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Surface-water Acidity in the River Dart Area Report for the West Country Rivers Trust

ECRC Research Report Number 154

Richard W. Battarbee, Ewan M. Shilland, Gavin L. Simpson, Jorge Salgado, Ben Goldsmith, Will Gray and Simon D. Turner

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Introduction

This report on the acidification of headwater streams of the River Dart follows the structure of the staged contract agreed with the West Country Rivers Trust (WCRT). Here we provide our responses to Stage 1 and Stage 2 of the contract. All tasks under Stage 1 and 2 have been completed. This report also refers to the ACCESS chemistry database already submitted to WCRT.

Stage 1:

"Is the situation on pH Dartmoor Natural? If yes then we need go no further because we would not want to seek to remediate a natural situation or is it anthropogenic? I.e. the pH is low due to a history of exceedance of critical loads for many years (if yes then we can proceed to stage 2)"

1. Collate, organise and inspect all existing historic water chemistry data for Dartmoor including critical load assessments

The chemical data we have assembled so far for Dartmoor and the Dartmoor region are presented in the ACCESS database provided to WCRT by Ewan Shilland. The database includes the following data-sets:

- UCL data from the original UK critical loads survey carried out by ENSIS-UCL under contract to the DETR (now Defra) in 1987 and 1988. The water samples were analysed by the Freshwater Fisheries Laboratory in Pitlochry and the results are identified in the database under the Chem Lab heading "MS" and coded CZSX or SSX in the database and Table 1 [below.](#page-5-1)
- under this contract with chemistry analysed at UCL and identified in Table 1 • UCL data from the 2012 survey of Dartmoor streams carried out by ENSIS-UCL [and the database as "UCL" with DLP codes.](#page-5-1)
- Generation Programme and DETR, and identified in the database and Table 1 • CEH data from a survey of surface waters in the Dart catchment in 1998-1999 carried out by Chris Evans (Evans *et. al.*, 2001; Evans, Cooper, and Gannon, 2001) under contract to National Power, PowerGen, the Western Power [as "CEH" with CE codes.](#page-5-1)
- headed "EApHdata". These sites are coded EA in Table 1. The data were • Environment Agency pH time-series data from several streams in the Dart catchment that have been continuously monitored for many years, although with differing start dates, and shown in the Database as a separate table [supplied by the Environment Agency via Dylan Bright \(WCRT\).](#page-5-1)
- Acid Waters Monitoring Network (AWMN) data for the Narrator Brook for 2012. Narrator Brook has been an AWMN monitoring site since 1988. The full timeseries data can be found in Shilland *et. al* (2012) and on the AWMN website (http://awmn.defra.gov.uk/resources/datasheets/site14_chem.pdf).

We have carefully checked the historical chemical data produced by third parties that are listed in the database and have found no obvious analytical errors. All site locations are shown in Google maps: <http://goo.gl/maps/Ayx6e>.

2. Collect, filter, and freeze water samples from 20 agreed locations including former CLAG sites and former sites in the Dart headwaters

Using all available data we selected 25 sites for full water chemistry (Table [1,](#page-5-1) Figure 1 and Appendix 1) including nine sites used in the original critical loads campaign of 1987-88, five sites used by CEH in their 1998-1999 project, three EA pH monitoring sites, two sites sampled by Wilson in 2002-2003 (Wilson, 2004) and six new sites sampled by ENSIS-UCL in 2012. The old ENSIS-UCL 1987-1988 sites were included to enable a comparison between past and present chemistry, and the new sites were selected to represent a downstream gradient in alkalinity from the most acidic streams in the headwaters to the less acidic ones below the moorland boundary. Five additional previously sampled sites, easily accessible during the water sampling programme in 2012, were sampled for field chemistry only (Table 1 and Appendix 1).

Sampling was carried out in April 2012 by Ben Goldsmith and James Shilland. pH, water temperature and conductivity were measured in the field and samples of stone biofilm were taken for diatom analysis (to be analysed under a separate inhouse UCL project on diatom biodiversity). Details of the field survey and results from field measurements are shown in the ACCESS database table headed "Field Survey" and Appendix 1. Water samples for laboratory analysis were filtered using a 0.45µm GFC filter, divided into two sub-samples and stored in a freezer at -18 $^{\circ}$ C at UCL.

