.9	-156
Maximum	1010	5.6	14.0	0.21	7.6	390
	Tanllwyth					
Average	311	1.6	4.1	0.04	5.4	5
High Gran Alk	135	1.9	3.3	0.04	6.4	71
Low Gran Alk	570	1.1	6.1	0.05	4.4	-48
Minimum	51	0.5	0.9	0.00	4.1	-113
Maximum	1020	2.4	30.3	0.10	6.9	160

Table 2. A comparison of Al, pH, Gran Alkalinity, EpCO$_2$, Si, DOC and F variations in groundwater within the forested part of the Upper Severn catchment. Averages for the top 10% (high) and bottom 10% (low) alkalinities are also presented.

	Al µg/l	Si mg/l	DOC mg/l	F mg/l	pH	G Alk µEq/l	EpCO$_2$ Atmos
Hafren 4 Borehole							
Average	120	2.5	0.6	0.1	5.1	27	27
High Gran Alk	25	4.0	0.5	0.1	5.8	181	40
Low Gran Alk	215	2.1	0.8	0.0	4.9	-9	13
Minimum	7	1.3	0.2	0.0	4.7	-12	1
Maximum	400	5.0	3.0	0.1	6.3	341	103
South East 1 Borehole							
Average	43	3.3	0.6	0.1	5.3	58	49
High Gran Alk	11	4.0	0.5	0.1	5.7	128	46
Low Gran Alk	96	2.4	0.7	0.1	4.9	4	40
Minimum	4	2.1	0.2	0.0	4.8	-0	17
Maximum	160	4.6	2.6	0.1	6.1	173	104
South East 3 Borehole							
Average	175	2.3	0.4	0.1	5.4	77	44
High Gran Alk	23	2.9	0.4	0.1	5.9	254	54
Low Gran Alk	320	2.2	0.5	0.1	5.2	24	32
Minimum	12	1.9	0.2	0.0	5.1	19	15
Maximum	439	4.7	1.2	0.2	6.2	415	98
Tan North Borehole							
Average	183	2.8	0.5	0.1	4.8	10	61
High Gran Alk	100	3.1	0.5	0.0	5.0	37	74
Low Gran Alk	299	2.8	0.6	0.1	4.7	-9	42
Minimum	23	2.0	0.2	0.0	4.2	-54	8
Maximum	848	4.6	1.4	0.3	5.3	89	111
Tan South Borehole							
Average	19	4.5	1.5	0.1	5.8	643	85
High Gran Alk	4	4.9	2.1	0.1	6.5	2029	106
Low Gran Alk	56	4.2	1.1	0.0	5.3	49	52
Minimum	1	2.9	0.5	0.0	5.1	25	20
Maximum	195	7.2	10.5	0.1	6.6	2293	139

