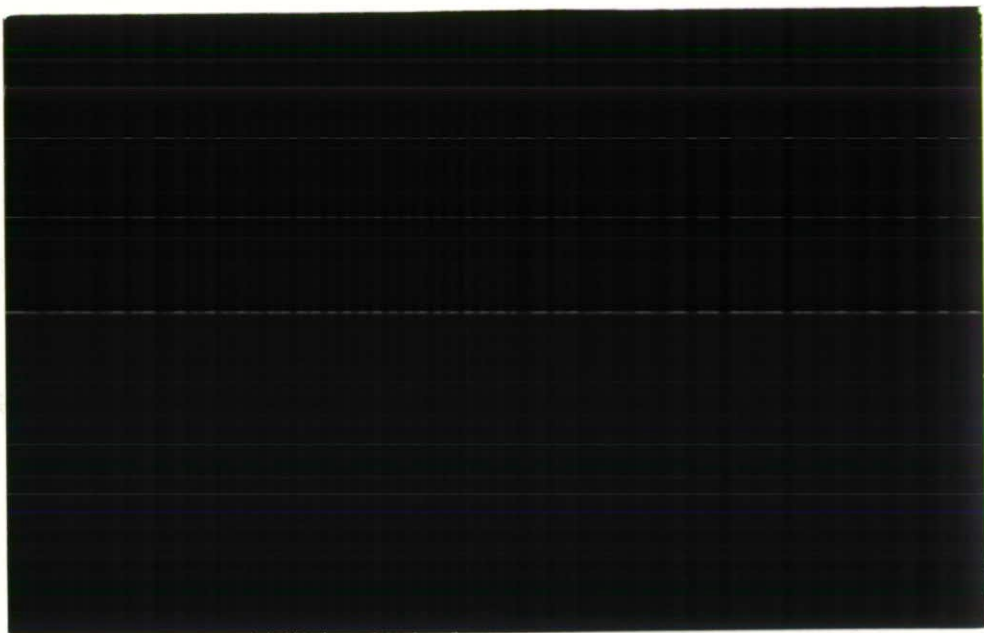




Institute of
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41022



CRITICAL LOADS

**Report to Department of the Environment
(IH Contribution to Study)**

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IH Project T04065N1
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8. Modelling Chemical Responses

8.1. Dynamic v Steady State Modelling

Two methods have been advanced for the calculation of critical loads for surface water, namely: steady state empirical and steady state mass balance techniques which are termed the level I approach and dynamic modelling, or level II approach. The steady state water chemistry (Henriksen) method, based on an empirically derived long term weathering rate for a site, is time independent and assumes steady state conditions. The time scale over which the new equilibrium at the biologically relevant chemistry will be achieved is irrelevant to the calculation. Clearly, this assumes that the rate of recovery at a site is unimportant, even over very long time frames (> 100 yrs) and, more crucially, that the site is not only capable of recovering to the biologically relevant chemistry level but also that prior to the onset of acidification the water chemistry was equivalent to or less acidic than the biologically relevant chemistry. Furthermore, the influence of the catchment soils, in particular their ability to adsorb and desorb ions through time, is only implicitly included in the empirical model which assumes that in the very long, or equilibrium, timescale the soil acidification process is completely reversible. Soil chemical processes may mitigate or delay acidification through sulphate adsorption and base cation exchange or extend the acidification effect after acidic deposition is reduced, through soil recovery processes whereby base cations are adsorbed and sulphate is desorbed.

Dynamic models, on the other hand, specifically account for changes through time such as the depletion of element pools in soils and changes in catchment land use. The long-term, process-oriented, hydrochemical model MAGIC (Model of Acidification of Groundwaters In Catchments) has been the main tool utilised for level II analysis within the framework of the UK freshwaters critical loads exercise. The model has been used primarily to address a number of time related questions in terms of future recovery of acidified waters, namely; (i) to identify the regional characteristics that determine critical and target loads; (ii) to determine the time dimension between achieving critical loads and ecosystem recovery; (iii) to determine the consequences, in terms of surface water, of not achieving a critical load; (iv) to examine the effect of land use

change, in particular forestry practice, on critical loads, and; (v) to determine the interaction between nitrogen and sulphur in the context of critical loads for total acidic deposition.

The real strength of these dynamic model applications in an applied sense within the framework of Integrated Assessment Modelling and emissions reduction negotiations, however, is in answering key policy questions such as; what degree, in time and space, of soil and water recovery can we expect from a given emissions reduction strategy ? and; what level of emissions reduction is necessary to achieve a given level of soil and water recovery within a given time scale ?

8.2. MAGIC and critical/target load calculation

MAGIC is a process oriented, physically based, lumped catchment model in which several key chemical processes are assumed to control responses of surface water chemistry to acidic deposition. MAGIC is based on mathematical representations of; anion retention by catchment soils (eg. sulphate adsorption); adsorption and exchange of base cations and aluminium by soils; alkalinity generation by dissociation of carbonic acid with subsequent exchange of hydrogen ions for base cations, and; control of inorganic aluminium concentrations through an assumed equilibrium with a solid phase of aluminium hydroxide. MAGIC uses these process approximations within a framework of; a set of equations which quantitatively describe the equilibrium soil processes and the chemical changes that occur as soil water enters the stream channel; a set of mass balance equations which quantitatively describe the catchment input-output relationships for base cations and strong acid anions in precipitation and streamwater, and; a set of definitions which relate the variables in the equilibrium equations to the variables in the mass equations.

MAGIC can be used to estimate critical loads by determining a time at which the defined critical water/soil chemistry is to be achieved. Since the "true" definition of critical loads is time independent and assumes equilibrium conditions in the future, the loads calculated using MAGIC should be assumed to represent target loads although this term has a political

interpretation and so the term critical load is retained. To estimate critical loads the model is calibrated to a catchment using available soil and water chemistry and land use data. The model is then used in predictive mode to determine the sulphur deposition required to achieve some pre-defined critical chemistry in soil or surface water at some pre-defined time in the future. Here, this critical chemistry is taken as surface water alkalinity of zero and soil water Ca/Al molar ratio of 1.5, although in practice a critical load can be determined on any chemical parameter in the soil-water system. The time scale used in the UK exercise is taken as 50 years as this is the most appropriate timescale over which deposition reductions and critical chemistry should be achievable. Again, in practice, any timescale can be chosen. The level of deposition required is assumed to be reached immediately and held constant at that level for 50 years. Clearly, this represents a best case scenario since deposition reductions are not going to be achieved so rapidly. MAGIC is then run repeatedly with different levels of deposition until the critical chemistry is achieved at the selected time in the future. This deposition is assumed to be the critical load for sulphur. For all cases it is assumed that the loading and catchment immobilisation of nitrogen compounds are not changed from present-day conditions.

These concepts are illustrated in a model application to the Allt a Mharcaidh and Round Loch of Glenhead (Figure 8.1). In the Allt a Mharcaidh (Figure 8.1a) current and past sulphur deposition is not sufficient to depress stream alkalinity below zero or raise Al/Ca ratio above 1.5, that is, the critical load is not currently exceeded at this site and so the sulphur deposition is increased in the model to achieve alkalinity zero and thereby quantify the critical load. At the Round Loch of Glenhead (Figure 8.1b) present deposition exceeds the critical load for water and so must be reduced to achieve alkalinity zero, although the soil is not as sensitive. The importance of the time dependency is further emphasised in Figure 8.2. At the Round Loch the critical load of sulphur increases as the timescale by which the critical chemistry is required increases, the maximum being some equilibrium time in the future. At Narrator Brook, an unacidified stream in SW England, the critical load is not currently exceeded and so a very high sulphur load is required to force surface water alkalinity to zero

within 10 years. Conversely, the required load to reach alkalinity zero in 100yrs is lower. This emphasises the point that the total flux of deposited sulphur is more important than the rate at which it is deposited and this has serious implications when planning emissions reduction strategies for the future.

The MAGIC model has been calibrated to 17 of the 22 sites in the UK Acid Waters Monitoring Network (AWMN). Those sites excluded currently lack sufficiently detailed soil chemical data for model calibration. The AWMN sites represent a range of acid impact and sulphur deposition flux across the UK and calculated critical loads are currently exceeded at 7 sites (Figure 8.3). The model reconstructions indicate that the 7 exceedance sites have not historically suffered a greater acidification than those not presently exceeded but started from a lower background alkalinity (Figure 8.3). This ties in with our knowledge of the factors influencing sensitivity to acidic deposition which come together in these areas.

A further modelling exercise has centred on a regional MAGIC model application to 39 lakes in the Galloway region of SW Scotland. The lakes are confined within an area of about 120 km² representing some sixteen 10km squares delineated in the UK freshwater critical loads mapping exercise. This area has been identified as having a large proportion of acidified surface waters following decades of acidic deposition. Many of the lakes and streams are susceptible to acidic deposition because of the relatively slow weathering and low acid neutralisation capacity of the bedrock, thin and acidic soils and extensive afforestation. Other freshwater in the area, lying predominantly on less sensitive geology, have a high positive alkalinity and are not currently acidified. This wide range of sensitivity to acidic deposition, with respect to both soils and waters, presents considerable problems for quantifying regional critical and target loads. To address this issue, data from these lakes, sampled in 1979 and again in 1988, was used in conjunction with detailed soil data obtained from the Macaulay Land Use Research Institute (MLURI) and forest management history from the Forestry Commission, to formulate a regional MAGIC application.