Sites ordered by ascending Ca, as measured in April 2012 survey.

Rivers data from ShareGeo Open (http://hdl.handle.net/10672/85)

Figure 1. Map of 2012 water chemistry sampling points. Numbers refer to Table 1.

3. Analyse samples for all determinands needed to calculate SSWC critical loads

Calculation of critical loads for acidity using the Steady State Water Chemistry (SSWC) method is based on the difference between base cations (Ca, Mg, Na, K) and acid anions (SO₄, CI, NO₃). Base cations were measured by ICP_AES and acid anions were measured by ion chromatography (IC). The results are shown in the ACCESS database table headed "Chemistry_Master" and designated as "UCL"

in the ChemLab column. In Figure [2 to F](#page-7-1)igure 8 cation and anion data for the samples analysed are shown.. All sites are arranged in ascending order of Ca, as measured in the 2012 survey. Sea-salt corrected sulphate data (used in the critical loads calculations) are shown in Figure [9. Field pH measurements are provided in](#page-10-1) Figure 10. Key features of the data are the low Ca concentrations for many of the sites, indicating their sensitivity to acidification, and the relatively low but nevertheless significant concentrations of non-marine sulphate indicating the continuing influence of acid deposition and its legacy in this area. Nitrate levels at many sites are also above background suggesting that N leaching is also taking place and contributing to the acidity of the streams. The very low pH at some sites is probably related not only to sulphate and nitrate concentrations associated with acid deposition and its legacy but also to the presence of organic acidity (as dissolved organic carbon (DOC) (not measured)), typical of waters draining upland peaty soils**.**

Figure 2. Calcium concentrations for water samples collected in April 2012 from Dartmoor streams

Figure 3. *Sodium concentrations for water samples collected in April 2012 from Dartmoor streams*

Figure 4. *Potassium concentrations for water samples collected in April 2012 from Dartmoor streams*

Figure 5. *Magnesium concentrations for water samples collected in April 2012 from Dartmoor streams*

Figure 6. *Sulphate concentrations for water samples collected in April 2012 from Dartmoor streams*

Figure 7. *Nitrate concentrations for water samples collected in April 2012 from Dartmoor streams*

Figure 8. *Chloride concentrations for water samples collected in April 2012 from Dartmoor streams*

Figure 9. Non-marine sulphate concentrations for water samples collected in April 2012 from Dartmoor stream*s.*

Figure 10. *pH for water samples collected in April 2012 from Dartmoor streams*

4. Calculate reference and present day ANC for the new 2012 samples and calculate critical load exceedance for them for the present day and 2020.

Acid Neutralising Capacity (ANC) for the 2012 data was calculated using the ion balance approach by subtracting the sum of acid anions from the sum of base cations. The reference ANC was calculated assuming that nitrate concentrations prior to acidification were zero and non-marine sulphate concentrations were at a low background level (allowing a natural non-marine component e.g. due to volcanism). Figure 1[1 compares these ANC values. The data indicate that the](#page-12-1) [reference ANC for all Dart headwaters except site 2 is greater than 30 µeq/l,](#page-12-1) [whereas current values for many sites remain significantly below this value](#page-12-1) [indicating those waters that remain acidified \(according to the assumptions made\).](#page-12-1)

Figure 11. *Histograms of ANC ref and ANC 2012 for the 25 sites analysed in 2012*

Critical load calculations were carried out on the data using ANC 20 as the critical value (ANC_{crit}) according to the national UK protocol (cf RoTAP 2012). Exceedance values are based on current (CBED 09-11) and future (FRAME 2020) S and N deposition data (provided courtesy of Jane Hall, CEH). The calculations presented here assume that deposition at all sites is to a moorland ecosystem. Adjustments for the proportion of stream catchments that are afforested need to be made when data on land-cover become available. The effect of such adjustments would be to increase the exceedance values as deposition over wooded surfaces are higher than over grassland ones. The results for the two dates are mapped in Figure 12 [and the values are compared on a site by site basis in F](#page-13-1)igure 13. The map uses the colour coding system of the UNECE in which black represents the highest exceedance and blue represents sites that are not exceeded. Units are in k eq H⁺ ha⁻¹ yr⁻¹.