Rivers



Groundwater

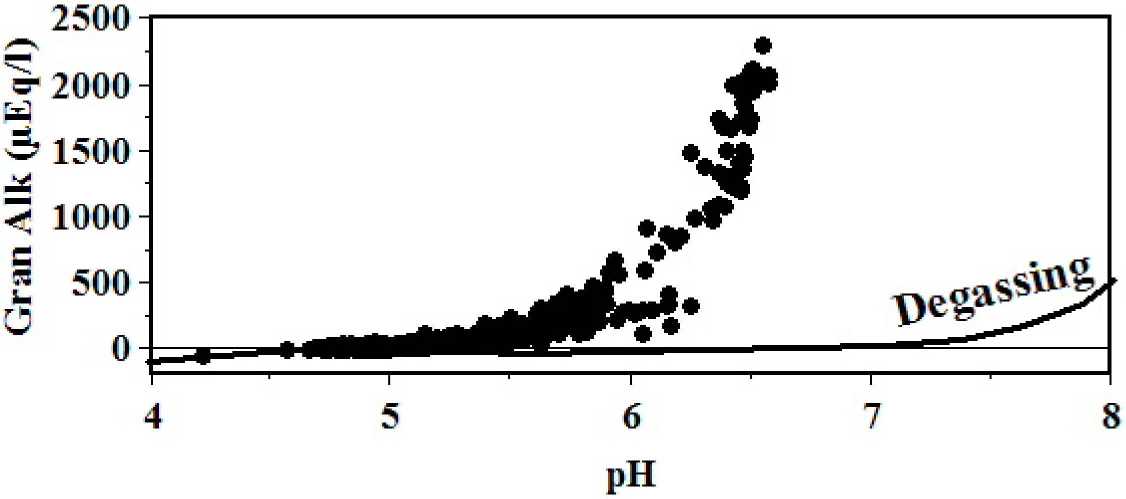


Figure 1. The relationship between pH and Gran Alkalinity for upper Severn rivers and groundwaters (with and without CO_2 degassing).