8.3. Comparison of Approaches

The comparison of empirical and MAGIC techniques for calculating critical loads demonstrate the differences between the dynamic and equilibrium assumptions utilised in the two methods (Figure 8.4). Across a wide range of critical loads, ranging from sensitive to extremely insensitive, differences mainly occur at the least sensitive sites (i.e. high critical loads) where the MAGIC critical load is generally higher than the Henriksen empirical critical load whilst at the most sensitive end of the range (i.e. low critical loads) the opposite is true. The less sensitive sites are characterised by well buffered water chemistry with high pH and alkalinity, influenced by soils which have retained a high acid buffering capacity. To deplete this soil store of base cations will either take many years of acid deposition at a relatively low sulphur loading, that is, as described by the equilibrium concept assumed in the empirical critical load, or fifty years of a higher critical load, that is, as described by MAGIC. Sensitive sites are characterised by low pH and low, or in many cases negative, alkalinity and have soils with low base saturation and a large adsorbed sulphate pool. At these sites the MAGIC critical load is lower than the empirical critical load. This results from the fact that the empirical approach assumes equilibrium conditions and an indefinite timescale for recovery and the dynamic modelling approach assumes a finite (50 yr) time scale. The MAGIC critical load tends to be lower, therefore, since these systems require longer than fifty years to recover and the base cation store in the catchment soils which have been depleted due to many years of acidic deposition and forest growth, must be replenished by weathering inputs before recovery can occur. This is further illustrated in Figure 8.5(a) which shows a comparison of critical loads calculated from the two techniques for the 39 lakes in Galloway. At sites which are not presently acidified no significant soil recovery occurs and MAGIC critical loads tend to be higher than the empirical calculations at these sites. It must also be remembered that the critical load estimated using MAGIC represents the change in deposition flux which must be made immediately to achieve zero alkalinity and so must be regarded as a best-case since sulphur deposition is more likely to be reduced gradually over a long time period. The implication for this region is that even if a low critical load (around $20 \text{ meq m}^{-2} \text{ yr}^{-1}$) is set some 40% of the surface waters in the region will not have achieved zero alkalinity within fifty years

(Figure 8.5b).

The question of uncertainty in critical load calculation is difficult to address since much of the variance in surface water chemistry at a site is due to changing flow regime, and in particular, the chemical changes associated with high flows. It must be remembered that the MAGIC model simulates only mean annual chemistry and takes no account of these flow-chemistry relationships. Uncertainty can be introduced into the model simulations, however, by incorporating known measurement errors and spatial variability in the parameters within the catchment at the calibration stage. In this way, uncertainty bands for the model simulations can be presented as maximum and minimum values for output variables, including critical loads (Figure 8.6). A range of critical loads can also be calculated empirically for samples collected across a wide range of flows. The ranges calculated from the two techniques demonstrate a good match (Figure 8.6) although these representations of uncertainty have little statistical or chemical significance and further work is necessary, particularly to assess the importance of episodes to biological response and to relate the mean chemistry to extreme events.

The relationship between soil critical loads calculated using MAGIC and the empirical Skokloster soil critical load sensitivity classification is poor (Figure 8.7). The Skokloster classification is primarily based on weathering and the ability of soils to provide acid buffering. In this application soils in the least sensitive class (critical load $> 200 \text{ meq m}^{-2} \text{ yr}^{-1}$) are set critical loads of $200 \text{ meq m}^{-2} \text{ yr}^{-1}$ thereby potentially causing an artificial lowering of the critical load classification for many catchments where base rich soils dominate. Nevertheless, even for the more sensitive classes the relationship is poor. MAGIC critical loads, on the other hand, are expected to be higher since a large soil calcium pool exists which would have to be depleted to reach the specified Al/Ca ratio. Furthermore, the Skokloster critical load classification is taken to represent only the top layers of the soil profile whereas MAGIC aggregates the chemistry of the entire soil profile. A two soil layer version of MAGIC is currently being applied to a number of the AWMN sites which show soil and water exceedences. Only the chemistry

of the upper box will be assessed for calculating the soil critical load and this is expected to substantially reduce the MAGIC critical load and lead to closer agreement with the Skokloster soil sensitivity classification.

8.4. Assessment of Future Emissions Reduction Scenarios

At the 7 AWMN exceedance sites, the surface water chemistry impact of two future emissions reduction scenarios have been assessed: (i) the Large Combustion Plant Directive (LCPD) emission strategy which calls for a 60% reduction in emissions by 2005 and it is further assumed that emissions are held constant, thereafter, until 2039, and; (ii) a more optimistic emissions reduction strategy involving an 80% decrease by 2005. Deposition data, in response to these emissions scenarios were obtained from the atmospheric transport model based at the University of Hull.

Taking positive alkalinity to generally represent a biological threshold, or critical chemistry, the model predictions for 2005 and 2039, compared to present day observations, show a consistent picture (Figure 8.8). The reduction in sulphur deposition to these catchments in response to the LCPD emissions reduction strategy (Figure 8.8a) is not sufficient to significantly improve the water chemistry status of these acid impacted sites. At the Round Loch of Glenhead (SW Scotland) the LCPD scenario is just sufficient to achieve an alkalinity of zero by 2039. At Llyn Llagi (N. Wales), the deposition reduction is too small to even halt the decrease in alkalinity which becomes negative by 2039. At Scoat Tarn (Lake District), on the other hand, the alkalinity increases in response to the decrease in deposition to 2005 but this is only temporary and a further decline to beyond the present day level occurs. The deposition reduction predicted from the LCPD is clearly not sufficient at Old Lodge (South Downs) and extreme acidification continues throughout the simulation period. Simulations for Afon Hafren (mid Wales) and Loch Grannoch (SW Scotland) are similarly pessimistic but are complicated by land use factors which are discussed in section 8.5.

The model results for the 80% emissions reduction scenario indicate a stabilising alkalinity

concentrations at present day levels, with some slight improvement at others (Figure 8.8b). This is a pessimistic picture in terms of recovery since it is unlikely that greater emissions reductions can be achieved.

Simulation of water chemistry using the regional model applied in Galloway suggest that acidified waters with negative alkalinities in the region will recover only marginally in response to the emissions scenarios by the year 2005 (Figure 8.9) and the total percentage of lakes with negative alkalinity (Figure 8.9a) and pH 5.0 (Figure 8.9b) will remain roughly the same. The location of these lake sites which require a much more dramatic decrease in emissions is mainly determined by the spatial extent of the underlying granitic geology.

8.5. Impact of Afforestation

Future land use policy within a catchment is another important factor in determining the rate of recovery of acidified soils and water in response to emissions reductions. In this respect, the role of trees in the critical loads concept requires careful consideration. As well as being sensitive receptors for which critical loads need to be determined, they play a crucial role in the soil and water acidification process by uptake of base cations during their growth, changing hydrological behaviour of the catchment especially by decreasing water outflux, and by filtering pollutants from the atmosphere thereby increasing the total deposition loading. No account is taken in this exercise of the input of base cations and nutrients during the life of the forest, for example dressing with calcium phosphate.

The model application at Loch Grannoch (SW Scotland) shows the more complicated situation which occurs when considering the issue of future afforestation policy (Figure 8.10). In general, two extreme future land use scenarios are possible: forest felled and replanted immediately and forest felled with no replanting. The latter option produces the best prediction of water chemistry recovery irrespective of the future emissions strategy employed. Clearly, the calculation of critical loads for soil and freshwater in areas where plantation forestry is a major land-use require that these impacts be considered. It is ironic that the areas where commercial

afforestation is presently concentrated in the UK largely coincide with the acid sensitive upland terrain which receives high sulphur loads in exceedance of calculated soil and water critical loads. These results underline the need to take land management into consideration in association with sulphur emission reduction strategies.

For the 39 lakes in Galloway, critical loads have been calculated under three afforestation scenarios in an attempt to quantify the forest effect (Figure 8.11). The base scenario represents the best estimate of critical load for a catchment assuming that the area of forest remains constant in the future and is harvested and replanted at 50 year interval. Critical loads calculated under this scenario are compared with those calculated under two further land use strategies. One assumes that all remaining land of forestry class 4, 5 and 6 is also planted to provide a maximum afforestation scenario. An alternative assumes that as existing forest stands reach 50 years age they are felled and not replanted to provide a minimum forestry scenario whereby within the 50 year time frame of the target load calculation, only moorland remains. The results clearly demonstrate that an increase in afforested area decreases critical loads for both soil and water and vice versa (Figure 8.11).

8.6. Impact of Nitrogen

A further development of the dynamic modelling approach is now underway to enable an assessment of the influence of nitrogen dynamics in the context of critical loads for total acidity and given the present and future commitments to nitrogen emissions protocols. In general terms increased nitrate leaching from a catchment may occur as a result of increased nitrogen deposition, decreased plant uptake of nitrate (perhaps due to sulphur induced stress on the organisms), or through a change in climatic conditions leading to increased mineralisation of nitrogen in the soil. As a "mobile anion" it is clear that if the nitrate concentration increases in surface waters, without any concomitant decrease in sulphur concentrations, the total anion load will increase with a resulting decreased pH and decreased alkalinity. Taking this argument forward to critical loads it is inappropriate that critical loads for sulphur and nitrogen are considered independently since the level of any one cannot be set

without consideration of the other. Although nitrogen is dealt with in an extremely simplified manner in MAGIC, uptake being modelled as first order functions, the model can be used to illustrate the influence of nitrogen dynamics in calculating target loads for sulphur. The model indicates that a "trade off" between the two critical loads, that is, lower sulphur deposition is required to maintain alkalinity zero in the light of increased surface water nitrate concentrations (Figure 8.12). It remains a task for the future to develop a long term dynamic model for nitrogen which incorporates the major processes controlling catchment nitrate leaching and coupled to the existing sulphur model so that surface water chemistry predictions can be made in response to a range of total acidity emissions reduction strategies.