SSWC Critical Load Exceedance

SSWC Critical Load Exceedance

Figure 12. *Critical load exceedance for the 25 sites sampled in 2012 for 2009-2011 and 2020 deposition respectively based on 2012 chemistry.*

Figure 13. Comparison between critical load exceedance for the 25 sites sampled in 2012 for 2009-2011 and 2020 deposition respectively based on 2012 chemistry (as for Figure 12).

The SSWC model data indicate that the critical load is currently exceeded at many sites, although none is in the highest exceedance category. The projections for 2020 show no or only slight exceedances remaining indicating that all sites should have recovered or almost recovered sufficiently to attain the critical value of ANC 20 (in µeq/l) and thereby support a relatively healthy fish population by that date.

It should be noted, however, that the SSWC model tends to provide "best case scenario" values (see below) and that there is underlying uncertainty in any model output where values are computed from single water samples from streams. The major ion chemistry of stream water is strongly influenced by discharge variability. More robust critical load evaluations therefore require data from samples collected under a range of flow conditions. Moreover attainment of an ANC value of 20 does not represent a full recovery. The target for a full recovery is the ANC reference value, although this is also an uncertain value as it is based on the same flow dependent chemistry.

Stage 2*:*

"If this situation is anthropogenic then we want to look at recovery, will it recover in the next 10 years? (if yes then we are better to wait and need progress no further) or the next 50 years (if yes then we can progress to stage 3)."

1. Comparison of major ion chemistry between sites sampled in 1987-1988 and 2012

An estimate of the extent of recovery can be derived from a comparison between the chemistries of the 9 sites sampled in 1987-1988 with those of the same sites sampled in 2012. However, allowances need to be made for the problems associated with potential differences in streamflow between the sampling periods and the different analytical methods and laboratories used. Unfortunately it was not possible to include the AWMN site Narrator Brook in the comparisons due to a change in sampling location at the site, moving position upstream of a coniferous plantation in 1991. Differences in ion chemistry between the two time periods for the nine sites are shown in Figure 14 [to](#page-16-1) Figure 18. The data show: (i) concentrations of Na and Cl are consistently higher in the 1987-88 samples suggesting that stream chemistry was more influenced by sea-salts and that flow may have been higher at that time; (ii) non-marine sulphate concentrations are significantly lower in the 2012 samples, very probably reflecting the effect of major reductions in S deposition that has taken place in the regions and across the UK over the last 25 years; (iii) there is little obvious difference in nitrate concentrations between the two surveys and, although low (<10 µeq/l), they remain higher than expected background levels; and (iv) despite the strong reduction in non-marine sulphate concentrations, pH values remain very low possibly due to the sulphate decrease being balanced by a reduction in labile AI (not measured) rather than H⁺ and possibly also due to the presence of relatively high DOC levels (not measured) in the streams as noted above.

The differences between the two surveys are in accordance with expectation based on the evidence of data from the AWMN that indicates strong reductions in non-marine sulphate, little change in nitrate and significant reductions in labile Al at the most acidified sites (Kernan *et. al*. 2010). pH increase is muted at such sites. Overall there is therefore no reason to doubt that the headwaters of the Dart catchment have been acidified as a result of acid deposition and are now recovering.