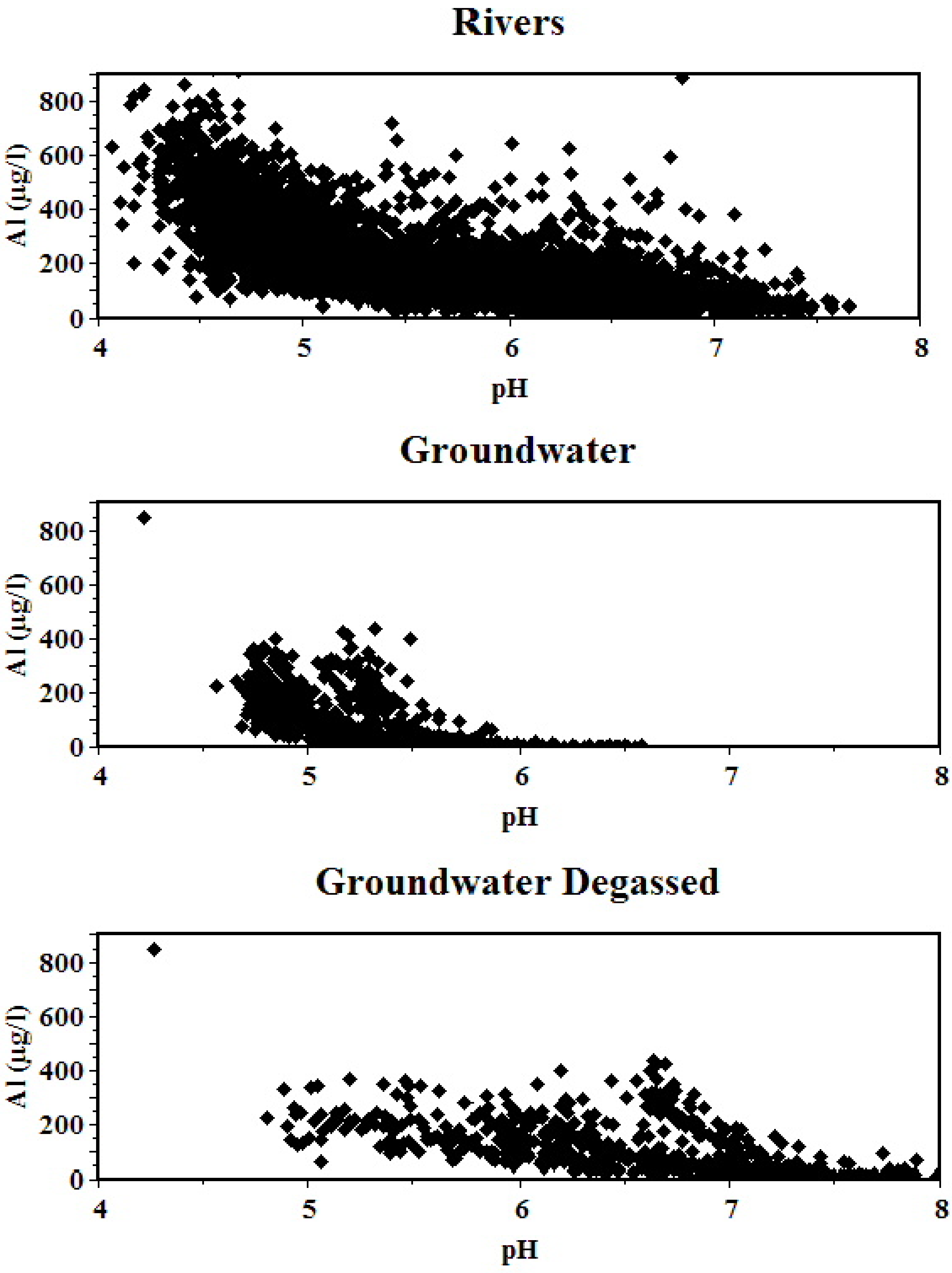

Rivers
Al (µg/l)
0
200
400
600
800
4
5
6
7
8
pH
Groundwater
Al (µg/l)
0
200
400
600
800
4
5
6
7
8
pH
Groundwater Degassed
Al (µg/l)
0
200
400
600
800
4
5
6
7
8
pH

Figure 2. pH versus Al for upper Severn rivers and groundwaters (with and without CO_2 degassing).

SI Al(OH)3 in streams

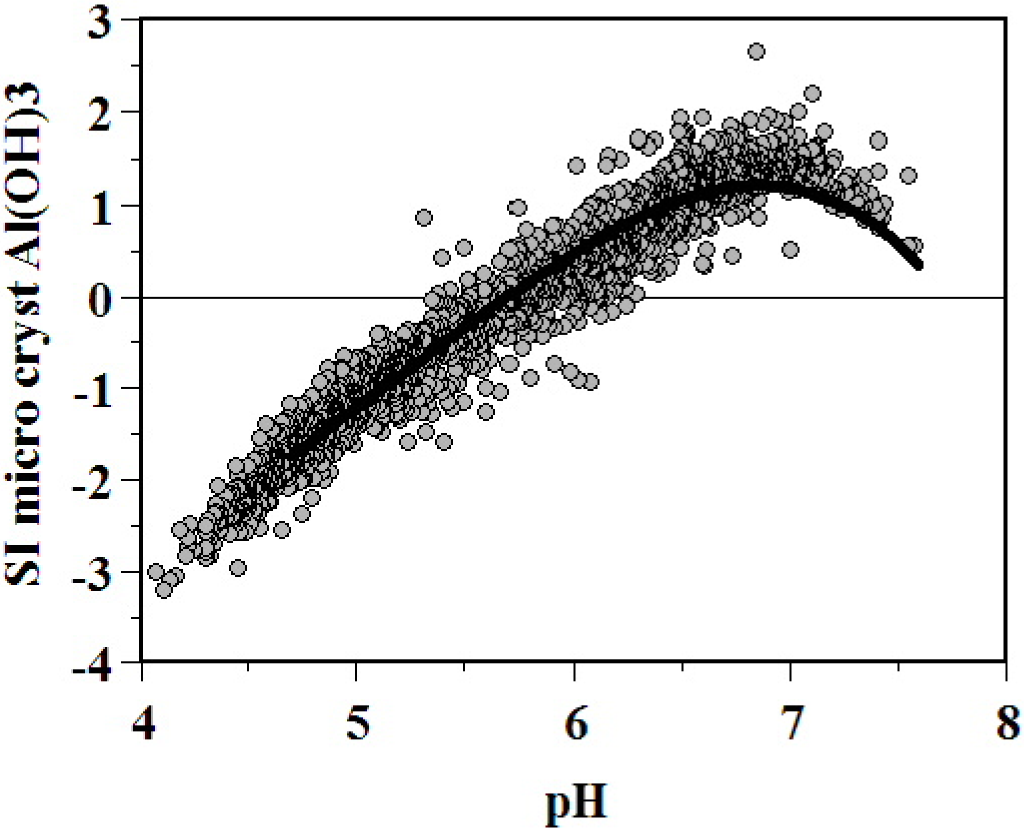


Figure 3. Microcrystalline gibbsite saturation for upper Severn rivers including a line representing the pH versus saturation level for micro crystalline $Al(OH)_3$.

