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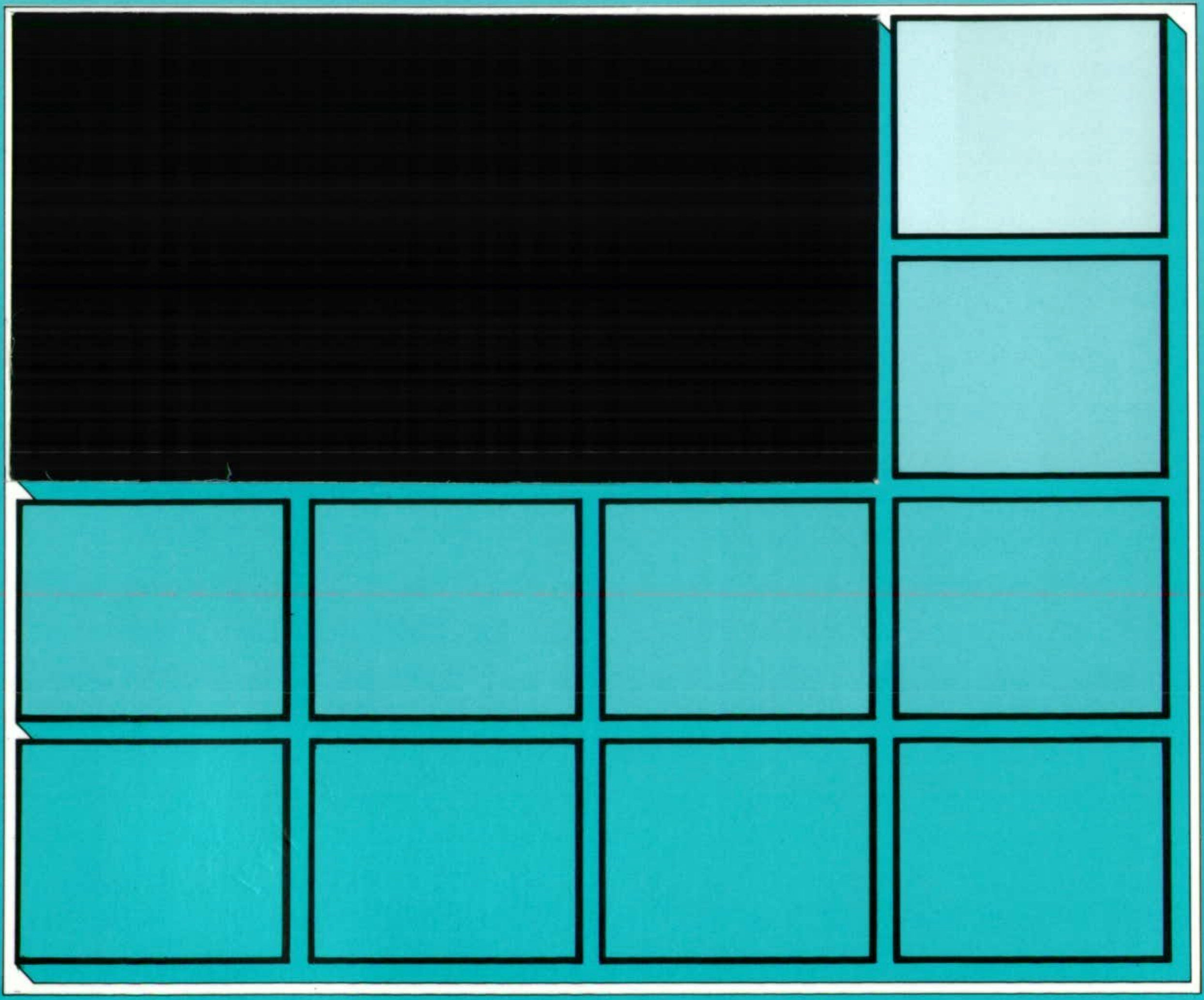

Forestry Impact on Upland Water Quality

INSTITUTE OF HYDROLOGY REPORT
TO THE
NATIONAL RIVER AUTHORITY

Project review: October 1990 to April 1991

C. Neal

FORESTRY IMPACT ON UPLAND WATER QUALITY

NRA PROJECT 114 (G/NRA1)

Project review October 1990 to April 1991

AIMS

The main aims of the project are two fold. First, the production of a wide ranging hydrochemical data set to establish the variations in stream water quality following tree harvesting. Second, the development of a model describing the chemical, hydrological and biological controls on a wide range of chemicals as they are transported through the catchment to the stream.

METHODS

The project involves three interlinked activities. First, the determination major, minor, trace and ultra trace element levels in rainfall, stemflow, throughfall, mist and stream water (felled and forested catchments) for weekly collections. This information is used to fingerprint the sources and amounts of components as they pass through the hydrological cycle. Second, continuous monitoring of pH and conductivity is undertaken for rainfall, stemflow, throughfall and stream water (felled and forested catchments) to provide detailed information on chemical variability during storm events: this supplements the weekly analysis. Third, analysis of the data using thermodynamic and time series analysis to assess the changes occurring. Emphasis is placed on assessment of the work programme and the publication of the findings.

RESULTS

The main portion of the work has involved chemical analysis at the Wallingford laboratories. Over 120 samples have been analyzed for major minor and trace elements during this reporting period to date: this figure will increase to over 160 by the end of March. Developments of analysis by inductively coupled plasma mass spectrometry has enabled about 200 analyses to be made for ultra trace element concentrations of samples retained since 1988 (see list in Table 1).

In the field, collection and processing of water samples has continued. Important modifications have been made to continuous monitors for rainfall, stemflow and throughfall: tipping buckets have now been installed which allows simultaneous determinations of flow pH, and conductivity; a new logger system has also been introduced to enhance data retrieval. A continuous monitor has also been established for the Afon Hafren upstream of the forest area. This allows monitoring of a peat moorland area and it provides new information on the dynamics of chemical inputs to the forested part of the stream.

Table 1 Ultra trace elements

	Rain ppb	Throughfall ppb	Stream water ppb
Cr	2.7	3.4	2.3 - 2.7
Ni	0.9	2.0	1.4 - 2.6
Rb	0.2	12.5	0.2 - 0.4
Sb	0.2	0.3	0.1
Cs	0.01	0.07	0.02 - 0.05
La	0.09	0.10	0.03 - 0.09
Ce	1.8	1.1	0.3 - 0.4
Pr	0.01	0.02	0.01
Pb	6.7	3.5	0.4 - 6.7
Th	0.01	0.02	0.01
U	0.007	0.016	0.007 - 0.008

Extensive analysis of the data has been undertaken and this has been linked to the IH modelling initiatives. Two papers have already been accepted for publication (see Appendix 1) and a further three papers are at the stage of submission or are under review. One major development has been the first analysis of the continuous pH and conductivity data. It is now clear that during the early parts of a storm, a significant amount of water is entering the stream which has hitherto not been identified. The contribution of this water varies from stream to stream: it has the greatest importance for the felled catchment stream.

FUTURE WORK

Over the next 6 months the monitoring will continue at present levels. Detailed analysis of the ultra trace element data will be undertaken together with an in depth time series analysis of the continuously monitored data.

Very high priority will be given to reporting the results in the peer reviewed scientific literature. Consideration will be given to the final report of the present contract. A book on activities at Plynlimon is planned for completion by December 1991. This book will bring together all the recent chemical, hydrological, geomorphological and biological findings within the context of climate and land use change.

PRESENT FUNDING

Funding details have been sent separately by IH accounts.

FUTURE FUNDING

The Plynlimon hydrochemical study is throwing new light on the effects of tree harvesting in the upland areas of the UK. The current study provides the most complete and extensive hydrochemical data set for any acidified catchment in the world. The results are showing that water quality changes are still occurring and that these changes are linked both to conifer deforestation and climate change. The results are also casting doubt over the applicability of currently used models for assessing environmental impacts. They also point the way for more appropriate modelling endeavours. Consequently, it is essential that continued funding is secured following the termination of the present contract in 1992.

Appendix 1 Papers accepted for publication over the past 3 months.

1. Predicting future episodic changes in stream water chemistry : Journal of Hydrology.

2. Describing anthropogenic impacts on stream water quality : the problem integrating soil water chemistry variability : Science of the total Environment.

Predicting future episodic changes in stream chemistry.

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ABSTRACT

Short term stream chemistry response in a small stream in upland Wales is characterised by applying a mixing approach whereby the flow is assumed to be a mix of water from two distinct sources. Acidic water from the upper soil horizons and well buffered water from deeper 'groundwater' sources are used to represent the two endmembers and a chemical hydrograph separation technique is used to estimate the mean proportions of mix. A long term simulation model, the Model of Acidification of Groundwater In Catchments (MAGIC) is calibrated in its two layer mode to these two endmember chemistries. The model produces a good fit to observed present day stream, soil and baseflow chemistry. Future predictions of changes in endmember chemistry are made so as to enable future episodic response to be modelled. Under a 60 percent sulphate deposition scenario the model predicts a lowering of hydrogen ion concentrations associated with high flows and even a marginal recovery in baseflow pH.

INTRODUCTION

An assessment of the impact of surface water acidification on ecosystems requires an understanding of changes in stream chemistry over two timescales. That is, the long term build up of chronic acidity over periods of years and the short term acute changes associated with storm events. These short term acidic pulses are superimposed on long term trends and reconciliation of the two timescales is difficult. Hydrochemical models have been developed to simulate either long term changes in mean concentrations of water quality variables (MAGIC;Cosby et al. 1985a: RAINS;Kamari et al. 1984), or have focused on short term hydrologically driven responses (ILWAS;Chen et al. 1984: TRICKLEDOWN;Schnoor et al. 1984: BIRKENES;Christophersen et al. 1982). None of these models have proved sufficiently robust to work across the two timescales.

The link between long term build up of acidity and the extinction of fish populations in many surface water ecosystems is now well documented (Haines, 1986). It is also established that the survival of fish in upland streams is dependant not just on mean stream pH but the duration and severity of acid episodes (Turnpenny et al. 1987). Little is known, on the other hand, about the link between mean acidity and extreme values during episodes. A long term decrease in mean pH could theoretically be accompanied by two alternative episodic responses; both baseflow and peakflow waters show a corresponding drop in pH or, baseflow waters remain well buffered but the severity of the acid pulses at peak flow increases. To distinguish between these possibilities it is necessary to identify the mechanisms of flow generation and the source areas of the flow components comprising the flows at all discharge levels.

In this paper the link between long term and episodic response is examined through the development of a technique for modelling the changes important to short term stream water quality variations under continued acid deposition. This involves, (1) a mixing model approach to identify simple flow pathways and components of stream flow (endmembers), (2) a two layer version of MAGIC calibrated to present day endmember chemistry and used to predict the changes which will occur in the endmembers under acid deposition, and, (3) an assessment of future short term water quality variations using the predicted endmembers. The technique is applied to the Afon Gwy a small, moorland catchment at Plynlimon in mid-Wales.

