

# LLYN BRIANNE ACID WATERS PROJECT

## SUMMARY OF INTERIM FINDINGS 1984-1986

The acidification of rivers and lakes has been the subject of increasing concern in Europe and North America in recent years. Declining fish stocks have been widely reported, and surface waters with previously productive fisheries have in many cases become fishless. In addition to the direct effects of increased acidity, an important factor in the observed decline appears to be the elevated concentrations of dissolved aluminium that are often found in low pH waters. In regions where geology and soil type dictate that the buffering capacity of natural waters is poor, dissolved aluminium can be acutely toxic to many forms of aquatic life. It has also been more recently suggested that the acidification of surface waters may have public health implications in remote areas where water treatment is rudimentary.

Acidic rainfall arising from industrial pollution has been implicated as the source of surface water acidity, but possible complementary or secondary effects arising from changes in land use have also been suggested. In particular it has been noted that waters draining conifer plantations on base-poor geologies are more acidic, contain elevated concentrations of toxic dissolved aluminium, and have impoverished biota by comparison with adjacent moorland catchments having similar soils. However, the detailed mechanisms involved are poorly understood, and little research has taken place to date in the U.K. into management strategies which could possibly mitigate the effects of surface water acidity.

The Llyn Brianne project aims to investigate the acidifying effects of both deposition and land use factors, and to quantify the relative importance of each. In order to establish management strategies to mitigate acidification, investigations are also being undertaken into various land treatments on both moorland and conifer catchments. Sophisticated equipment packages on each of the study

catchments enable continuous monitoring of pH and other parameters, with biological monitoring on all the study streams both before and after land treatment. Laboratory based process and toxicity studies complement the field investigations. The Mid Wales study area contains soil types and land uses which are widely found in other sensitive upland areas of the U.K.

The project commenced in September 1984, although preliminary studies had been undertaken in the area before that date. Most of the sites selected for study were instrumented by summer 1985, although the additional ones (dependent on the increase in funding awarded in March 1986) were instrumented in summer 1986. This document summarises progress to the end of 1986 both in the various field studies and in the laboratory-based process studies. It must be stressed that these findings are preliminary only, since in some cases they are based on short data runs. In other cases corroboration is required from replicate studies before the conclusions can be regarded as other than tentative. However, even at this early date it appears that the project is producing data which may have considerable policy implications.

## SUMMARY OF INTERIM FINDINGS 1984-85

### 1. Deposition

- \* Data from this study confirms the results of previous investigations, that rainfall in mid Wales is on average at least five times more acidic than unpolluted rain, although among the least acidic in Europe. Rainfall in 1986 had a volume-weighted mean pH of 4.6, and individual events with pH 3.9 were recorded.
- \* Snow samples collected in February 1986 after a prolonged period of easterly winds had pH values as low as 3.5. A concurrent survey showed that atmospheric oxides of nitrogen in the area were considerably elevated reaching 15 parts per thousand, or some 4-5 times previous levels. However, the snow contained about equal concentrations of both nitrate and sulphate, suggesting that deposition of sulphur compounds may have been as high as that of nitrogen compounds.
- \* A "wet-only" precipitation collector was deployed in summer 1986. Initial results demonstrate that "bulk" and "wet-only" pH were within 0.1 units of each other on just under half of the recorded occasions. "Bulk" pH was, however, between 0.2 and 1.5 units more acid than "wet only" pH on a similar number of occasions. This implies a significant contribution to "bulk" deposition from the "dry" and "occult" components under certain conditions. Further attention will therefore have to be given to quantifying the "occult" and "dry" deposition of sulphate and oxides of nitrogen.

### 2. Throughfall and stemflow

- \* Throughfall is more acid than precipitation under 25 year old sitka spruce in late winter and early spring, but less acid at other times of the year. It is likely that the discrepancy is due to the incidence of easterly winds during late winter and early spring.