8.7. Summary of the Level II Approach

The dynamic modelling analysis indicates that recovery depends on the timescale over which the emissions reductions are made. It is also clear that whilst the critical load may be achieved at a given site within a given time frame, the water chemistry may at that time still be unsuitable for aquatic organisms because of the inherent time lags in the catchment system which slow the rate of recovery of surface water chemistry. In this respect, the model reinforces the fact that the inherent neutralising ability of a catchment (weathering and ion exchange) determines the degree and rate of reversibility of acidification but future land use policy might conspire to modify the time lag between deposition reduction and ecosystem recovery. This has implications for the way in which the critical load exceedance maps for 2005 are interpreted. It is possible that in areas where critical loads are currently exceeded but which are predicted to be 'protected' under an emissions reduction strategy in the future (ie. whereby critical load is achieved), surface water chemistry will not have recovered to the designated biological threshold.

At sites where large (c. 80%) reductions in emissions are not predicted to lead to a substantial recovery in surface water chemistry, the question which should perhaps be addressed is whether other mitigation techniques such as terrestrial source area liming might prove a cost-effective supplement to the emissions reduction programme. Clearly the use of dynamic

acidification models provides an invaluable insight into the environmental effectiveness of proposed sulphur emissions reductions and as such, have a clear role to play within the wider concept of Integrated Assessment Modelling.

The level II analysis shows that it is not possible to calculate a critical load for surface waters without due consideration to the future land use policy within the catchment. Furthermore, specification of a critical load for sulphur in the absence of knowledge of how the nitrogen dynamics within the catchment system might change in the future is inappropriate since employing the model to determine the rate and degree of ecosystem recovery in response to some sulphur emissions reduction strategy demands assumptions regarding controls on nitrogen dynamics in catchments. Such a change in nitrogen cycling may be brought about by land use change and/or increased deposition of nitrogen species. Other environmental factors could also be important, particularly, the potential for changing water flowpaths, soil chemistry status and mineralisation rates associated with long term climate change. It is clear, therefore, that nitrogen and sulphur emissions strategies must be considered simultaneously.

Further development of catchment scale models to explore scenarios relating to potential changes in sulphur and nitrogen driving variables are now required to provide for integrated assessment modelling of total acidity. At the same time, validation of dynamic models using experimental manipulations and long term monitoring data is crucial if policy makers are to be confident of the long term impact of their negotiations

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8.4. Comparison of empirical and MAGIC calculated water critical loads at a range of sites in the UK AWMN.

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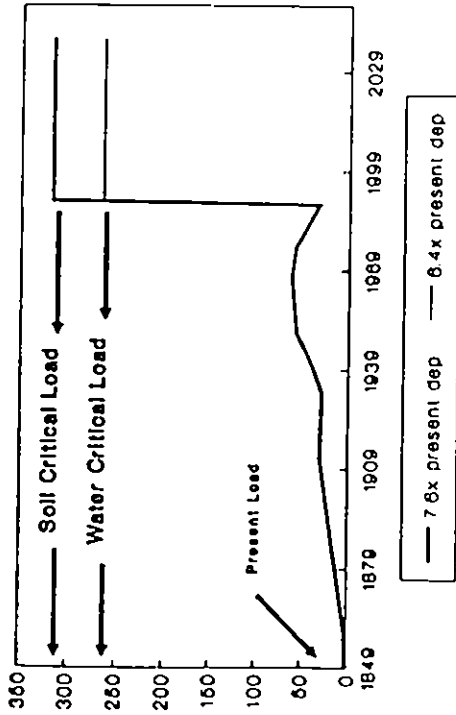
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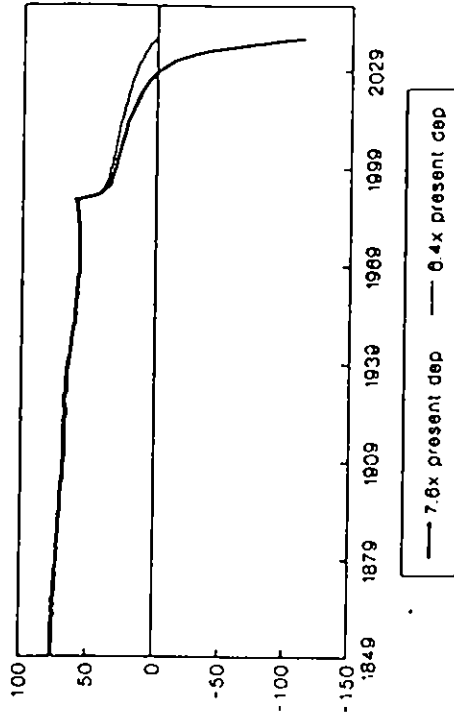
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8.12. MAGIC predictions of critical loads for surface water at the Round Loch of Glenhead based on achieving alkalinity zero by 2039. Presently, NO₃ concentrations in surface waters are low reflecting only direct input to the lake itself (100% immobilisation within the terrestrial catchment) and the present S critical load (1) of c. 105 meq m⁻² yr⁻¹ is calculated under this assumption. If NO₃ deposition increases, SO₄ critical load decreases to maintain zero alkalinity according to the relationship shown as line (2). If NO₃ immobilisation in the terrestrial catchment decreases to 50%, at the present level of NO₃ deposition the S critical load (3) would fall to c. 70 meq m⁻² yr⁻¹ to achieve zero alkalinity and if NO₃ deposition increased further reductions in the S critical load would be necessary in accordance with line (4).

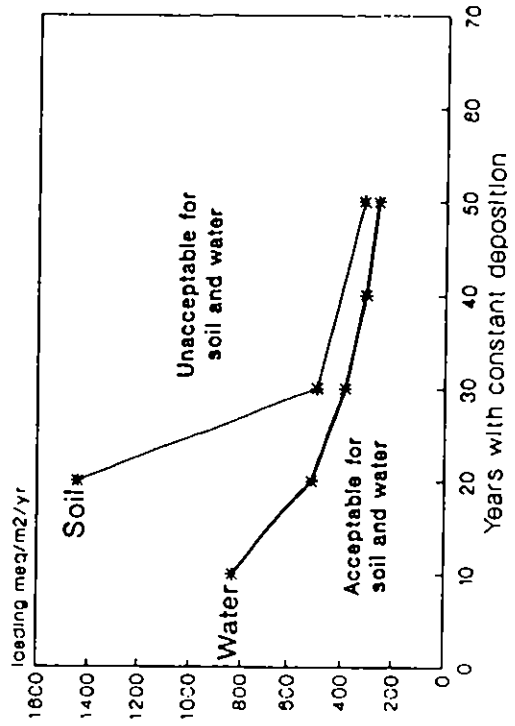
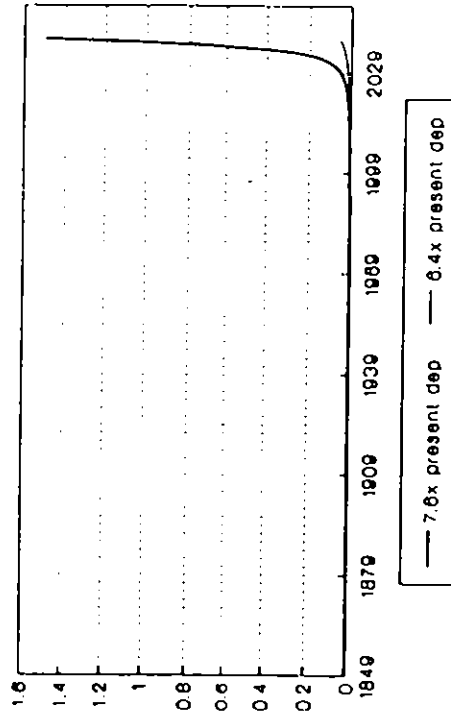
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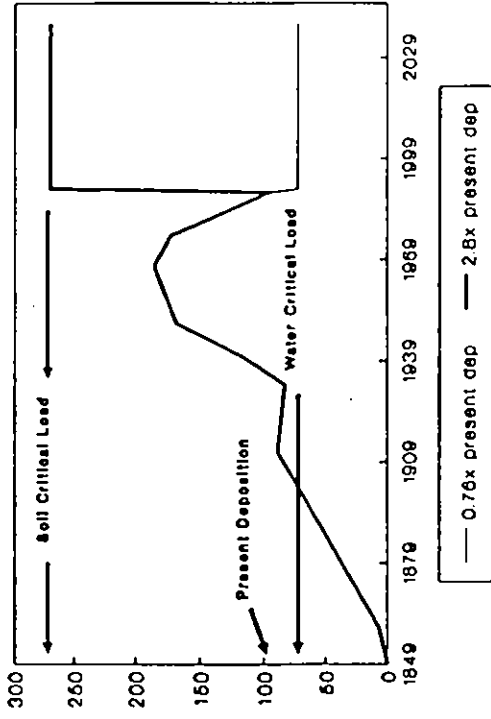
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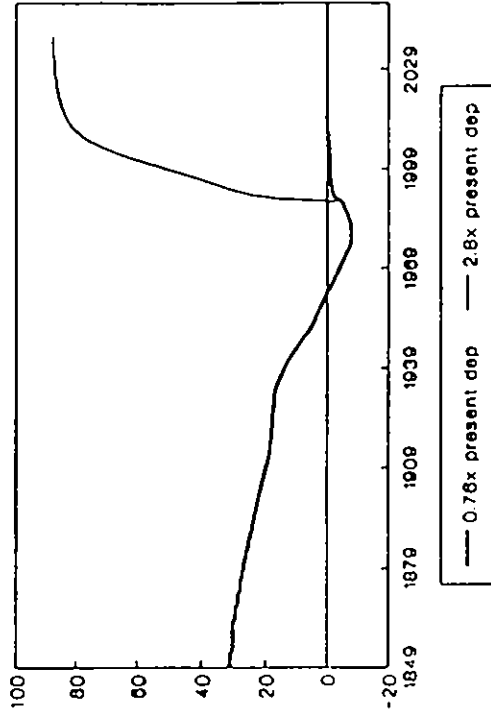
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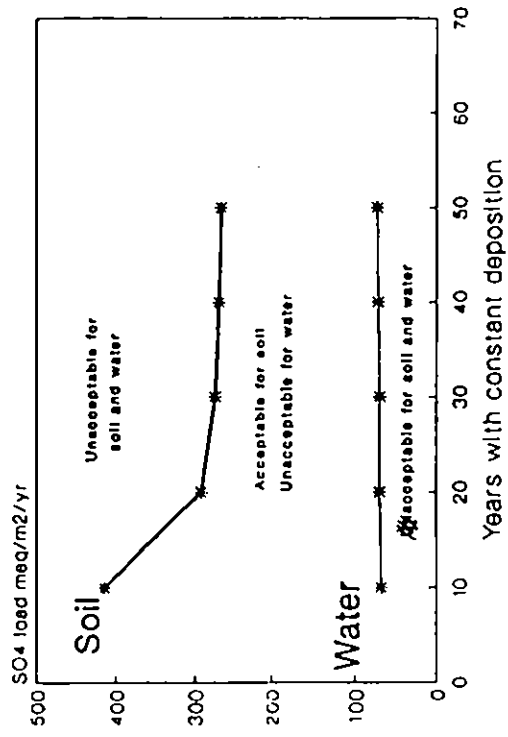
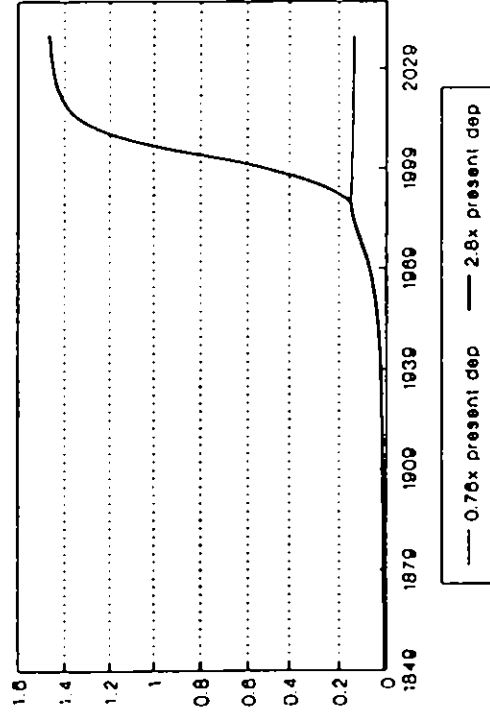
Excess SO4 loading meq/m2/yr