THE STUDY SITE

The Afon Gwy catchment forms part of the headwaters of the river Wye. The geology consists of lower Palaeozoic mudstones, shales and grits with locally derived glacial and postglacial drift. Soil types include peats, brown earths, stagnogleys and stagnopodzols. The vegetation is acid grassland dominated by Nardus, Festuca and Agrostis species. Mean annual rainfall and runoff for 1983 - 1984, 1984 -1985 was 2385 and 2111 mm/year, respectively. Average rainfall, stream water and soil water chemistry is shown in Table 1 together with the stream water composition at baseflow, that is, from samples taken during very low flow periods when the water is assumed to originate from deeper, 'groundwater' sources and so is characterised by low acidity and high alkalinity.

THE MIXING APPROACH

The essence of the mixing approach is the concept that stream waters are generated by the mixing of chemically distinct water types (Christophersen et al., 1990; Hooper et al., 1990; Neal et al., 1990). The mean composition of each of these components (endmembers) is assumed to change only slowly and at most from year to year. The rapid chemical changes seen in the stream, in response to rainfall, are assumed to be the result of mixing varying proportions of the endmembers. The quantity or proportion of each endmember contributing to the stream is determined by changing catchment flowpaths as the storm intensifies and recedes.

The choice of characterisic endmembers for the catchment is based on the ion-flow relationships in the stream. Chemical response of the Gwy is typical of many British upland streams in that during high flow the pH falls, aluminium levels rise and base cation concentrations decrease (UKAWRG, 1988). At times of low flow the stream waters are well-buffered, of high pH and relatively rich in base cations. A simple interpretation of this can be made. During peak flows, when the water table is high, waters move through the acidic upper soil layers to the stream. During low flow, waters originate from deeper sources where weathering reactions with the bedrock occur (Neal et al., 1985). Only two components of flow are identified at this stage but this helps to limit the complexity of the modelling work and fits with observed variations (Neal et al., 1990; Robson and Neal, 1990; Kleissen et al., 1990). The natural choice is to take soil water as one endmember and a well buffered deep water (ground water) as the other. The rationale for the choice of these two components is discussed further in Neal et al. (1990). The soil water endmember chemistry is derived from L, O, E and B horizon soil water chemistry . The deep water component, however, has not yet been sampled directly and the composition of these waters is inferred from the chemistry of the baseflow waters seen in the stream.

To calibrate the MAGIC model, a mean annual proportion of mix between the two endmembers is required to fix the flow pathways in the model. This proportion of mix can be calculated by using a conservative chemical characteristic as a tracer such as the acid neutralising capacity (ANC). ANC is defined by:-

ANC = Sum "strong" base cations - Sum "strong acid anions"

and is determined from the chemical composition of the water, all terms being expressed in μEq/l. The ANC distinguishes well betwen the two chosen endmember water types and it is unaffected by CO_2 degassing. Extensive details of the use of ANC in hydrograph separation are given in Neal et al., (1990) and Robson and Neal, (1990). Calculated ANC for stream water, soil water and baseflow water is given in Table 2.

Since ANC is conserved during mixing the average proportion of soil water can be derived;

$$\text{Average proportion soil water} = \frac{\text{ANC deep water} - \text{ANC stream}}{\text{ANC deep water} - \text{ANC soil water}}$$

Using this relationship, the calculated mean flow-weighted proportion of soil water for the Gwy was approximately 0.48.

Clearly, a number of limitations exist in the use of this mixing approach and it is necessary to assume that, (1) streamflow is generated by water from two sources, (2) the direct contribution of rain to the stream is negligible, (3) a single soil endmember is representative of the upper soils even though the soils show heterogeneity both spatially and with depth, (4) the deep water component has uniform composition, and, (5) the chemistry of the endmembers remains constant during a storm.

Given the limitations of these assumptions and analytical error in the chemical measurements, a perfect match between the modelled and the observed chemical species in the stream is unlikely. The ANC gives a good indication of the overall composition of a water sample and whereas some deviations in individual determinands are acceptable, it is important that the modelled ANC is accurate.

THE MAGIC MODEL AND APPLICATION TO THE GWY

The MAGIC model uses equilibrium equations to describe soil processes and mass balance equations to describe catchment input-output relationships. Detailed descriptions of the conceptual basis of tha model and the equations on which it is based are documented elsewhere (Cosby et al.,1985 a,b). In this application a two layer version of MAGIC is used (Jenkins and Cosby, 1989) enabling the simulation of two chemically distinct waters. Here, the waters are chosen to correspond with the flow components identified from the mixing considerations outlined earlier. That is, the top layer represents the lumped L, O, E and B soil horizons while the bottom layer represents the C- horizon and deeper till layers. Similarly, the flow proportions included in the model are those suggested by the mixing approach. That is, all rain passes through the upper soils (top layer) and 42% of that percolate contributes directly into the stream whilst the remainder is routed via the deeper zones (bottom layer) to the stream (Figure 1.).

Concentrations of chloride and sulphate in the rainfall and stream were adjusted for occult and dry deposition of sea-salts and anthropogenic sulphur compounds. Between 1844 and 1984 the modelled rainfall inputs were varied according to the deposition sequence outlined by the Warren Springs laboratory (1983).

The two layers in the model were conceptualised such that different reaction mechanisms dominate each layer since they generate waters with distinct chemistries. The water from the upper soils is acidic and aluminium rich suggesting that ionic exchange mechanisms are the most important influence on soil water chemistry. Water from the deeper sources is rich in base cations indicating that it comes from a high weathering zone. In this application, therefore, it is assumed that ion-exchange occurs in only the top layer and that the ion exchange capacity of the lower soils and till layers is small enough to be neglected. On the other hand, weathering is assumed to take place predominantly in the deeper layers. A source of base cations was found to be essential in the upper soils, however, in order to fit the observed ANC. This may be attributed to biological activity or cycling. Only weathering inputs for calcium and magnesium were necessary in the top layer. Observations of throughfall chemistry support this: concentrations of calcium and magnesium are 15 and 18 μmol/l, respectively in throughfall compared with 4 and 10 μmol/l, respectively, in rainfall, allowing for evaporation: for sodium the throughfall concentration (94 μmol/l) is little different from rainfall (85 μmol/l) and so no extra input to the top layer is necessary.

The soil characteristics used in the model are given in Table 3. The depth of the upper soil (0.4m) corresponds to the average combined depth of the L, O, E and B horizons. An average depth of 1m is assumed for the remainder. The bottom layer is denser and of lower porosity. The partial pressure of carbon dioxide is assumed to be 30 times atmospheric for both layers (Neal and Whitehead, 1988). For the stream the pCO_2 was set to 3 times atmospheric pressure (Neal, 1988 a,b). The organic acid concentration in the two layers was calculated from the average observed DOC concentration assuming 9 carbon atoms per molecule. Dissociation constants were specified according to previously used values for similar sites in Scotland and are the same for each layer.

MODEL CALIBRATION

The model was calibrated to the chemistry of the stream water, the soil water and the deeper groundwater by adjusting weathering rates, uptake rates and the initial soil base saturation. The optimised values for the adjustable parameters are given in Table 4. Sulphate adsorption in the model is described by a Langmuir isotherm which has two parameters (Hornberger, 1986). These are calibrated on the assumption of a present day steady state condition with respect to sulphate input and output. Unique isotherms were calibrated for each layer under the assumption that the bottom layer has a greater capacity to adsorb sulphate than the top layer.

Nitrate and ammonia were modelled by calibrating catchment uptake to match the difference between inputs and outputs. Nitrate input was further increased to account for the high nitrate levels in the top layer resulting from a combination of dry deposition and biologically activated nitrogen mineralization.

RESULTS

The results from the calibrated model, shown in table 5, demonstrate a good agreement with stream chemistry although soil and groundwater chemistry are less well simulated. Given the variability of soil water chemistry with depth and aerially across the catchment, however, it is encouraging that each of the determinands falls within the measured range of soil water chemistry. The chloride concentration in the bottom layer is lower than observed in stream baseflow and is a consequence of the assumption of chloride conservativity in the model: this forces the chloride concentration in all of the model compartments to be constant. As a result of the low chloride level, simulated base cation concentrations are also lower than observed in the bottom soil layer.

Simulated stream ANC lies within 1 ueq/l of the value calculated from observed stream chemistry and the simulated ANC in the top soil layer is well within the observed range for soil waters. The simulated ANC for the lower box, however, is slightly higher than for stream baseflow water, probably because at baseflow the stream water includes a small soil water component. In this case the "true" groundwater endmember may be characterised by a higher ANC than that of stream baseflow.

The time trends of reconstructed soil, ground and stream water chemistry from 140 years ago, that is pre-acidification, up to the present day, are shown in figure 2. The pH (Figure 2a) of the stream falls rapidly as deposition increases in the 1950's and levels out in the 1980's in response to decreases in atmospheric deposition in recent years. The pH of the two endmembers changes similarly, but to a lesser degree, through the same period as a result of the higher partial pressure of carbon dioxide in the two layers. As a consequence of CO_2 degassing, the pH of the stream is not always bounded by the two endmember pH values, espescially at higher pH levels.

Sulphate concentrations in all three model compartments increase through time (Figure 2b) in line with the assumed increase in sulphate deposition. The variation in response between the endmembers reflects the sulphate adsorption constants chosen in the calibration whilst the stream concentration represents a direct mix of the two components. Calcium, magnesium (Figure 2c, d) and aluminium concentrations also increase in response to sulphate input whilst soil exchangeable bases (top layer) decrease (Figure 3). Exchangeable magnesium decreases most quickly, relative to the other exchangeable cations. This is a direct consequence of the Gaines - Thomas expression used to model ion exchange, whereby the most abundant ion is preferentially leached.

The model has also been used to estimate changes in stream, soil and deep water components into the future under two sulphate deposition reduction scenarios (Figure 2a-d); a reduction to 30% and 60% of present day levels by the year 2000 and held at a constant level thereafter.

Stream water pH improves in response to increasing pH in both soil layers and the greatest recovery occurs in response to the larger deposition reductions. Sulphate concentration in both endmembers decreases and the model predicts a reversal in sulphate concentration gradient between the upper and lower soils. Prior to the 1970's, modelled groundwater sulphate concentrations are lower than in the upper soils. In future years, as a consequence of the chosen sulphate adsorption constants sulphate concentration in groundwater takes longer to decline than the upper soil water. By the year 2100 the sulphate concentrations have equilibriated with the lowered input and there is no longer a variation between the layers.