- \* Sulphate and chloride concentrations are elevated beneath conifers. This almost certainly results from a combination of atmospheric "scavenging" by conifer needles, and the concentration effect arising from increased evapotranspiration by conifers.
- \* Throughfall beneath oak is generally less acid than precipitation. Further neutralisation takes place in the ground flora (of which there is none under conifers). Concentrations of sulphate and chloride are higher than precipitation, but there are also sufficient base cations for neutralisation to occur.

### 3. Soil Water

- \* For any given soil type, concentrations of aluminium in soil water are between two and three times higher under 25 year old conifers than under moorland. Sulphate and chloride concentrations are also elevated, being around twice as high as under moorland.
- \* Aluminium appears to be derived from ion exchange sites within soils. Mobilisation of aluminium is driven by the elevated sulphate and chloride concentrations, and possibly by organic anions.
- \* For a given soil type, aluminium concentrations under 12 year old sitka spruce are similar to those under moorland. This suggests that there is an "age effect", with scavenging and increased evapotranspiration only becoming important at the closed-canopy phase of forest development. This requires testing on a fuller age sequence.
- \* For a given soil type, higher concentrations of aluminium are found beneath larch than beneath spruce (of similar ages). Throughfall beneath larch is consistently more acid than throughfall beneath spruce of a similar age on the same soils. The flux of sulphate is also greater beneath larch than beneath spruce.

#### 4. Stream chemistry

- \* The overall mean pH of the moorland streams of the Camddwr catchment is 5.32, compared with 4.75 from the untreated mature conifer catchments. Sulphate levels in the moorland streams are on average 93.25 u Equiv.l<sup>-1</sup>, and 160 u Equiv.l<sup>-1</sup> in the afforested ones. The sulphate levels are slightly greater than those in bulk precipitation in the moorland streams, but around twice the precipitation levels in the mature forest streams.
- \* 25% of stream samples have pH <5.0 in the moorland Camddwr catchments CI3 and CI4, whereas 25% have pH <4.6 in the mature afforested catchments. Mean aluminium levels in the moorland and forest streams are respectively 0.13 mg l<sup>-1</sup> and 0.40 mg l<sup>-1</sup>. The moderately high levels in the moorland streams are related to acidity and to the poor buffering capacity of the catchment soils.
- \* The stream in the juvenile forest catchment (LI8) behaves more like a moorland stream than a forest one. Mean pH is 5.38, and 25% of samples exhibit pH <5.0. Nevertheless, acid events do occur, with the minimum pH of 4.4 being almost as low as in the mature forest streams.
- \* Continuous monitoring of stream chemistry using the sophisticated instrumentation has identified rapid and severe deteriorations in water quality that were not detectable by the previous less intensive monitoring.
- \* During snow-melt conditions in March 1986, pH dropped from 6.0 and 4.0 at afforested LI1 and from 5.6 to 4.7 at moorland CI5 within an eleven hour period. Normally well buffered streams were also affected, although to a lesser extent. Aluminium levels exceeded 1.0 mg l<sup>-1</sup> at afforested LI1. The changes recorded are attributable to a combination of reduced buffering capacity arising from frozen soils and reduced groundwater flows, combined with rapid run-off of material deposited from the atmosphere during the preceding cold period.

- \* Even during summer storm events, pH regularly dropped to 4.2 in afforested LI2. Such short duration flushes have been shown to be ecologically significant. Whilst certain invertebrate groups (e.g. mayflies) are able to take advantage of any temporary improvements in water quality to produce a short-term increase in diversity, fish populations can be eliminated by single acidic episodes.

## 5. Stream biology

- \* Biological impacts of surface-water acidity in Welsh rivers and lakes are amongst the most important consequences, involving effects on primary production, invertebrates, fish and on birds which depend on water-courses as a food supply.
- \* Fish are absent from afforested streams, but present in acidic moorland streams despite a low abundance of invertebrates. Terrestrially derived prey may be important in the moorland, but more data are required.
- \* Aluminium concentrations in forest streams, particularly the labile fraction, are well above the toxic threshold for salmonids, and a clear toxic effect has been shown with caged fish exposed to natural episodes.
- \* Field toxicity tests with experimentally induced episodes revealed enhanced breathing frequency and dramatically enhanced mortality amongst salmonids exposed to low pH and elevated aluminium. Aluminium under these circumstances accumulates at the gill surface.
- \* Forest presence also has physical influences on stream ecosystems, including altered temperature regimes which may reduce fish growth.
- \* Invertebrate faunas in Welsh streams show marked and clear relationships with water chemistry, amongst which pH, aluminium concentration and total hardness figure prominently.