Stream alkalinity ueq/l



Al/Ca soil solution eq/eq



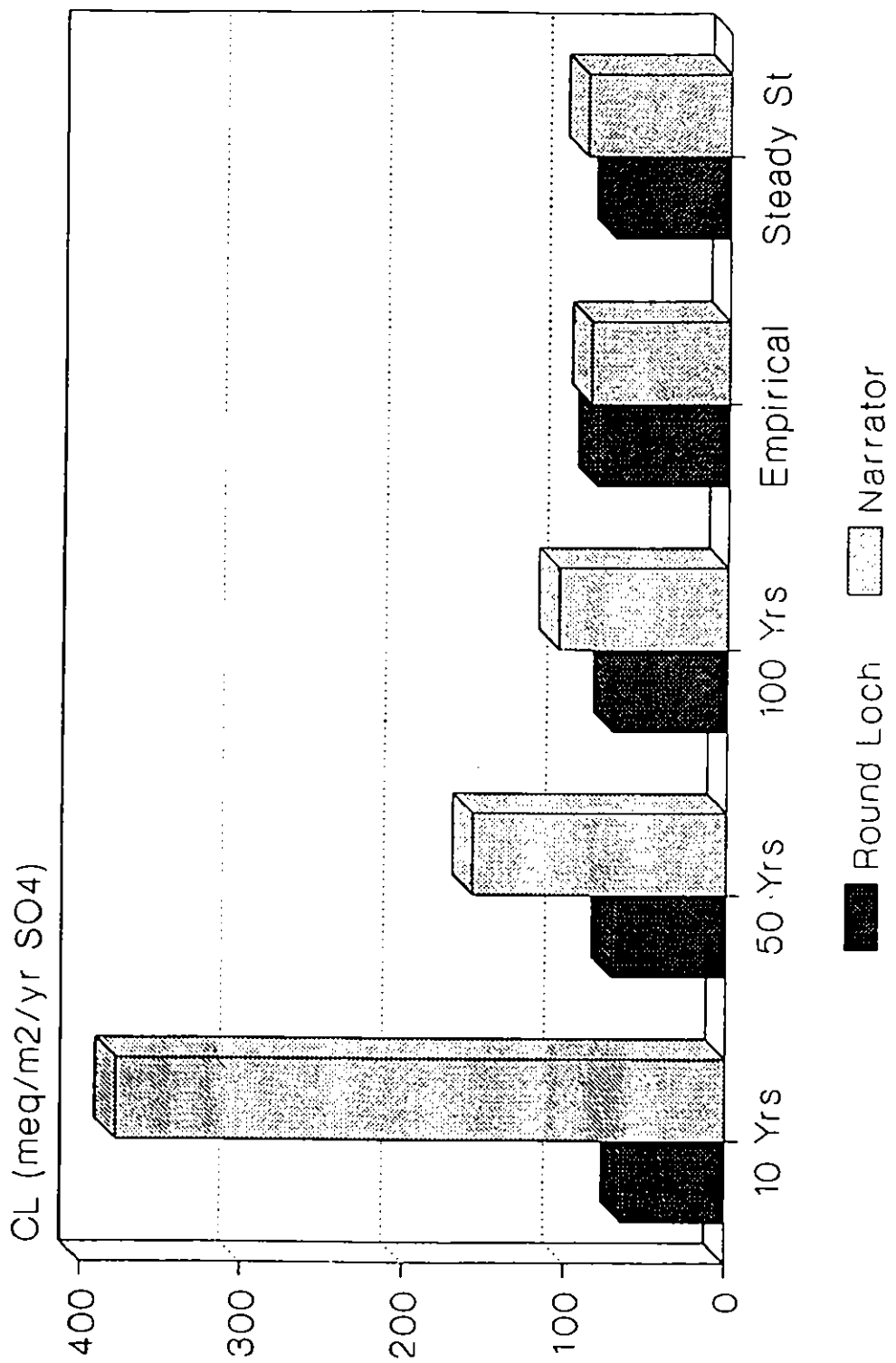
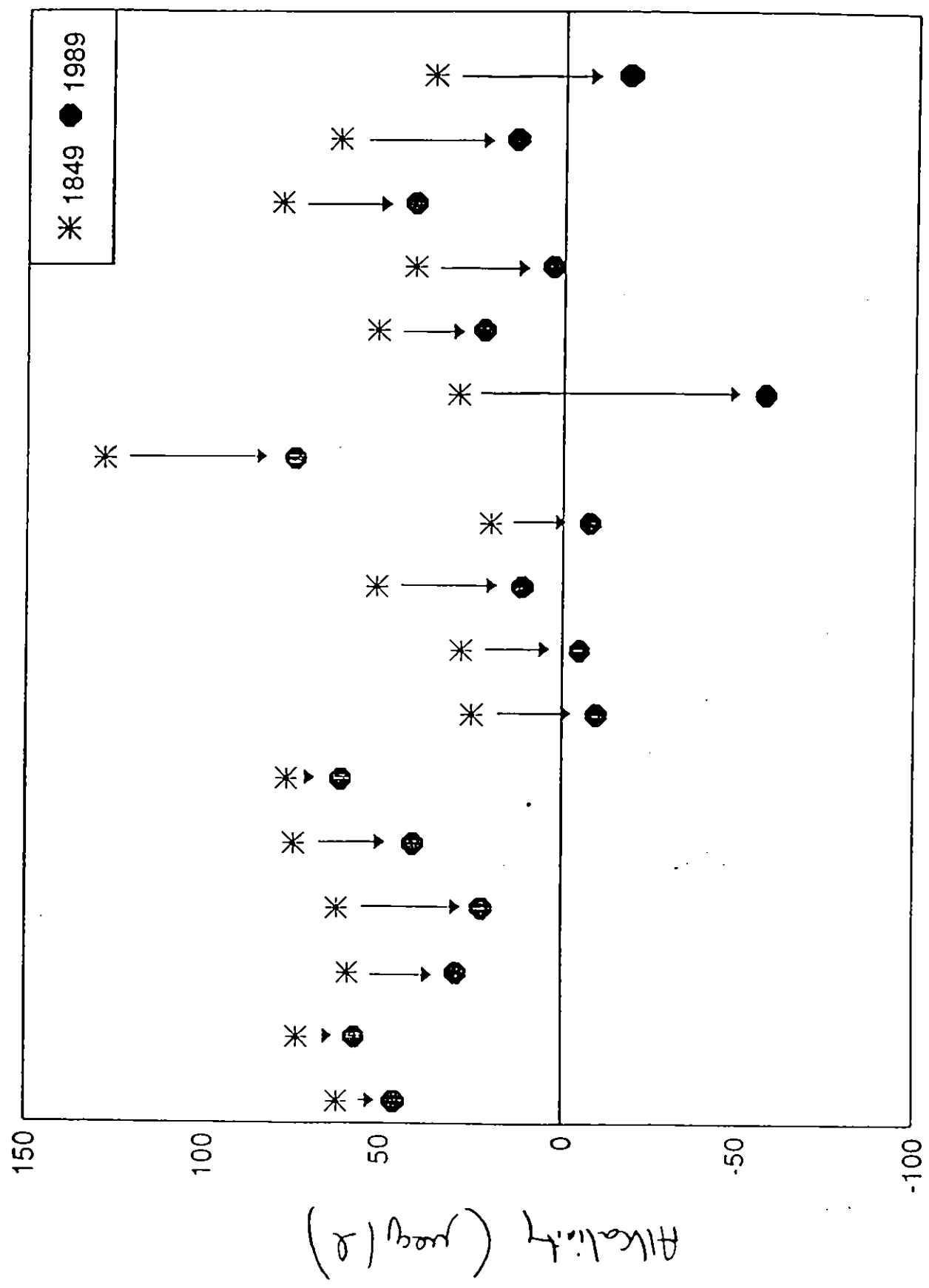
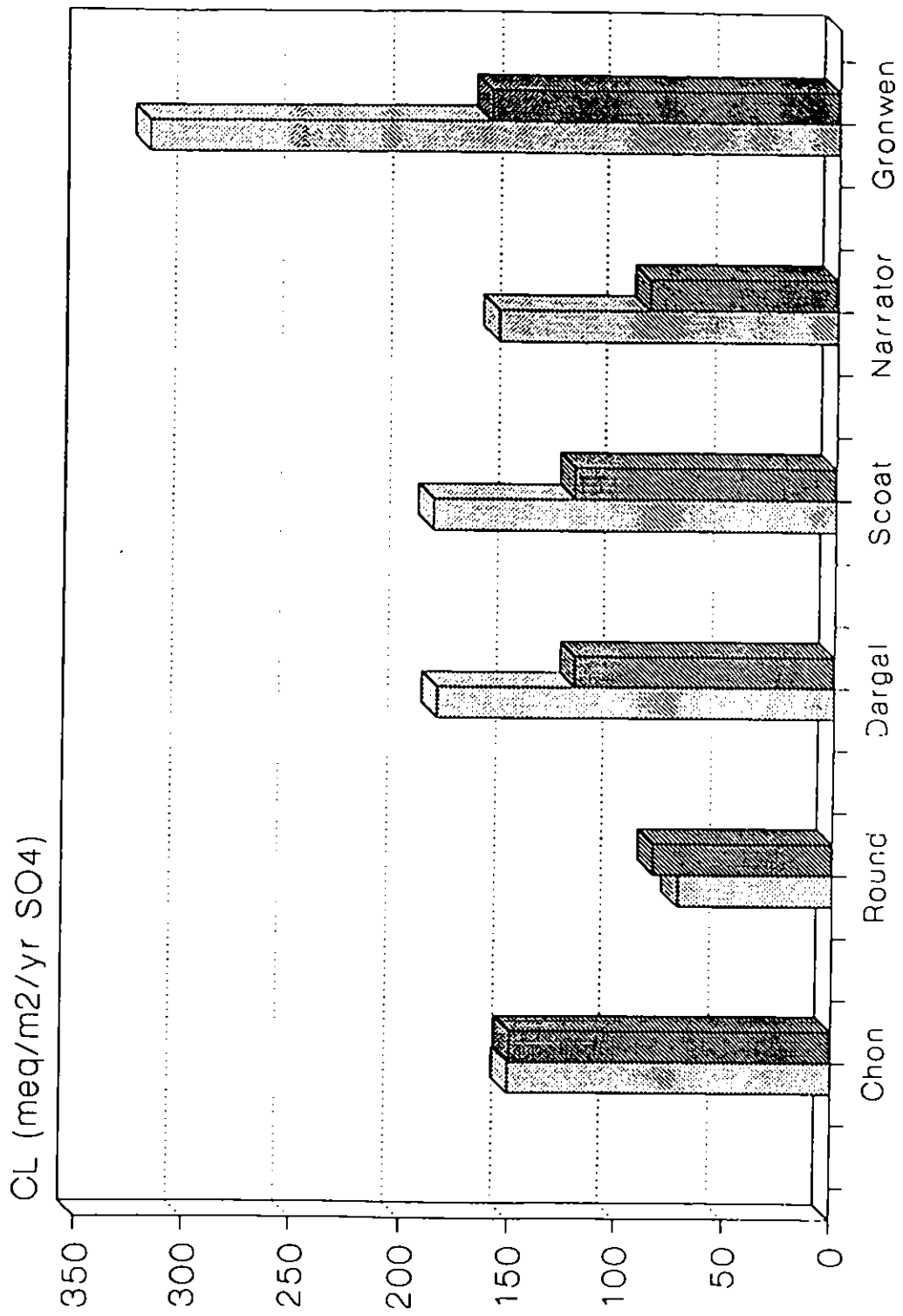