Simulated aluminium concentrations fall, in line with sulphate reduction. The results give only a broad indication of likely trends since the cubic equilibrium conditions assumed in MAGIC may well not hold during episodes (Neal et al, 1989); this does not affect hydrogen ions or other base cations to any significant degree. The response of the base cation concentrations is more complex (Figure 2c, d). As sulphate input is reduced, fewer cations are exchanged from the soils and so cation concentrations decrease in both endmembers. The decrease is rapid for the first 10-20 years and then slows, directly reflecting the mobile anion input to the system. Under a 60% deposition reduction, some long term recovery is predicted but a 30% reduction is insufficient for any recovery in the model. In terms of the catchment soils (upper box), a 60% reduction in sulphate input produces a significant improvement in cation exchange capacity (Figure 3).

To assess the performance of the two layer model, a basic one-layer version of MAGIC was also calibrated to the Gwy catchment. Where possible identical values of the fixed parameters were chosen. The parameters for the aggregated soil layer were lumped according to standard practice (Jenkins and Cosby, 1989). As expected, the results show a broadly similar pattern of behaviour. The one-layer stream water chemistry falls well within the range spanned by the predicted endmembers from the two-layer model (Figure 4). However, the optimised one layer model estimates a significantly lower weathering rate than was found for the two layer version. As a consequence, the simulated background and predicted future stream chemistries from the one layer model are more acidic and the one layer model is less responsive to the variations in atmospheric deposition. The major differences between the approaches result from the inclusion of an additional body of well buffered water in the two-layer model.

DISCUSSION

During the next 140 years the predicted changes in endmember chemistry will produce a significant improvement, relative to present conditions, in the chemistry of the streamwater, especially at high flows. For example, the model predicts that whereas the difference in cation concentrations at high and low flows will remain the same, relative to each other, the predicted recovery in the upper soil water chemistry and the assumed dominant contribution from that source at high flows will lead to a decrease in the peak concentrations of hydrogen and aluminium. Concentration of both hydrogen and aluminium at baseflow is currently low and this situation will continue.

The incorporation of short term stream chemistry dynamics into models of long term response to changing acid deposition has obvious benefits in determining critical loads to ecosystems. At present, critical load estimation is based only on predictions of mean chemistry (Nilsson and Grennfelt, 1988) and yet stream biota can be seriously affected by short term acid pulses. This is not neccesarily a result of the peak levels of toxic species reached during an event, but may also be a function of the duration of the toxic conditions. If the critical load is to accurately represent the point at which biological life becomes seriously at risk then it must account for these dynamics. Through the technique developed here short term water quality responses can be quantified.

The two layer MAGIC model predicts enhanced recovery relative to the one layer model. Further work is required to see if this result holds in general as present day regional assessments may be too pessemistic.

CONCLUSIONS

1. A simple 2-layer model structure gives a good fit to observed endmember and stream water chemistry.

2. The model predicts that the chemistry of the endmembers has changed historically. Both soil waters and deep waters have acidified and the cation exchange capacity of the soils shows a large decrease.

3. Under reduced deposition the model predicts that the most significant changes in stream chemistry will occur at peak flow with greatly reduced levels of acidity and aluminium. Baseflow chemistry will also improve slightly. Recovery is greatly enhanced by a 60% reduction as opposed to a 30% reduction.

4. The approach may be expanded to model dynamic storm response using mixing principles and can provide valuable information for establishing an episodic basis for critical load estimation.

5. Greater recovery from reduced emission strategies are suggested with the two layer model in comparison with the one layer MAGIC model.

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Table 1.

Rainfall, stream water, soil water and baseflow water chemistry. Units are µEq/l except Al and Si (µmol/l) and pH.

	Rainfall	Stream	Baseflow	Soils		
				Oh	Eag	Bs
Ca	8	36	58	14	20	14
Mg	10	54	70	40	44	40
Na	85	143	166	100	187	173
K	2	3	2	8	4	4
NH_4	17	<5	<5	<5	<5	<5
Si	<2	35	54	18	42	36
SO_4	42	72	74	68	87	71
Cl	106	155	170	124	209	184
NO_3	12	15	4	29	39	28
H	21	13	1	77	55	44
pH	4.7	4.9	6.3	4.1	4.3	4.4
HCO_3	<1	35	27	-	-	-
Al	<2	3	2	10	18	15

Table 2.

Stream water, soil water and baseflow Acid Neutralisation Capacity. Units are µEq/l.

	Stream	Soil			Baseflow
		Oh	Eag	Bs	
Sum cations	236	162	255	231	295
Sum anions	242	221	335	283	248
ANC	-6	-59	-80	-52	47

Table 3.

Soil characteristics used in the two-layer MAGIC model

	Units	Top Layer	Bottom Layer
depth	m	0.4	1
porosity	frac	0.55	0.35
bulk density	kg/m^3	1060	1460
CEC	meq/kg	70	0.1
Organics	µmol/l	56	10
Temperature	°C	7.6	7.6
PCO$_2$	atm	0.009	0.009
$\log_{10}(K_{Al(OH)3})$		7.8	8.6

Table 4.

Calibrated parameters for the two-layer MAGIC model

		Top Layer	Bottom Layer
SO_4 Halfsat	µEq/l	80	5
SO_4 MAXcap	µEq/l	2	9
pk1 (organics)		4	4

Weathering/Uptakes	Top Layer	Bottom Layer
NH_4	-92	0
NO_3	0	-88
Ca	2	43
Mg	14	28
Na	0	36
K	0	0

Selectivity coefficients

Ca	2.7
Mg	3.27
Na	-0.65
K	-4.7

Initial base saturation: 35.0

Table 5.

Modelled stream and endmember chemistry. Bracketed values are the field measurements. A range is given for the O-B horizons in the soil. Units are μEq/l except pH.

	Stream		Top Layer		Bottom Layer	
Ca	36	(36)	16	(14-20)	55	(58)
Mg	54	(54)	41	(40-44)	66	(72)
Na	143	(143)	126	(100-183)	159	(166)
K	3.2	(3)	3.2	(4-8)	3.3	(2)
NH_4	1.5	(<5)	1.5	(<5)	1.5	(<5)
SO_4	72	(72)	71.0	(68-87)	73	(74)
Cl	155	(155)	155	(124-209)	155	(170)
NO_3	16	(15)	29	(28-39)	3.5	(4)
H^+	18	(13)	60	(44-77)	3.6	(1)
pH	4.8	(4.8)	4.2	(4.1-4.4)	5.4	(6.3)
Al^{3+}	7	(9)	46	(28-55)	1.0	(5)
ANC	-5	(-6)	-69	(-52 - -80)	54	(47)