Figure 14. *Comparison of sodium for 9 sites sampled in 1987-88 and 2012.*

Figure 15. *Comparison of chloride for 9 sites sampled in 1987-88 and 2012.*

Figure 16. *Comparison of non-marine sulphate for 9 sites sampled in 1987-88 and 2012.*

Figure 17. *Comparison of nitrate for 9 sites sampled in 1987-88 and 2012.*

Figure 18. *Comparison of pH for 9 sites sampled in 1987-88 and 2012.*

2. Comparison between critical load exceedances for 1987-88, 2012 and 2020

The rate of improvement (and extent of recovery) at the Dart sites can be further assessed from a comparison between the SSWC critical load exceedance values for 1988, 2012 and 2020 (Figure 19 [and](#page-20-1) Figure 20). The 1988 values use the 1987-88 chemistry data from samples collected by ENSIS-UCL and analysed by the Freshwater Fisheries Laboratory (Pitlochry) at the time of the original national critical loads survey and modelled S and N deposition data for 1986-1988 (courtesy of Ron Smith, CEH). The 2012 values use the 2012 chemistry data from samples collected and analysed by ENSIS-UCL and CBED (Concentration Based Estimated Deposition) modelled deposition data for 2009-2011 (courtesy of Jane Hall, CEH), and the 2020 values use the 2012 samples for chemistry and deposition values modelled using FRAME (also courtesy of Jane Hall, CEH).

Figure 19. *SSWC-based critical load exceedances for 1988 (based on 1987-88 chemistry and 1986-1988 modelled deposition), 2012 (based on 2012 chemistry and 2009-2011 CBED modelled deposition) and 2020 (based on 2012 chemistry and 2020 FRAME modelled deposition)*

Figure 20. *Comparison of SSWC-based critical load exceedances for 1988, 2012 and 2020 as for Figure 19.*

The data (Figure 1[9 and F](#page-20-2)igure 20) show that critical load exceedances have reduced from 1987-88 to the present day and that a further reduction is expected by 2020 to the extent, as pointed out above, that all of the sites sampled are projected not to, or only slightly to, exceed the ANC 20-based critical load by that date. The trend in exceedance reduction suggests that conditions for fish recruitment and survival should gradually improve and, all things being equal, the streams should be capable of supporting a healthy brown trout population within 10 years.

However, there are a number of caveats:

- As already indicated, the comparison between the critical load exceedance values for 1988 with those for 2012 and projected for 2020 needs to take into account seasonality and the uncertainty caused by differences in flow conditions between the two sampling periods (Curtis and Simpson, 2011). The lower non-marine base cation concentrations of the 1987-88 samples and the higher Cl levels compared with the 2012 samples suggests that flows were higher and more influenced by sea-salts during the earlier sampling period, a difference that would potentially cause the extent of recovery to date to be over-estimated.
- The critical load exceedance values presented here are based on the SSWC model. The model assumes there is a steady state between acid anion deposition and anion leaching. This assumption is not upheld, however, in cases where N deposition and nitrate leaching are not in balance. The First Order Mass Balance Model (FAB) then becomes the preferred critical load model as this model accounts for nitrogen dynamics in catchment soils and it can be used to predict the extent of nitrate leaching to surface waters as the soil's capacity to store or use N is exhausted. Although N deposition on Dartmoor and nitrate concentration in the Dart headwaters is not high, both are significantly above background values. Consequently, despite the reduction in N emissions that is taking place in the UK, nitrate concentrations in streams, including the Dart streams, may not necessarily decrease and may even increase should soils in the catchment become saturated by N. It is possible therefore that, in contrast to the SSWC model, the FAB model could indicate continuing critical load exceedance in 2020. As these two models represent the best and worst-case scenarios respectively the true exceedance values are likely to lie between them. One of our recommendations is to acquire the additional information needed on catchment soils to run FAB on the 2012 samples with both 2009-2011 and 2020 deposition fields.
- The critical load exceedance calculations do not take into account the potentially harmful effects of acid episodes associated with high runoff following storm events. We note that Wilson (2004) used continuous monitoring of two Dart headwater tributaries in 2003-2004 to demonstrate sustained pH depression from pH 6 to almost pH 4 after severe rainfall events. The severity of such events should decrease as sulphate levels fall, but acid episodes may continue to cause problems for fish and invertebrate populations even when critical loads are theoretically not exceeded (i.e. when ANC concentrations reach 20 µeq/l and over).
- Although the probability of brown trout occurrence at a site can be predicted from ANC concentration, a better predictor is labile monomeric aluminium (Malcolm *et. al.*, in