Figure 8.3

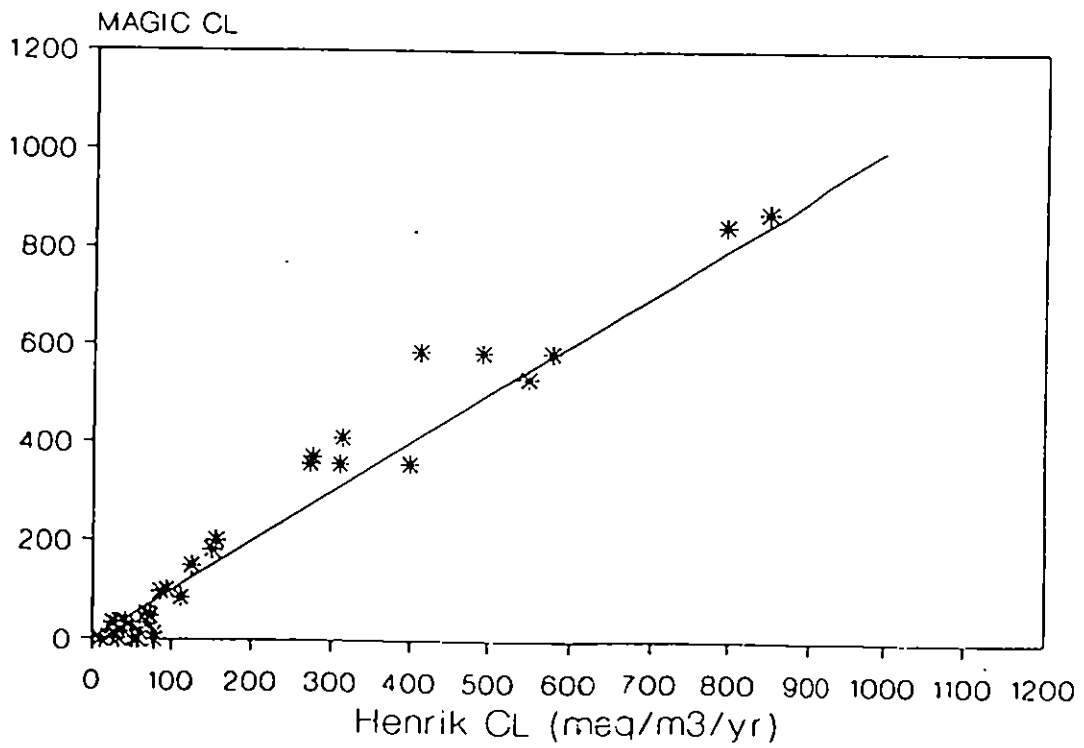
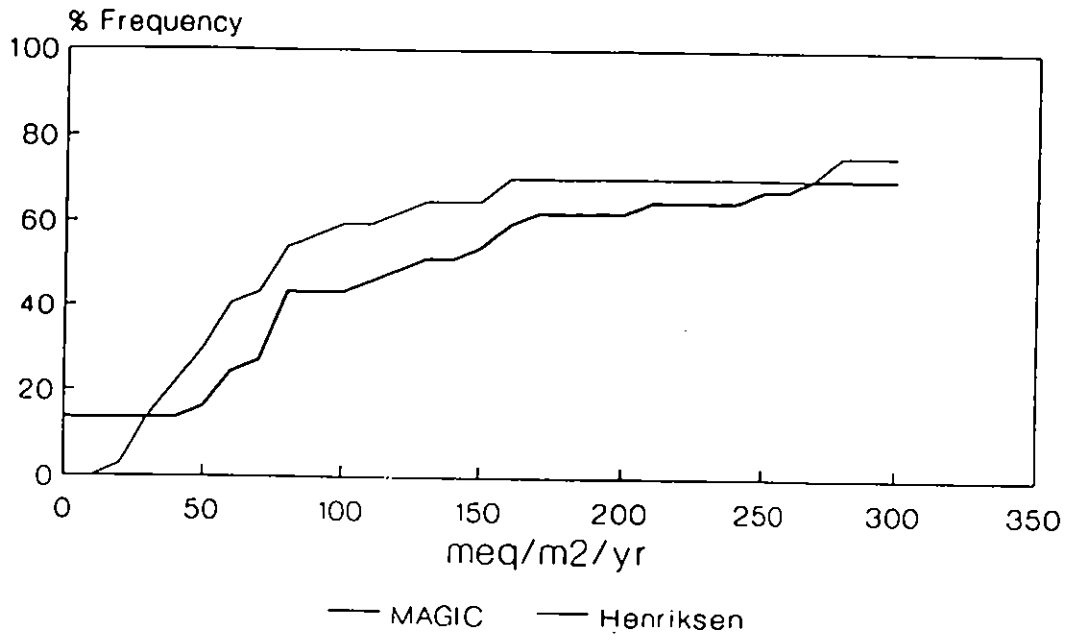