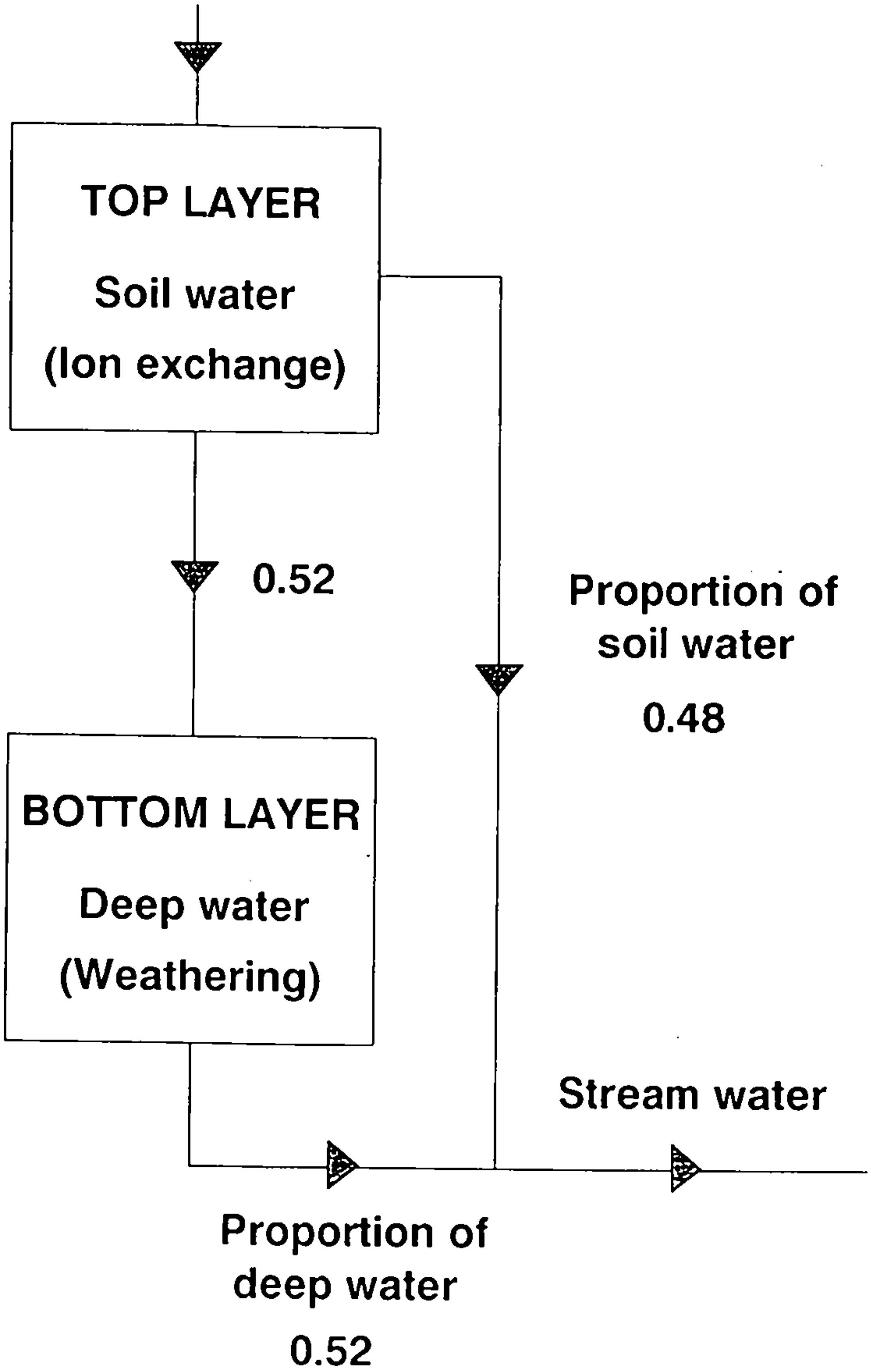
Figure Legends

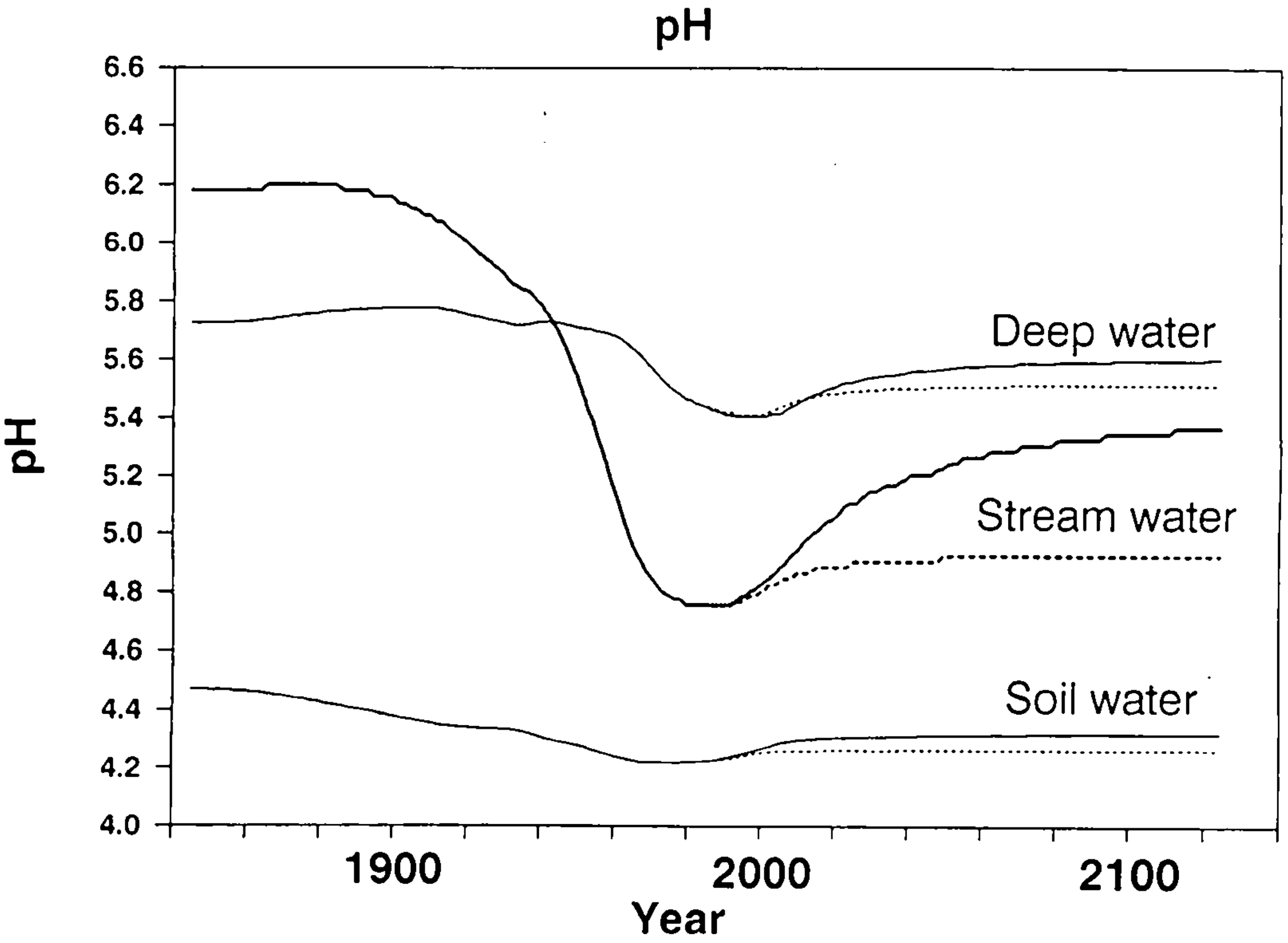
Figure 1. Flow routing for the two-layer MAGIC model.

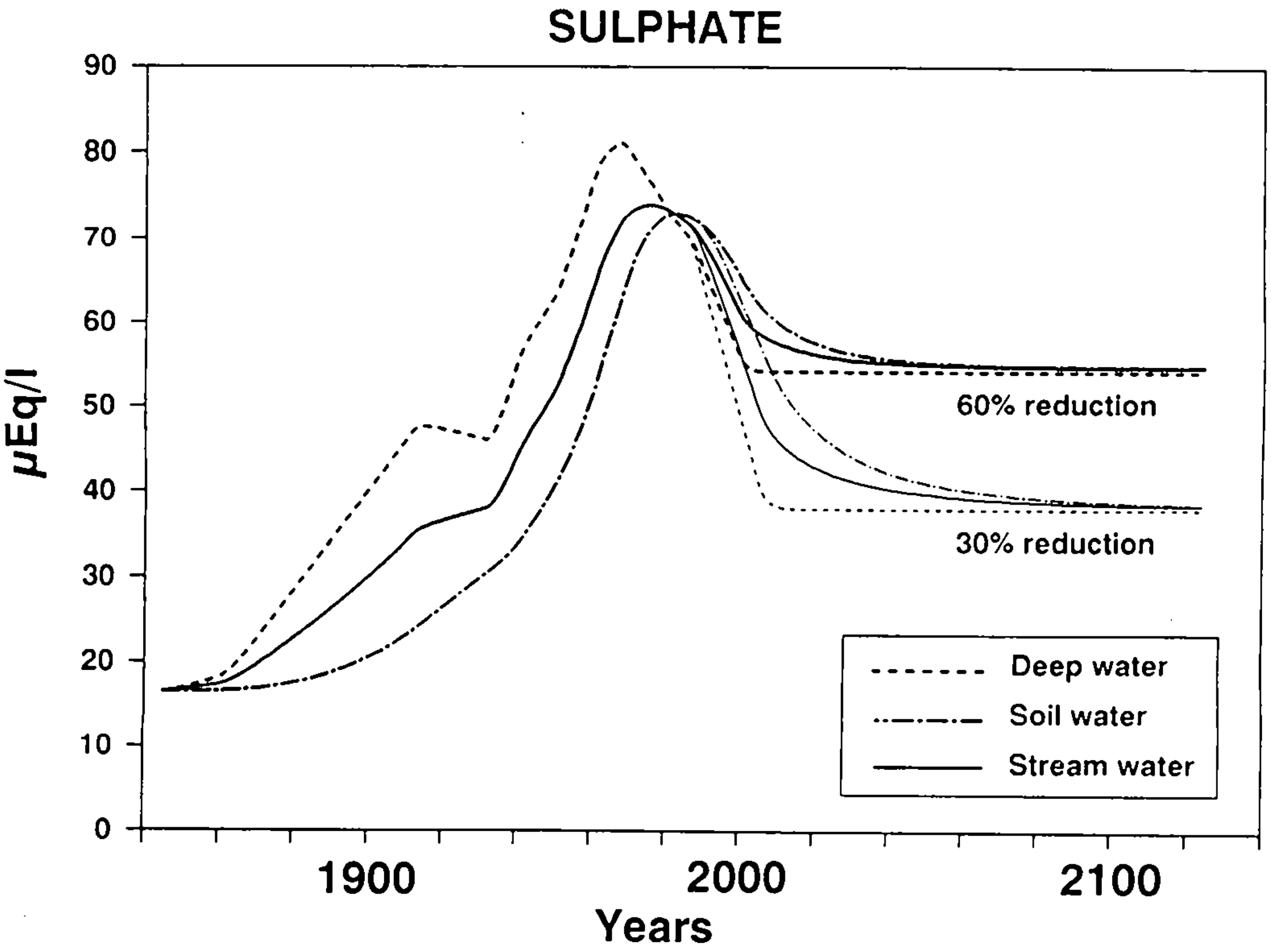
Figure 2. Modelled stream and endmember chemistry; (a) pH, (b) sulphate, (c) magnesium, (d) calcium. For a, c and d solid lines show the predictions for 60% and the dotted lines for 30% reduction.

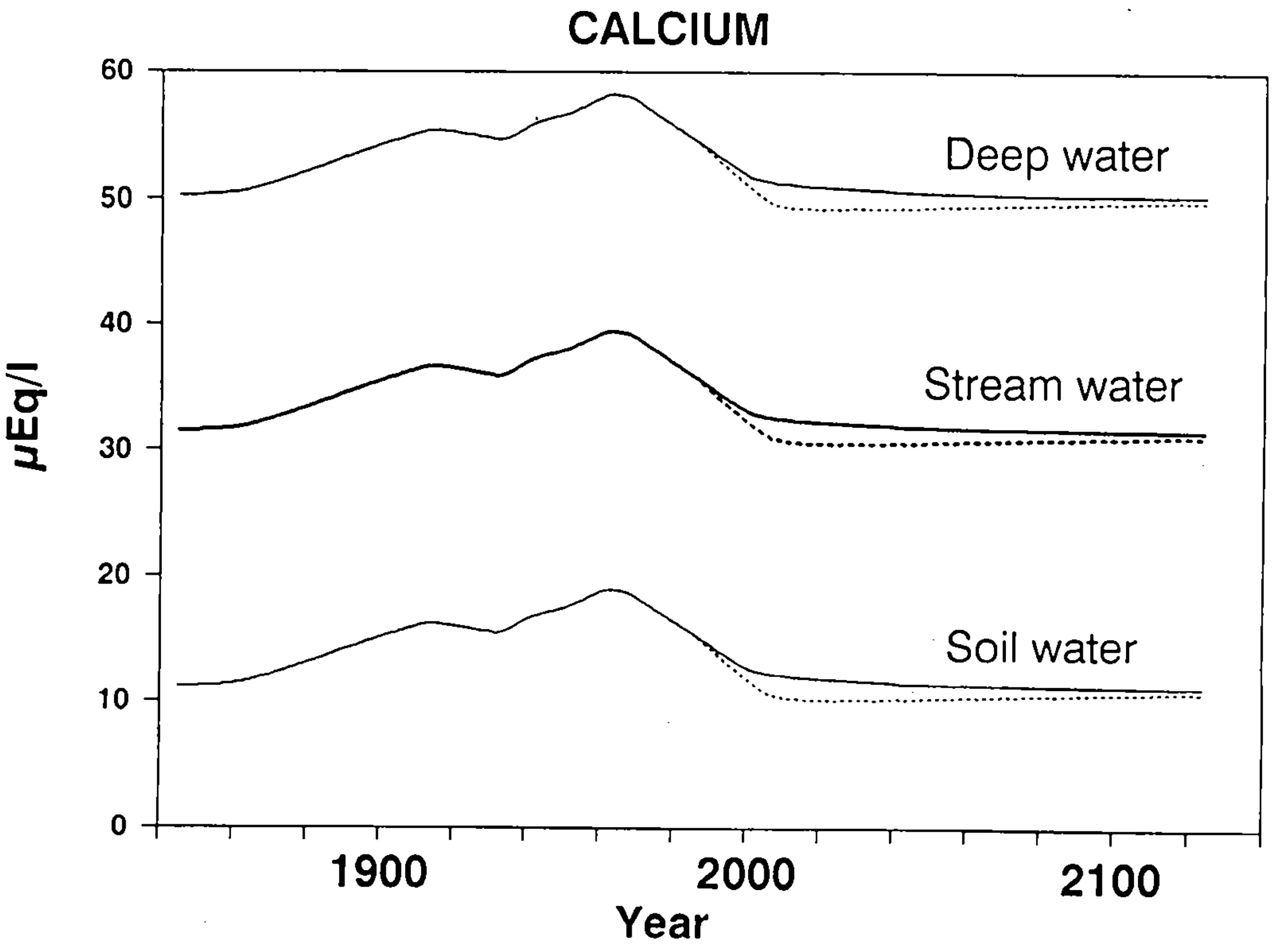
Figure 3. Simulated cation exchange capacity in the top soil layer.