- \* Invertebrate densities were generally lower in acidic moorland streams than in circumneutral streams and forest streams (except following bankside clearance). Circumneutral streams had the most mayfly nymphs and caddis larvae, whilst acidic streams were dominated by stoneflies.
- \* The quality of algae and bacteria, used as food by some invertebrates, differs between streams. However, experimental pulses of acidity and elevated aluminium have a marked influence on mayflies. Both indirect and direct effects of low pH on invertebrates are, therefore, possible. More data are required on impacts of acidity on primary production, and its relationships with invertebrate fauna. More evidence is also required on the trophic and chemical effects of forest presence on invertebrates, ideally through experimentation.

## 6. Process investigations

- \* Previous field investigations have estimated the concentrations of dissolved aluminium in streamwater using the "filterable" criterion (i.e.  $<0.45 \mu\text{m}$ ), and so the ionic species present were not known. Laboratory studies in this project have determined the levels of inorganic monomeric aluminium in natural waters using a modification of the Driscoll method to provide increased accuracy. The inorganic monomeric form is the most toxic form of aluminium, and was found to be highest in streams draining afforested catchments during high flow events.
- \* A more rapid method of aluminium fractionation than that outlined above has also been developed, enabling large numbers of samples to be analysed. When applied to field samples, it was found that total, filterable and labile aluminium concentrations were all highest in forest streams. More data are required on episodic changes, but there are indications of a direct correlation between "filterable" and "labile" aluminium at  $\text{pH} < 5.0$  and aluminium  $> 0.1 \text{ mg l}^{-1}$ .

- \* Only a very small proportion of measured inorganic monomeric aluminium is complexed by fluoride or by humic acids. However, the large quantities of particulate and colloidal matter found in suspension during high flows can effectively regulate the amount of inorganic monomeric aluminium in solution.

## 7. Treatments

- \* Agricultural improvement (ploughing, liming, reseeded) of part of a moorland catchment did not affect water quality significantly in the first four months after treatment. During a storm event in October 1986, toxic conditions were experienced with pH falling to 5.0 and aluminium concentrations reaching  $0.13 \text{ mg l}^{-1}$ . However, some improvements may become apparent in the longer term, since magnesium limestone is known to take some time to leach out.
- \* Bankside clearance of conifer forest (carried out in 1983) had no significant effect on water quality, with pH  $< 5.0$  being recorded on most storm events after treatment. Biological monitoring since 1984 has indicated that some impoverishment of invertebrate communities has taken place since the clearance was carried out.
- \* Bankside clearance and liming had a beneficial effect on water quality in the short term, with pH rising to 6.0 from a pre-treatment maximum of 4.8. However, during storm events pH dropped as low as 4.5, almost as low as the lowest pH's previously recorded. The longer term effectiveness of this treatment as the limestone is leached through the soils has yet to be determined.
- \* Liming of a small lake in the Brianne area has shown that water quality can be improved sufficiently to permit the introduction of a thriving brown trout population in what was an extinct fishery. Annual re-dosing is, however, required. An evaluation of flow-related river liming would be most valuable.



## 8. Modelling

- \* Long term simulations of catchment behaviour indicate that there has been significant acidification over the past hundred years. A half-unit pH decline has been calculated for moorland catchment CI5, similar to the amount inferred by diatom studies on nearby moorland lakes.
  
- \* A short-term flow-hydrogen ion response model has also been applied to afforested catchment LI1. The model produces a satisfactory simulation of hydrogen ion concentration, and indicates that hydrology plays an important role in catchment acidity.
  
- \* A model relating invertebrate assemblage to water chemistry has been derived. It will have value in prediction and in backwards reconstruction when used in conjunction with hydrochemical models.