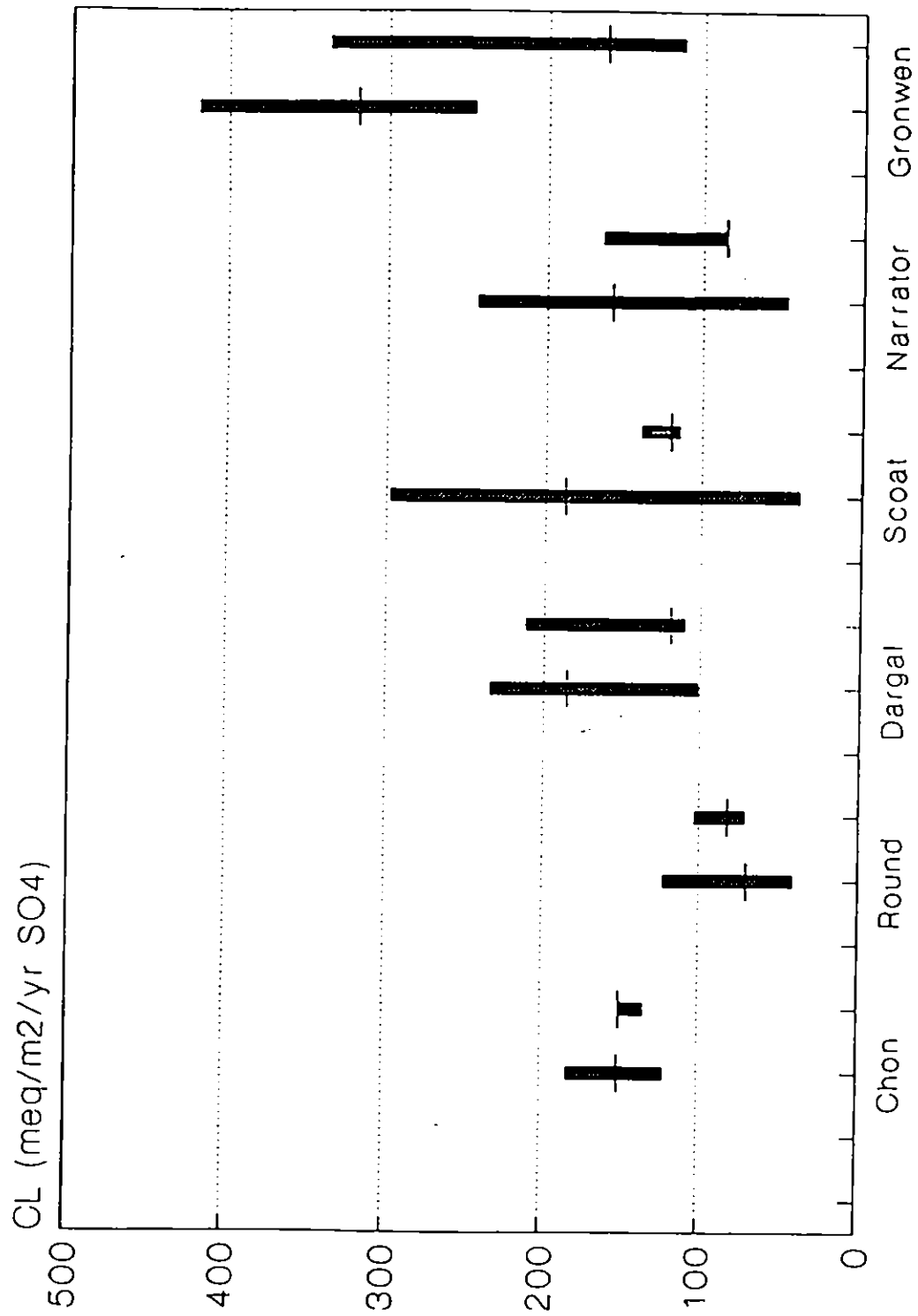
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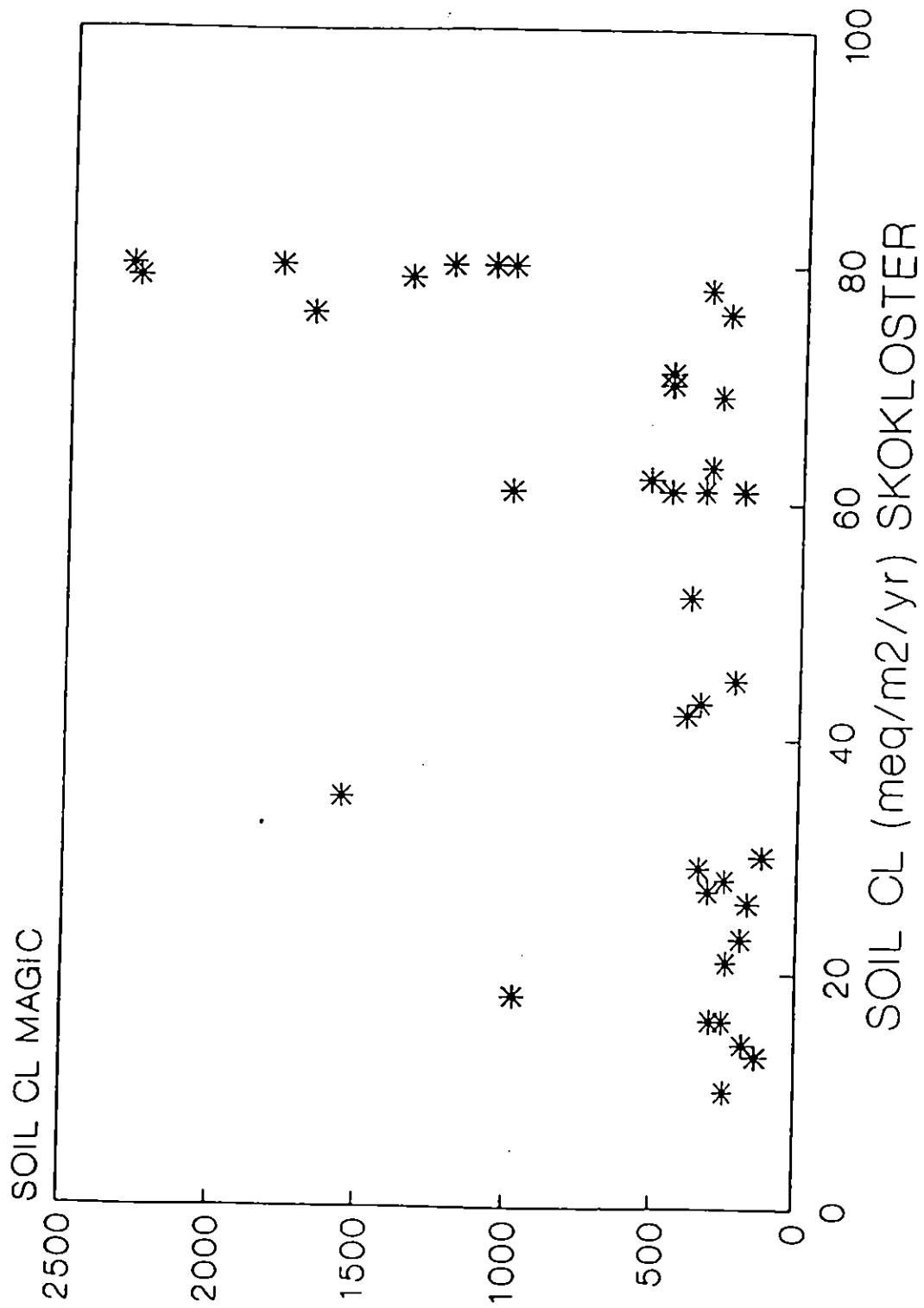


Galloway

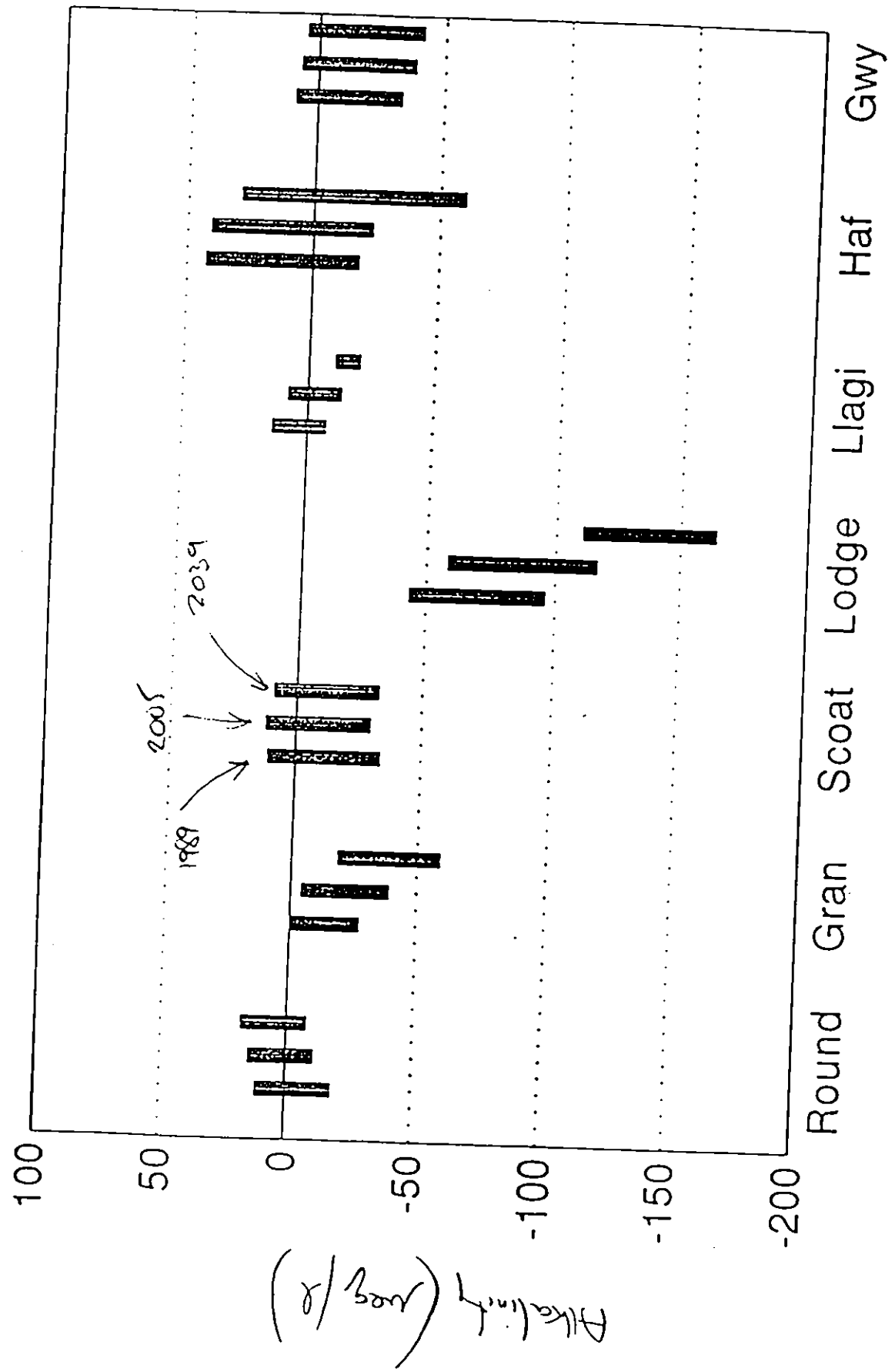
Surface waters survey 1989







60% Emissions Reduction (LCPD)