Figure 4. Comparison of Acid Neutralisation Capacity for the one layer (line with markers) and two layer (no markers). Solid lines show the predictions for 60% reduction and dotted lines for 30% reduction.

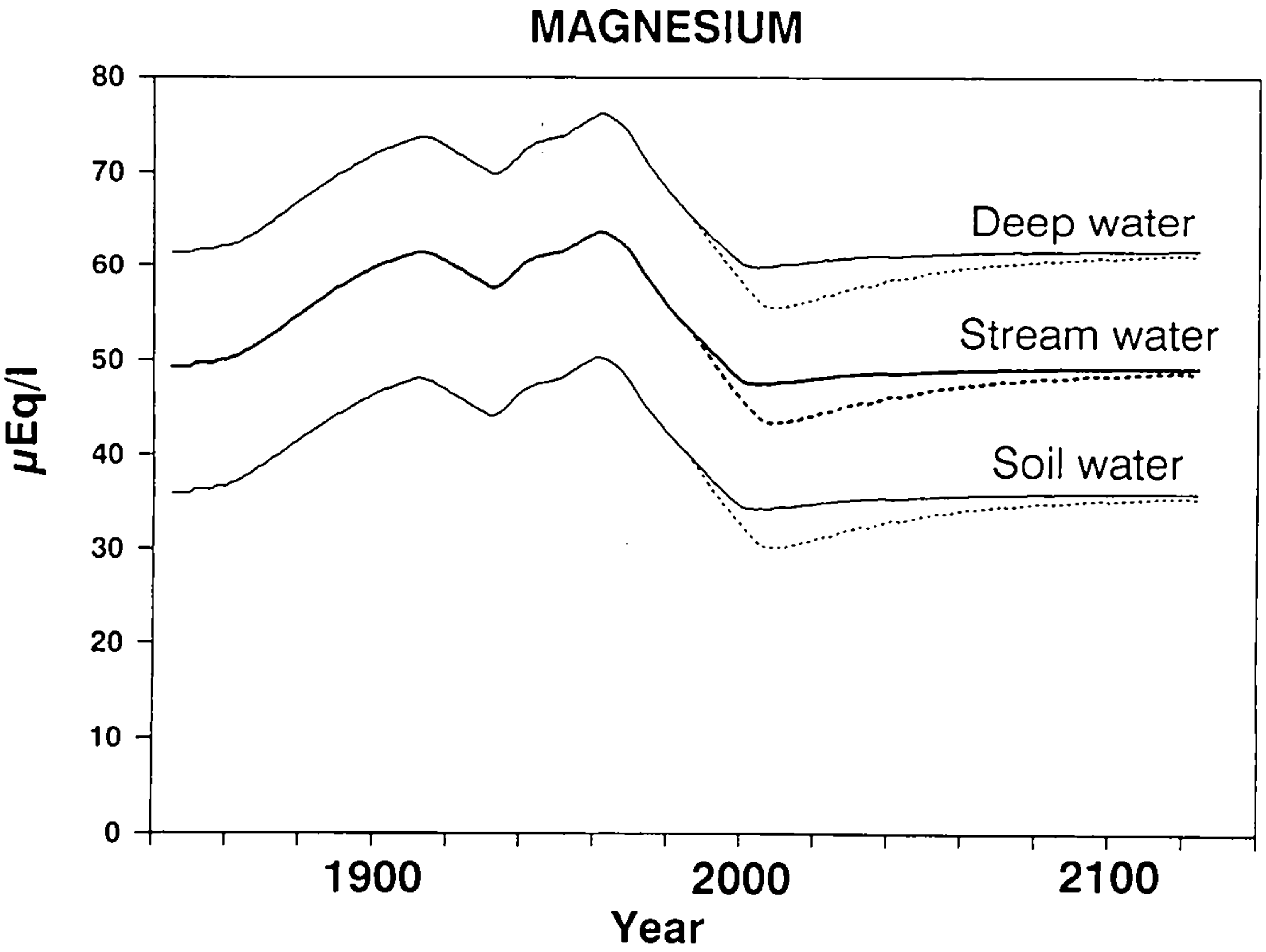

TOP LAYER
Soil water
(Ion exchange)
0.52
Proportion of soil water
0.48
BOTTOM LAYER
Deep water
(Weathering)
Stream water
Proportion of deep water
0.52

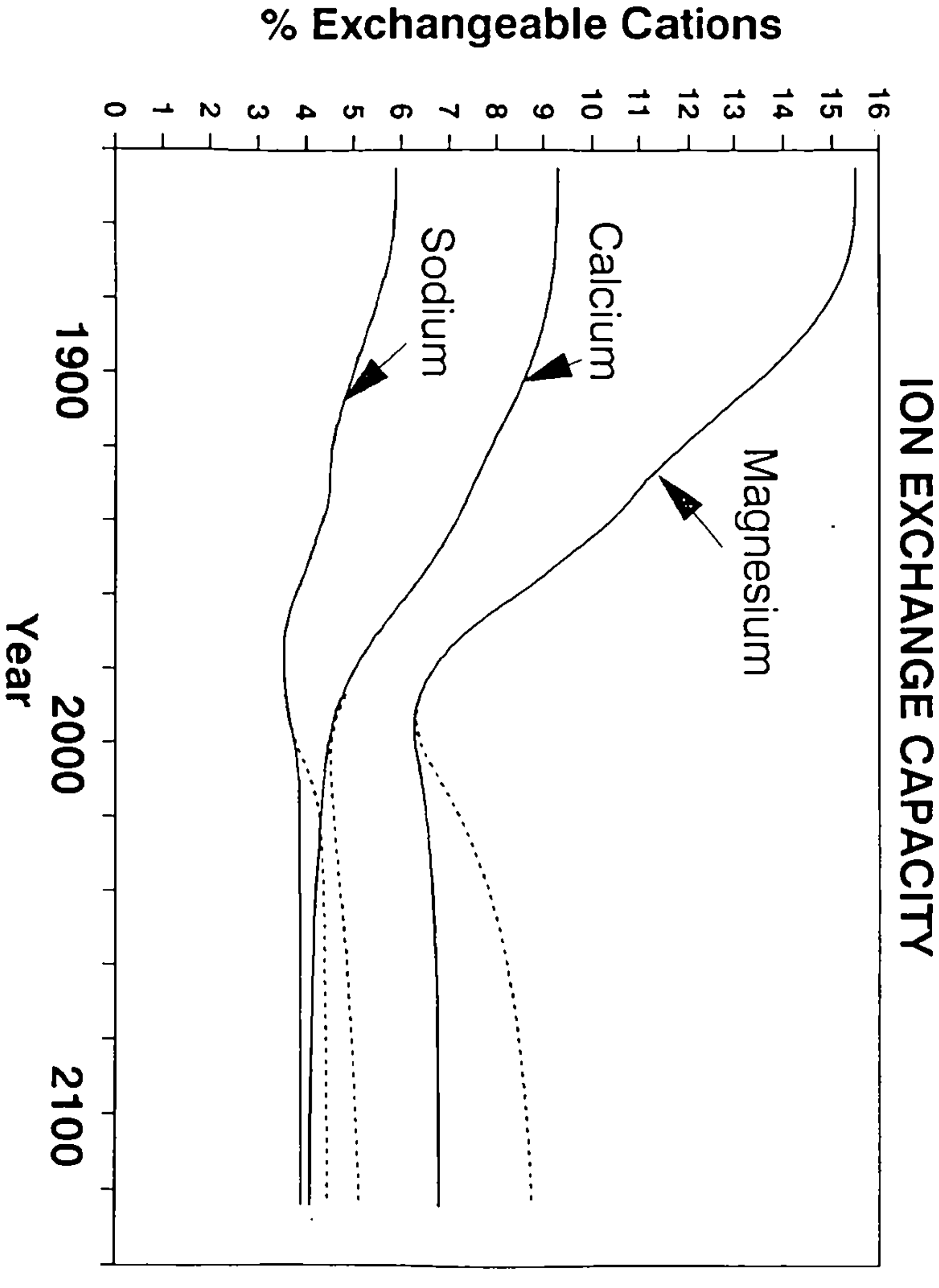

pH
6.6
6.4
6.2
6.0
5.8
5.6
5.4
5.2
5.0
4.8
4.6
4.4
4.2
4.0
pH
Deep water
Stream water
Soil water
1900
2000
2100
Year

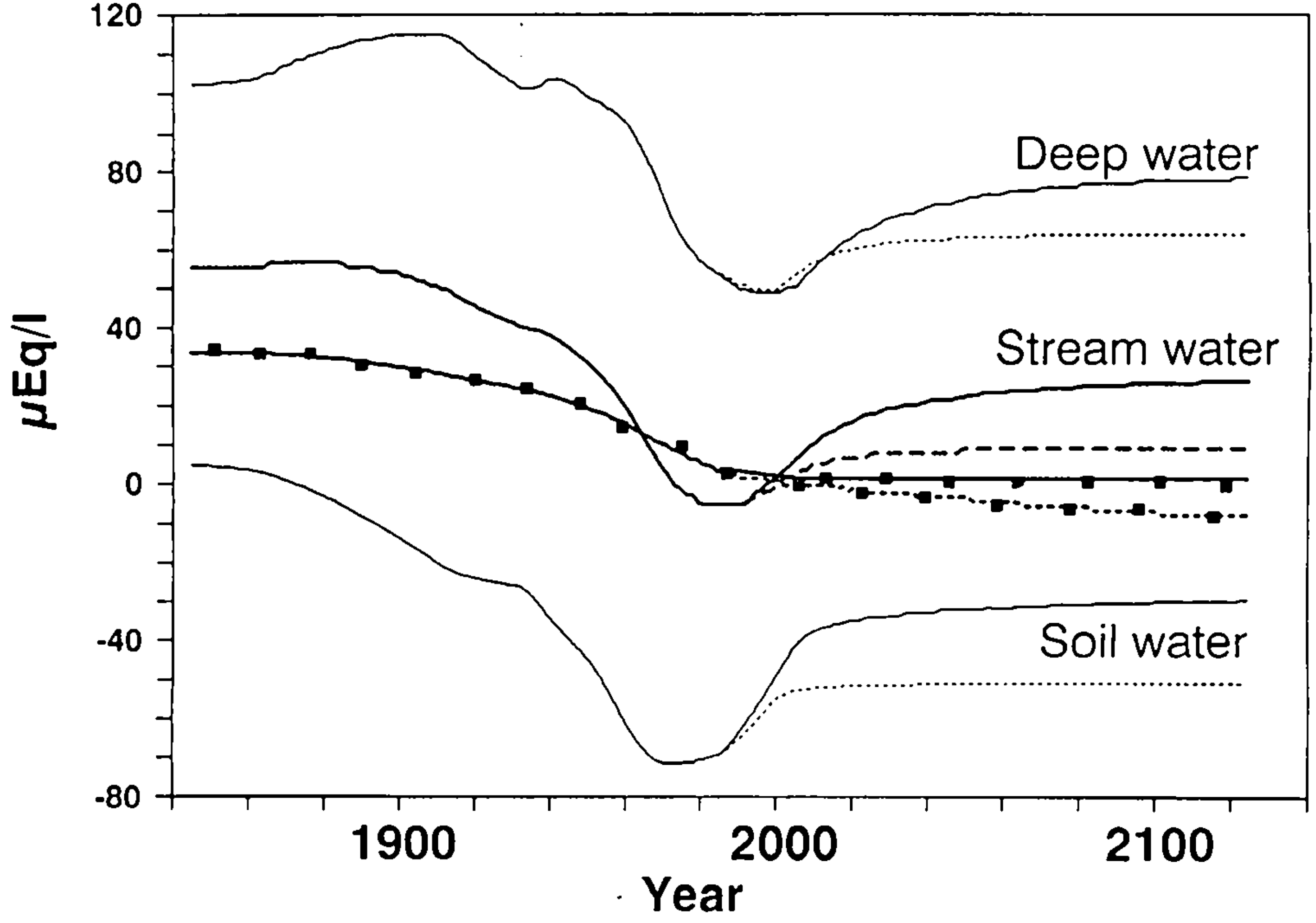

SULPHATE
μEq/l
0
10
20
30
40
50
60
70
80
90
1900
2000
2100
Years
60% reduction
30% reduction
Deep water
Soil water
Stream water