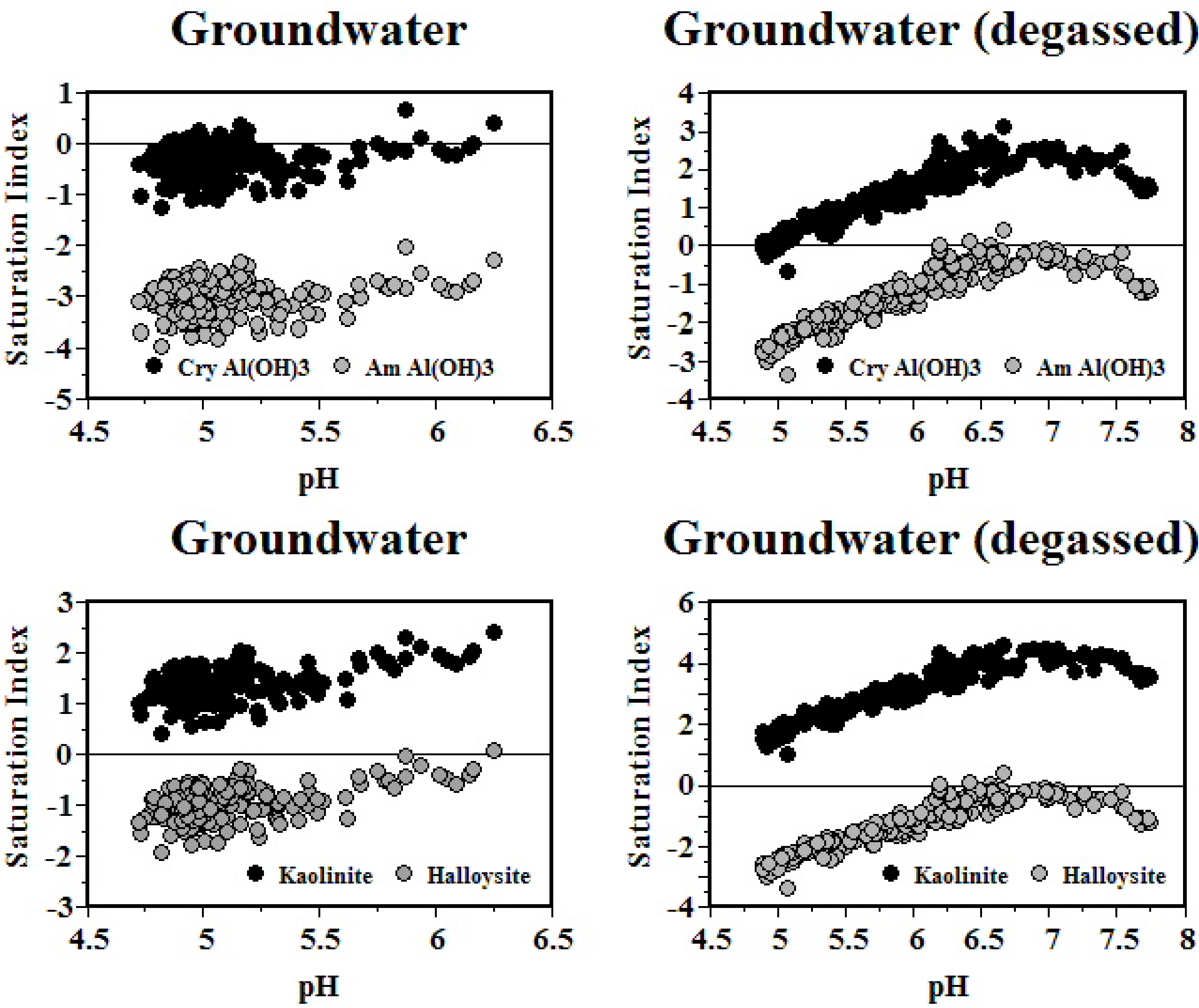

Groundwater
Groundwater (degassed)
Saturation Index
pH
Cry Al(OH)3
Am Al(OH)3
Kaolinite
Halloysite
1
0
-1
-2
-3
-4
-5
4
3
2
6
-4
4.5
5
5.5
6
6.5
7
7.5
8

Figure 4. $Al(OH)_3$, kaolinite and halloysite saturation indices for upper Severn groundwaters (with and without CO_2 degassing).