80% Emissions Reduction

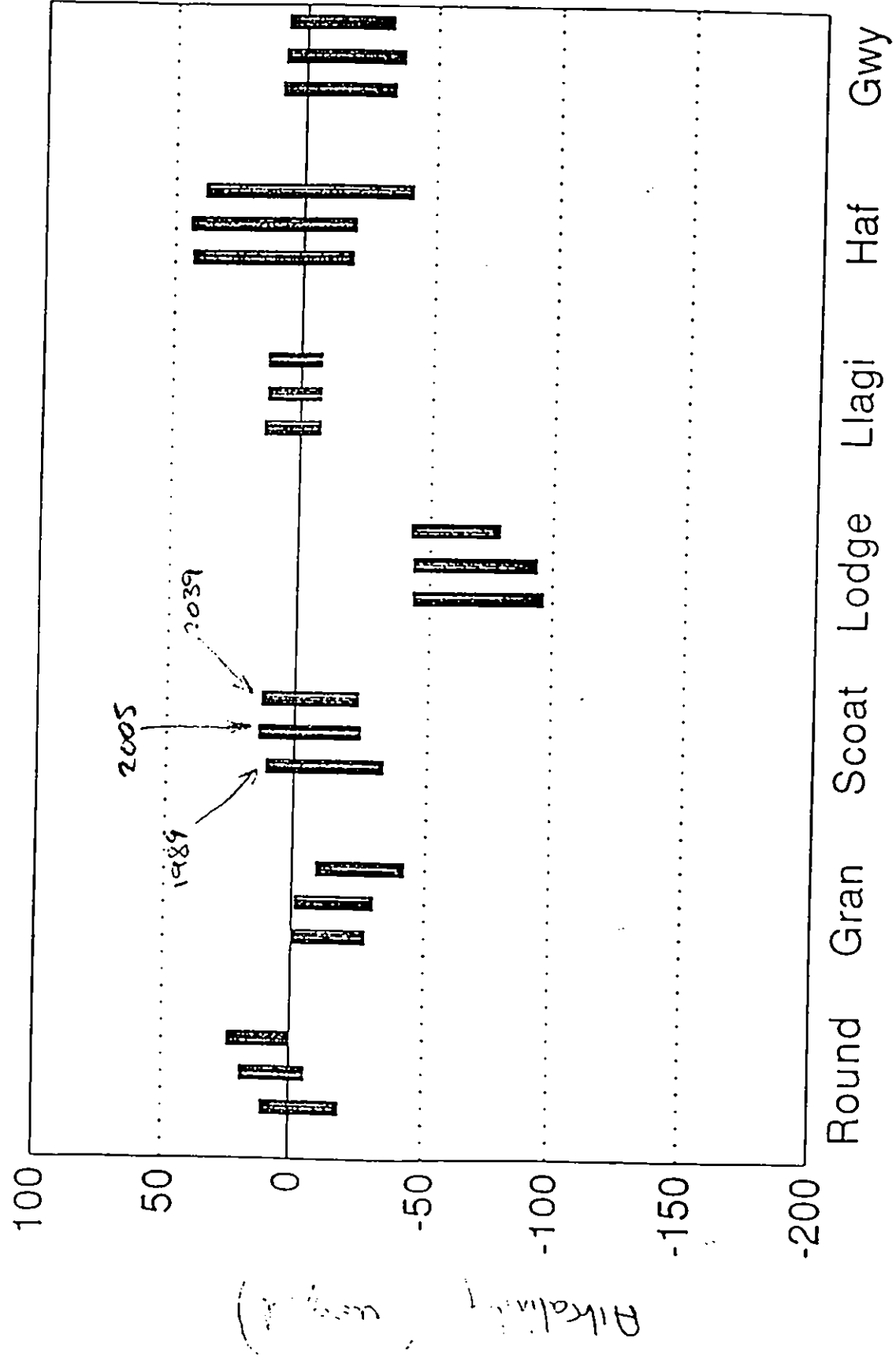
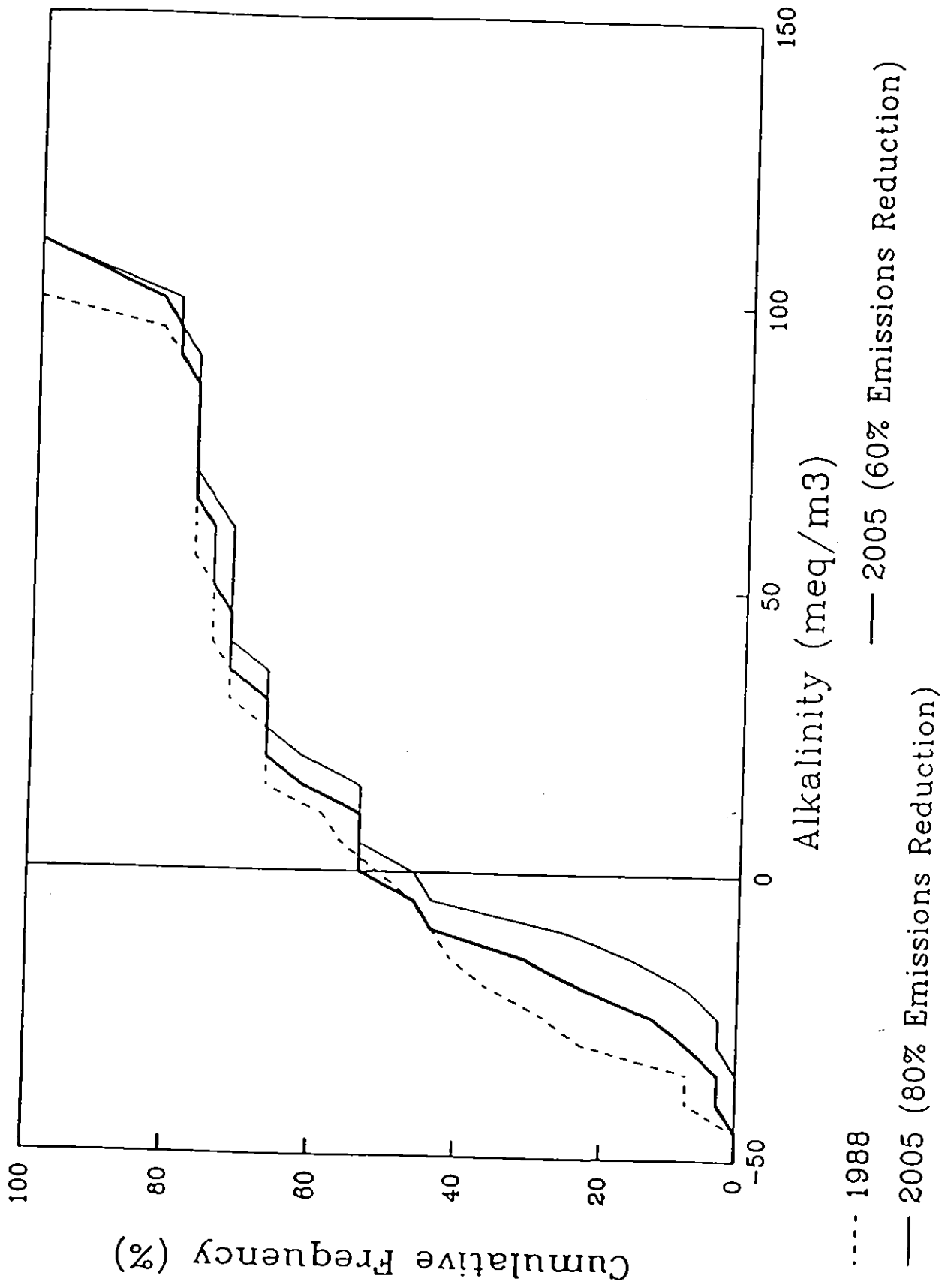
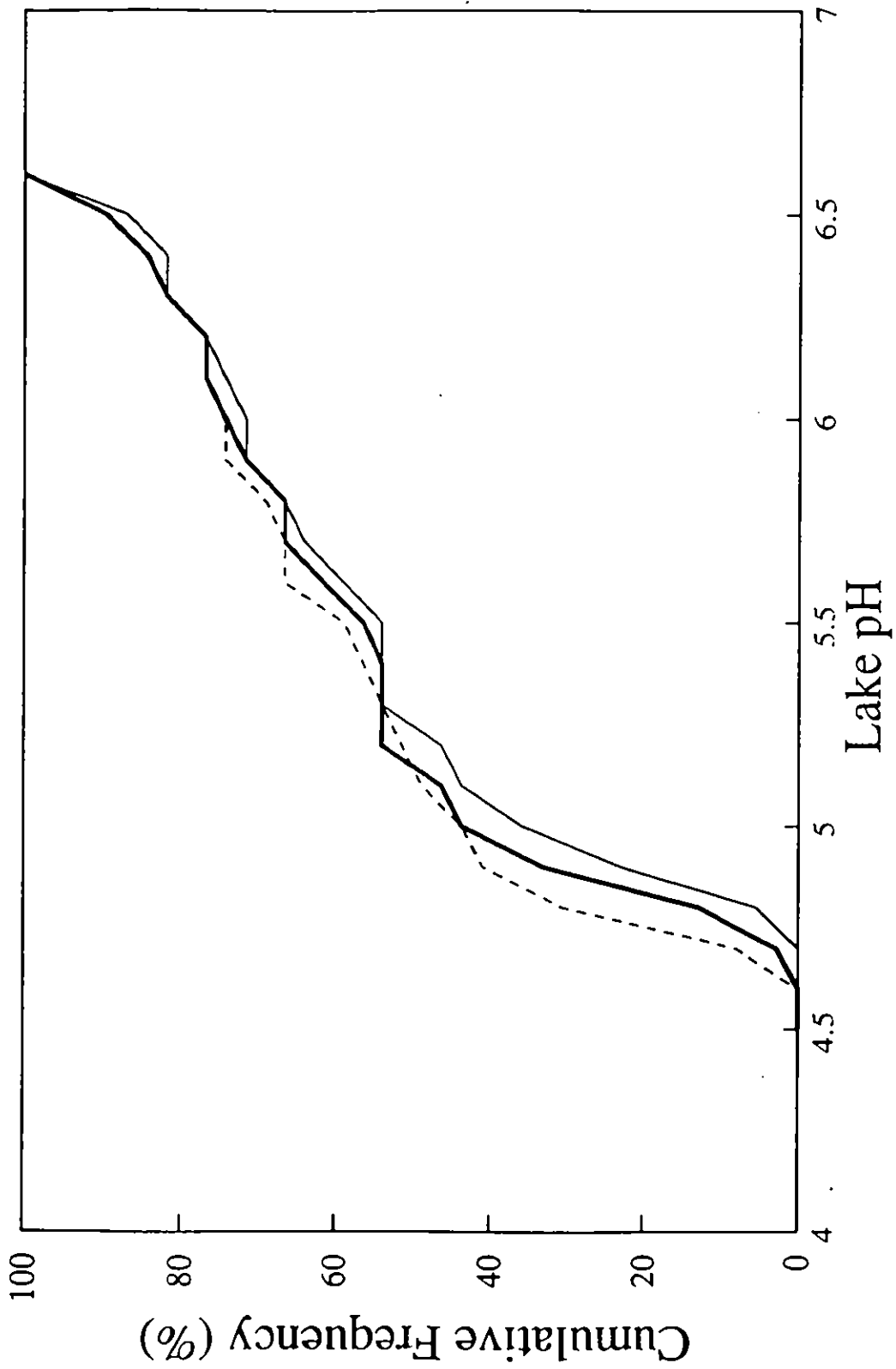