CALCIUM
60
50
40
30
20
10
0
µEq/l
Deep water
Stream water
Soil water
1900
2000
2100
Year

[illegible] 2d


MAGNESIUM
µEq/l
80
70
60
50
40
30
20
10
0
1900
2000
2100
Year
Deep water
Stream water
Soil water


ION EXCHANGE CAPACITY
% Exchangeable Cations
Year
Magnesium
Calcium
Sodium
0
1
2
3
4
5
6
7
8
9
10
11
12
13
14
15
16
1900
2000
2100



ACID NEUTRALISATION CAPACITY

COMPARISON OF ONE-LAYER AND TWO-LAYER MAGIC

Describing anthropogenic impacts on stream water quality: the problem of integrating soil water chemistry variability.

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ABSTRACT

Problems encountered when (a) lumped soil water information is used to assess the relevance of cation exchange equations in the soil and (b) lumped mathematical models are used to describe the hydrochemical behaviour of catchments, are discussed. To highlight the difficulties and to focus the discussion, an example is provided using synthetic data. This data is generated using a mathematical model employing simple cation exchange reactions to describe water chemistry within the microporous regions of the soil. The proportion of the individual cations is assessed by varying the strong anion content within the micropore. These solutions are then mixed and the resultant chemistries are compared with the cation exchange formulations. It is taken that, on transfer from the micropore to the soil water sampler, the mixed solutions do not participate in cation exchange reactions: the chemical speciation programme ALCHEMI is used to characterise the chemical speciation changes occurring after mixing. The model is calibrated on the basis of average soil water data from two acidified spruce forest sites. The results show that by lumping the soil chemistry data, the averaged values for the chemical constituents systematically deviate away from the underlying theoretical cation exchange equations when differing cation charges are involved: no deviations occur when the charges are the same. The findings are extended to suggest that, for the chemically heterogeneous catchments being studied, the use of lumped mathematical models, which smooth out and ignore this variability, nullifies the theoretical equations on which the models are based. An appeal is made for (a) more detailed field studies to determine the degree of catchment inhomogeneity for soil properties and chemistry and (b) an assessment of the importance of catchment heterogeneity within a modelling framework.

INTRODUCTION

The hydrochemical behaviour of catchments is extremely difficult to describe. Not only is one dealing with a complex set of chemical, biological and hydrological processes but the catchments themselves are highly heterogeneous (1,2). For example, soils vary in their thickness and chemical composition across catchments in irregular ways. Correspondingly, macroporous and microporous flow processes occur and vary to different extents. These flow processes, while known to occur, are both poorly described and not easily describable within a process based model. They vary according to location within the catchment and other hydrological factors such as moisture content and storm intensity (1,2).

In order to describe catchment response to anthropogenic change, studies have been undertaken in the laboratory and in the field, on plot and catchment scales, to assess the dominant processes occurring (1-3). These studies have been augmented by intensive modelling activities (1-5). Within hydrochemical process studies on acidic and acid sensitive catchments, emphasis has been correctly placed on field observation since, by bringing catchment samples from the field into the laboratory, one perturbs the system in a manner different to that occurring in the environment (6). The best examples of this come from studies for soils and bedrock where field and laboratory determined weathering rates differ by up to three orders of magnitude and where soil disturbance produces large changes in soil water chemistry (6). However, in undertaking field studies, one has to cope with the heterogeneous nature of the catchments (eg large variations in the soil water and throughfall chemistry and cation exchange complement): a situation unimportant in laboratory studies where one can, for example, homogenise soil samples and undertake reactions under very controlled conditions.

In this contribution one of the problems of using field information is considered: the characterisation of cation exchange processes in the soil based on lysimeter information. The work is set in relation to field and modelling studies of acidic and acid sensitive, spruce-afforested, catchments at Plynlimon in mid-Wales (7) and at Birkenes, southern-Norway (8). The analysis provides an example of where combining (herewith termed lumping) samples to obtain average soil water chemistries for the soil leads to loss of information for elucidating the cation exchange processes occurring and thus leading to misleading conclusions. The arguments presented are extended to comment on the value of lumped, process-based, models in describing catchment response.

THEORETICAL CONSIDERATIONS

A homogeneous model for cation exchange in soils

Consider the case of cation exchange reactions in soils which obey simple relationships of the type

$bA^{a+} + aAds(B) = aB^{b+} + bAds(A)$.

Here cations A and B, of charge a and b respectively, interact with a solid phase cation exchanger (Ads). For this reaction an equilibrium constant ($K_{A,B}$) is defined by the expression

$K_{A,B} = (\{A^{a+}\}^b*NIC(B)^a)/(\{B^{b+}\}^a*NIC(A)^b)$ Equation 1,

where {} refers to the chemical activity and NIC(), the notional interfacial content, denotes the amount of component adsorbed (9,10).

Under the conditions pertaining in the soils of concern here, the amount of cations on exchange sites is large relative to the corresponding amount in the soil solution. For this circumstance, the ratio $NIC(B)^a/NIC(A)^b$ remains relatively constant, say at a value of $NIC(Ratio)_{B:A}$, and hence

$\{A^{a+}\}^b/\{B^{b+}\}^a = K_{A,B}/NIC(Ratio)_{B:A} = a\ constant\ (K_{A,B})$ Equation 2.

The chemical activity of A and B will change in the soil solution as the total anion concentration changes (eg during storm events when water moves through the different soil layers and during dry periods when evaporation processes are important). However, the relative changes in the chemical activities will be fixed by the power term given by equation 2. For example, cation exchange reaction involving hydrogen ions and trivalent aluminium will be manifest by a cubic relationship between H^+ and Al^{3+} activities: i.e.

$\{H^+\}^3/\{Al^{3+}\} = K_{H,Al}$.

A heterogeneous model for cation exchange

In sampling soil water using tension lysimeters, an integrated sampling of waters in the vicinity of the collector is made. Similarly, when lysimeter samples are mixed together to save on the analytical chemistry load, an integrated sample is collected. Assume there exists a cation exchange equilibrium, of the type described in the previous section, within very localised areas in the soil (microporous water in intimate contact with the soil cation exchange surface). Assume also that during transport from the micropore to the collector, and during mixing of the various sources of water, reactions with the solid phase do not come into play. Under these circumstances, and when lysimeter samples are mixed, the chemical variations will be averaged out to some degree. In the case of a component, say C, which conserves its chemical activity (i.e. it does not participate in complexation, solubility and carbon dioxide degassing reactions during and subsequent to mixing) the mean activity in the bulked solution (*C*) is given by the equation

$$C = \Sigma(\{C_i\}*v_i)/\Sigma(v_i) \qquad \text{Equation 3.}$$

Here, v_i is the volume of a subsample collected and i is the identifier: Σ represents a summation from i = 1 to i = N, N is the number of collections or water types. For the situation where non-conservative processes are operative, there are two possibilities. First, if the data is collected individually, equation 3 can be applied, together with a speciation model, to calculate the net changes occurring: this type of approach is used in the calculations described below. Second, if the samples are mixed together before chemical analysis has been performed, the net chemical composition will be directly determined; equation 3 will not hold.

One general point can be made over the ratios of the mean chemical activities and *K* for conservative cations. Consider mixed soil water solutions obeying the above rules for two conservative cations P and Q of charges p and q respectively; mean chemical activities {*P*} and {*Q*} respectively. Combining equations 2 and 3 gives

$$\{P\}^q/\{Q\}^p = K_{P,Q}*(\Sigma Q_i^p*(v_i/\Sigma(v_i))^q)/(\Sigma Q_i^p*(v_i/\Sigma(v_i))^p) \qquad \text{Equation 4.}$$

When the charges on the cations P and Q are the same (p = q) then

$\{P\}^q/\{Q\}^p = K_{P,Q}$.

When q > p then $\{P\}^q/\{Q\}^p > K_{P,Q}$ since

$(v_i/\Sigma(v_i))^q < (v_i/\Sigma(v_i))^p$ and $0 < v_i < \Sigma(v_i)$.

By the same argument, when p < q then $\{P\}^q/\{Q\}^p < K_{P,Q}$.

In other words, the averaged estimate of $K_{P,Q}$, $\underline{\underline{K}}_{P,Q}$, is systematically biased when P and Q are of different charge:-

if p > q then $\underline{\underline{K}}_{P,Q} > K_{P,Q}$;

if p < q then $\underline{\underline{K}}_{P,Q} < K_{P,Q}$;

if p = q then $\underline{\underline{K}}_{P,Q} = K_{P,Q}$.

An application of the heterogeneous model using synthetic data

In order to use an heterogeneous model for examining the effects of mixing processes it is necessary to consider a practical example. This is required since the above theory cannot describe directly non conservative behaviour and the extent of the deviations. To do this an example is provided here which examines soil water chemistry with variations in salt content using synthetic data. The method follows that employed by Christophersen and Neal (11) to examine hypothesis testing of chemical reactions in soil and stream waters. This is required since (a) there is insufficient field information available for direct assessment of variability in the soil micropores and macropores and (b) an ideal case has been chosen free of the complicated field situation where cation exchange formulations, hydrological, biological and chemical pathways are uncertain.

Here an analysis is made using field information from spruce forest soils at Plynlimon, mid-Wales, (12) and Birkenes, southern Norway (8). The field data is used simply to provide approximate, but hopefully realistic values for $K_{p,Q}$, ranges in ionic strength and average soil water compositions encountered in the upper soil horizons. Using this information a set of soil water compositions are determined which cover the range in observed soil water ionic strengths. This is undertaken by using a speciation programme, ALCHEMI (13), in conjunction with equation 2 and the net charge balance. Within the calculations allowance is made for (a) cation exchange reactions involving Na, K, Mg, Ca, inorganic aluminium and protons, (b) complexation of aluminium with fluoride, sulphate, silicate and dissolved organic matter, (c) dissolved organic matter protonation (a triprotic acid is considered) and (d) the inorganic carbon dioxide system. The effects of mixing these soil micropore waters to simulate the bulking of information is made by considering three ranges of ionic strength: the full ionic strength range is considered as this represents the long term variation in soil water chemistry: ranges spanning the lower and upper halves of the ionic strength range as they describe more localised and lower variability effects. Determination of the effect of mixing waters from each range of ionic strengths is as follows. Random proportions of water from the top middle and lowest ionic strength value for each range are mixed and equation 4 is applied. Subsequently, the ALCHEMI programme is used to calculate the resultant solution composition following changes in speciation. Within the calculations the ranges chosen for the total anion concentrations are 100 to 800, 100 to 450 and 450 to 800 µEq/l while $K_{Na,H} = 2$, $K_{Na,Ca} = 10^{-3}$ and $K_{Na,Al} = 2*10^{-7}$.

The results of this exercise are summarised in figure 1 and tables 1 and 2. They show that the mixed solutions provide data that fits closely to the theoretical line when a non-conservative component is involved (eg H^+) only for the case where the charges are identical ($\{Na^+\}$ vs $\{H^+\}$, Figure 1). For the conservative cation case there is an exact fit to the theoretical line when the charges are identical (Na^+ and K^+; Ca^{2+} and Mg^{2+}): see theory above. In the cases where the charges differ, the concentration of the mixed solutions plot in a region defined by the theoretical curve and a straight line joining the two extreme values ($\{Na^+\}$ vs $\{Ca^{2+}\}$; $\{Na^+\}$ vs $\{Al^{3+}\}$; Figure 1): this property seems to occur for both conservative and non-conservative cations. These results all show that for components with differing charges the mixing process gives data that is systematically biased to the convex side of the theoretical curve. Further, in the differing charge case the data approximate to straight lines (Tables 1 and 2) and the power terms are closer to 1 (Table 1). In the cases where smaller ionic strength ranges are used the scatter is limited to an area much closer to the theoretical equation. For the straight line regression cases, both the gradients and the intercepts vary according to the anion concentration ranges chosen (Table 2): the power terms also vary according to the concentration range chosen (Table 1)

DISCUSSION

The results show that in sampling and lumping chemical information together, for systems which are non-linear, the averaged values do not correspond with the theoretical equations. There are two very important consequences to this finding. First, lumped field data cannot be used to directly infer whether or not non-linear reactions are occurring when the system shows large spacial variation in its chemical composition. Second, lumped hydrochemical models cannot be used, without reservation and questioning, in conjunction with theoretical or laboratory established non-linear equations, when the system being studied is of variable chemical composition.

Although it is very widely accepted that soil lysimeters collect a mixture of waters in the field, the extent of the chemical variability of the water being collected is not known in any detail. Therefore, it remains uncertain, generally, as to the extent that mixing processes will obscure the underlying chemical processes operative: results will vary from catchment to catchment as well as with the location and type of collector used.

However, there is widespread indirect evidence for suggesting that mixing of distinct water types is occurring. Five examples are provided to show this. First, in the case of the Hafren spruce forest, very marked linear trends in element concentration occur which mirror the behaviour described above (12): straight line relationships are observed between $\{H^+\}$ and $\{Al^{3+}\}$ for each soil horizon and the power relationship is much less than 3 (about 1.5). Second, studies at the Allt na Mharcaidh catchment in the Cairngorms, Scotland show soil water chemistry which displays linear relationships between monovalent and divalent cations and low correlations for other cations (7,15,16). Third, at the Birkenes catchments in southern Norway, soil water solutions have chemical compositions which provide power relationships less than the theoretical value when cations of different charges are considered (8). Four, for a variety of soil lysimeter data the results indicate a $\{Al^{3+}\}$ vs $\{H^+\}$ relationship of power 1.66 (17) as opposed to a value of 3 from the theory given above. This power term is far too low even for the most recent and most appropriate cation exchange model, CHAOS, which allows for the cation exchanger having variable surface charge (18). Five, the chemical inputs to the upper soil layers in forested catchments (as throughfall) can vary substantially over very localised areas. Indeed one of the major difficulties in obtaining averaged throughfall concentrations is having sufficient samplers to lower the standard error to an acceptable amount (25): it was estimated that over 100 samplers were required under a hardwood forest to obtain mean throughfall concentrations for the major cations within 10% of the true mean with 95% confidence for individual storms (25). Furthermore, there is strong field evidence of large scale and localised variability of water chemistry in a given soil horizon. For example, examination of small samples of soils from grassland areas in Oxfordshire show soil water chemistry to vary substantially on metre scale collection (14). Therefore, there is a strong basis for questioning the value of most of the field information collected, using lysimeter or lumping procedures, with regards to the identification of the chemical processes: the data can still be used for flux and residence time analysis. If mixing occurs to the extent described in the modelled case then information on process controls is clearly lost. For example, tables 1 and 2 provide correlation coefficients for linear and power terms which are very similar. The independent observer would have great difficulty distinguishing mixing and cation exchange reactions given the information provided in these two tables. Table 1 shows that for cations of different charges there are large deviations away from the theoretical power terms that correspond with the field observations described above.

In order to test for chemical equilibrium within the fine pores of soils it is therefore essential that new experiments be performed using waters collected from very localised areas within the soil. For example, the recently developed liquid displacement technique to remove solutions from soils immediately after collection (14,19) could be valuably employed.

Within environmental studies there never seems to be the time or the manpower to collect sufficient information to identify how rainfall is modified as it progresses to the stream (20). For logistical reasons, it has been necessary to limit the number of collections made and/or to combine data together to reduce the analytical load. The consequences of this are two fold: the degree of catchment inhomogeneity has been inadequately monitored; identification of the underlying chemical processes has been obscured. On this basis it is strongly argued here that this shortfall needs readdressing.

Modelling the effects of acidic deposition and land use change has necessitated a major simplification of the processes operative within the catchment. For example, the most widely used short term hydrochemical model, the Birkenes model (21,22), assumes soil and ground water layers which are constant in there chemistry over daily periods. Correspondingly, the most widely used long term model, the MAGIC model (23,24), assumes similar constancy but over a yearly time step. In neither case is allowance made for the soils having a variable structure, cation exchange complement and soil solution chemistry. In simplifying the system down to this extent a inconsistency has been introduced corresponding to the lumping problem described above. Indeed, the situation is worse than that described above since there are very large chemical gradients within the soil profile and the relationship between cation concentrations is very different for each soil horizon (1, 2, 8, 12): the mixing model used above only allows for variations within a single layer. One simply cannot, ad-hoc, use a lumped model with theoretical equations that match, or are presumed to match, processes occurring within micropores. Further, when field observations based on lumped information (eg soil lysimeter data) do not tally with modelling assumptions (as is the case with cation exchange and aluminium hydroxide solubility controls) then the model structure is incorrect: the integrated soil water samples, when lumped for the various soil horizons, provides the nearest analogue to the estimated average soil water chemistry using the lumped model. In order to progress further with modelling work some attempt must be made to assess how heterogeneity will affect the reliability of predictions. Again this points to the urgent need for a more rigorous assessment of variability in the field.

CONCLUSION

The results presented here bring into the open the question of the limits to which process-based hydrochemical models, and detailed plot and laboratory studies, can be used to describe environmental processes on the catchment scale. They suggest that greater emphasis be placed on establishing the chemical and hydrological variability within catchment: the need for stochastic based models is also implied. The value of chemical information from lysimeter collections is questioned.

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FIGURE LEGEND

Figure 1,{Na^+} relationships with {H^+}, {Ca^{2+}}, and {Al^{3+}} for soil waters with anion concentrations in the range 100 to 800 µEq/l. The solid line represents the cation exchange relationship in the

Table 1. Regression data linking p$\{Na^+\}$ to pH, p$\{Ca^{2+}\}$ and $\{Al^{3+}\}$ for mixed soil solutions: p denotes $-\log_{10}$.

p$\{Na^+\}$ vs pH

	Gradient	r^2
Full range	0.915±0.007	0.998
Lower range	0.983±0.006	0.999
Upper range	0.846±0.004	0.943
Theoretical value	1.00	

p$\{Na^+\}$ vs p$\{Ca^{2+}\}$

	Gradient	r^2
Full range	1.30±0.05	0.954
Lower range	1.42±0.05	0.959
Upper range	1.90±0.03	0.991
Theoretical value	2.00	

p$\{Na^+\}$ vs p$\{Al^{3+}\}$

	Gradient	r^2
Full range	1.95±0.07	0.948
Lower range	2.37±0.09	0.952
Upper range	2.64±0.03	0.933
Theoretical value	3.00	

Table 2. Regression data linking $\{Na^+\}$ to $\{H_+\}$, $\{Ca^{2+}\}$ and $\{Al^{3+}\}$ for mixed soil solutions.