Figure 8.9 (a)

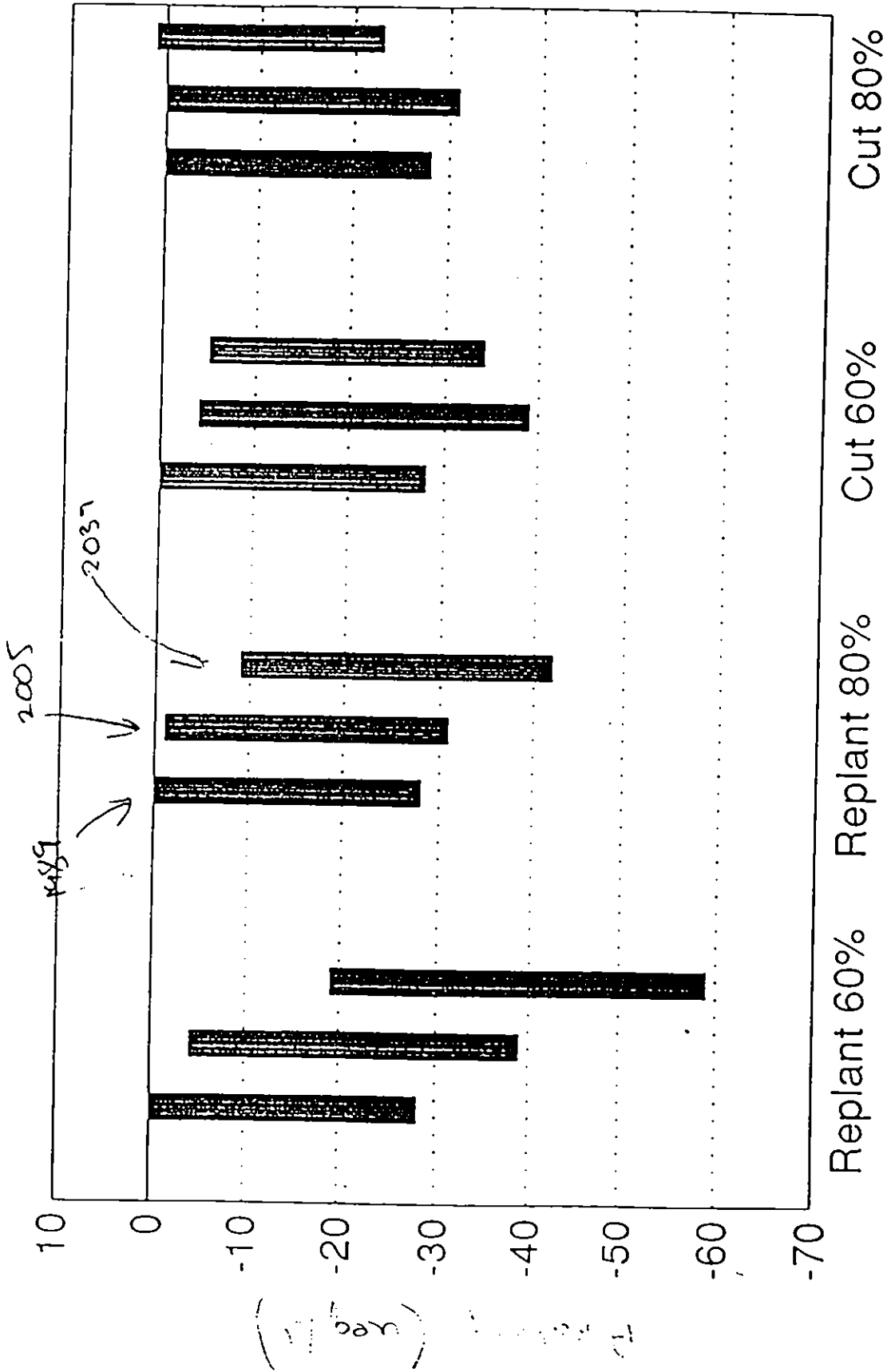




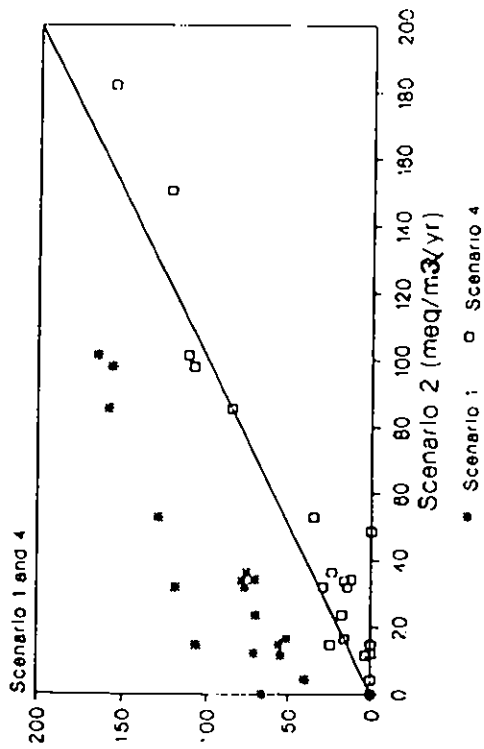
..... 1988
—— 2005 (80% Emissions Reduction)
—— 2005 (60% Emissions Reduction)

Loch Grannoch

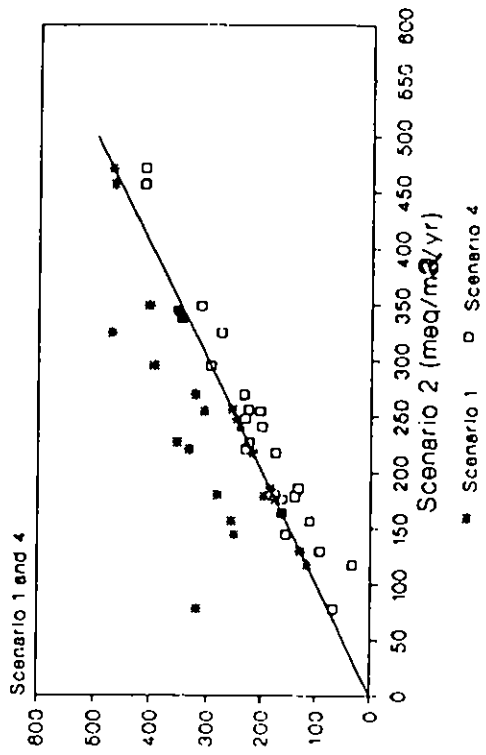
Forestry Impacts



Water CL (MAGIC)



Soil CL (MAGIC)



Round Loch of Glenhead