$\{Na^+\}$ vs $\{H^+\}$

	Gradient	Intercept	r^2
Full range	0.604±0.006	$(8.3\pm1.1)*10^{-6}$	0.996
Lower range	0.660±0.004	$(1.7\pm0.5)*10^{-6}$	0.998
Upper range	0.540±0.004	$(19.8\pm1.2)*10^{-6}$	0.940

$p\{Na^+\}$ vs $p\{Ca^{2+}\}$

	Gradient	Intercept	r^2
Full range	0.266±0.010	$(8.6\pm1.9)*10^{-6}$	0.947
Lower range	0.207±0.007	$(-5.6\pm0.9)*10^{-6}$	0.954
Upper range	0.407±0.006	$(-36.4\pm0.3)*10^{-6}$	0.991

$p\{Na^+\}$ vs $p\{Al^{3+}\}$

	Gradient	Intercept	r^2
Full range	0.258±0.011	$(-16.4\pm2.2)*10^{-6}$	0.928
Lower range	0.163±0.002	$(8.9\pm0.9)*10^{-6}$	0.933
Upper range	0.444±0.004	$(-52.0\pm0.2)*10^{-6}$	0.996

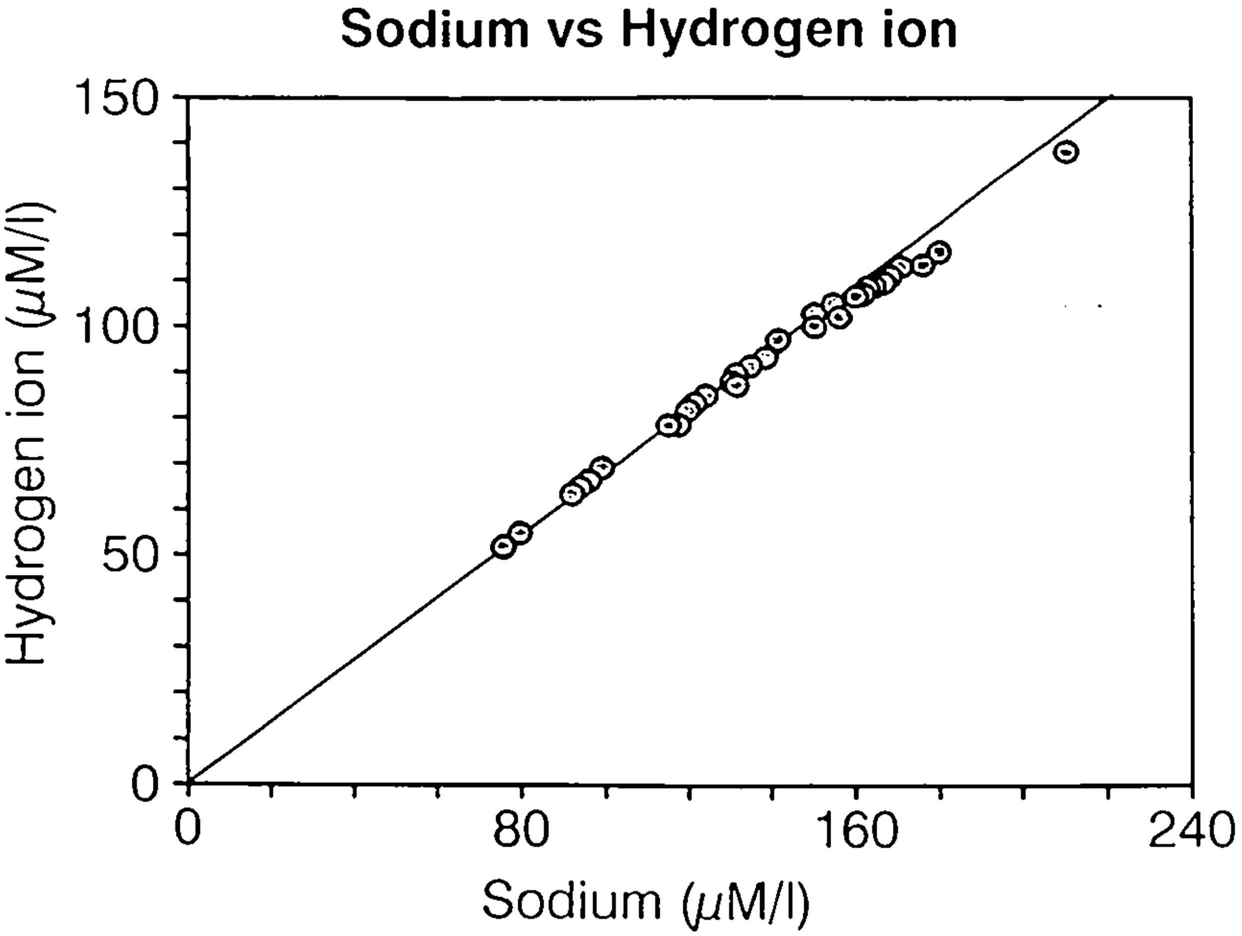
Sodium vs Hydrogen ion
150
100
50
0
Hydrogen ion (μM/l)
0
80
160
240
Sodium (μM/l)

Fig 1a

Sodium vs Calcium

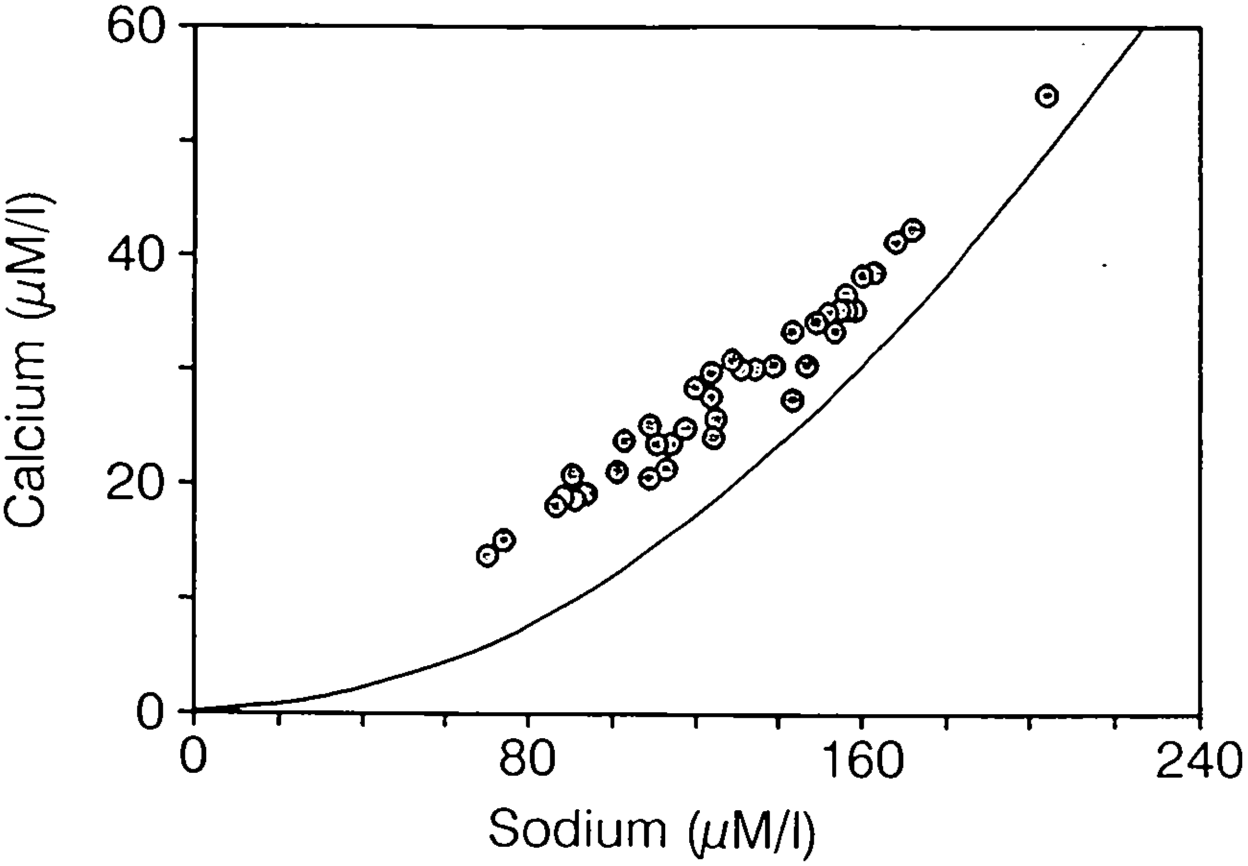

Fig 16

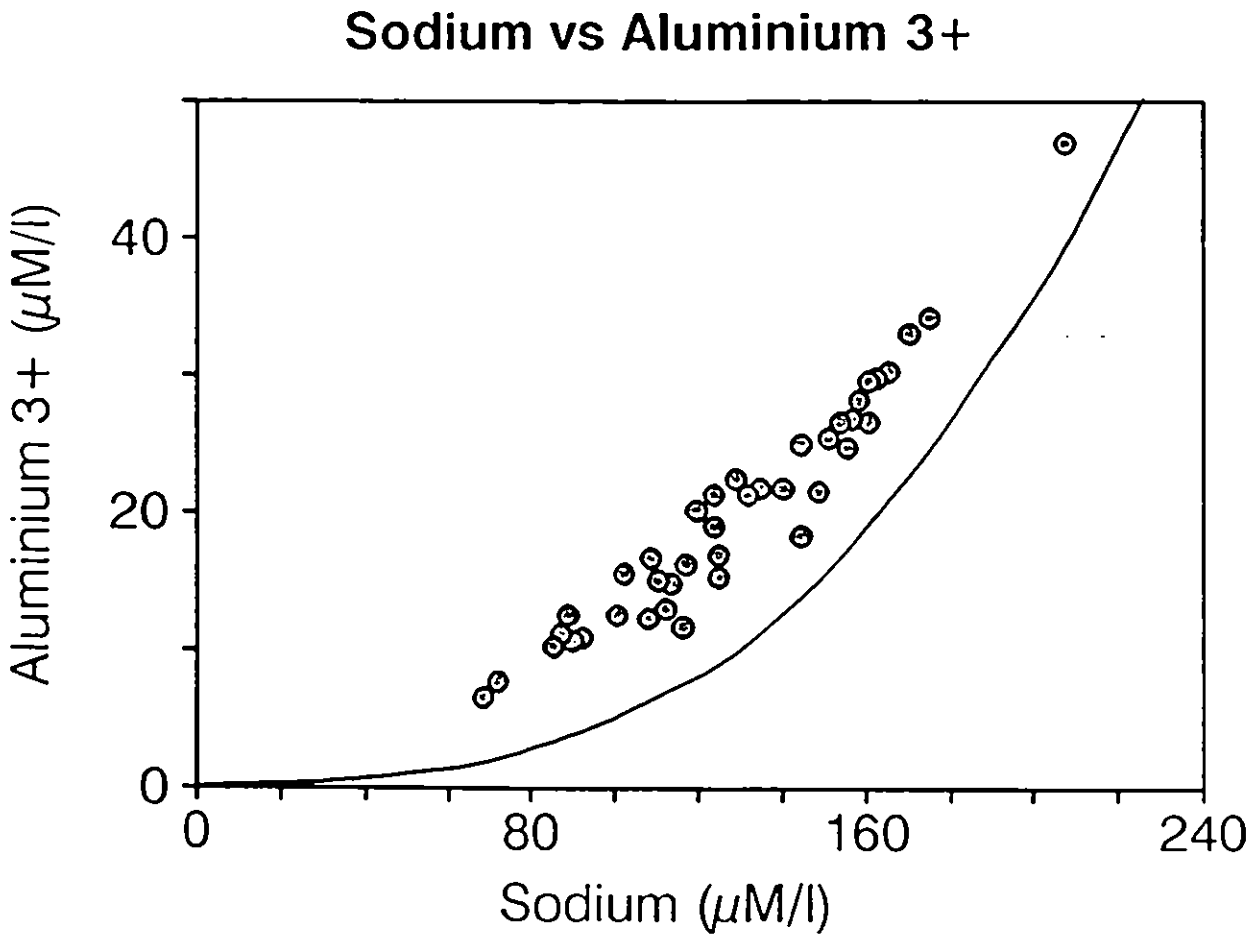
Sodium vs Aluminium 3+
Aluminium 3+ (μM/l)
0
20
40
0
80
160
240
Sodium (μM/l)

Fig 1C

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