press) the concentration of which depends principally on catchment lithology, pH and DOC. There are no measurements of Labile-Al yet available for the Dart headwaters, although measurements at the nearby AWMN Narrator Brook site show concentrations that vary between approximately 0 and 50 µg/l with a mean of about 25 µg/l. It is likely therefore that concentrations in the more acidic headwaters of the Dart are higher than this, and that Labile-Al is indeed at concentrations likely to cause damage to fish. As recovery continues and pH and probably also DOC continue to increase Labile-Al concentrations should fall and become less toxic. Analysis of Dart samples to measure current labile-Al concentration is recommended to assess conditions for fish survival more accurately.

Summary and conclusions

- Headwater streams of the River Dart have been severely acidified by the effects of acid deposition.
- Following the major reduction in sulphur dioxide emissions that has taken place in the UK over the last 25 years sulphate concentrations in the streams have decreased strongly and ANC has increased.
- Nitrate concentrations are relatively low but well above the expected background at some sites.
- The lack of a decrease in pH between 1987-88 and 2012, despite the decrease in sulphate, may be due to changes in labile aluminium and DOC concentrations (not measured in this survey).
- Calculations of reference values for ANC indicate that all sites sampled in the Dart system had ANC values above 20 µeq/l prior to acidification and were therefore capable of supporting healthy populations of brown trout at that time.
- Fish populations at the present day are likely to be limited by high labile aluminium concentrations (not measured) that probably prevail in the headwater streams.
- SSWC model projections suggest that critical load exceedances will be eliminated or almost eliminated at all sites by 2020 and conditions for brown trout recruitment and survival should improve accordingly.
- Allowance needs to be made, however, for the potential impact of acid episodes that are likely to continue occurring following high rainfall events although the severity of these should decrease as conditions improve.
- The SSWC model gives results that can be regarded as representing the best-case scenario as the model does not take into account the possibility of any increase in nitrate leaching.
- There is uncertainty over the behaviour of N in catchment soils. It is possible that nitrate leaching could increase, and, as a strong acidifying anion, offset some of the gains that are being made from reductions in sulphate.

• We believe the data are well founded and accurate, but we should stress the limitations of drawing conclusions and making predictions for the future on the basis of single water samples.

Recommendations

Although there are many uncertainties, as described above, the data suggest that recovery is underway and that the rate of improvement is sufficiently rapid for liming of the upper moor not to be necessary. Before making any decision on liming we recommend that:

- the FAB model is used to calculate worst case exceedance values for 2020. The model uses the same water chemistry as the SSWC model but needs data on catchment soils;
- analysis of labile-Al and DOC concentrations are carried out to assess better the probability of brown trout occurrence using the new WFD fish tool;
- samples for one or more of the most acidic sites are collected and analysed on a fortnightly or monthly basis to assess variability in chemistry over an annual cycle.

If a decision is made to lime on a trial basis we recommend as previously advised that:

- the minimum amount of lime is added to minimise damage to algal and plant communities in the streams;
- biological surveys of the sites to be limed are carried out for at least one year before liming and two years after;
- one of the headwaters of the Dart remains un-limed to act as a control;
- waters below the limed sites are monitored to assess the effect of liming on downstream communities.

In the context of both the local region and the UK as a whole, we also recommend that the West Country Rivers Trust consider setting up one of the Dart headwater sites as a longterm monitoring site to become part of the new Upland Waters Monitoring Network (UWMN) that will supersede the AWMN, and as such, complement the Narrator Brook. In this way the chemistry and biology (including fish populations) of representative sensitive upland streams in the region can be tracked in response to future changes in acidity, nitrogen leaching and climate change and compared to changes at sites elsewhere in the UK.

Next steps

The two remaining Stages are:

Stage 3: could the addition of lime mitigate the effect? yes (go to stage 4)/no (stop work)

Stage4: what is the best method based on case studies? What are the implications for the riverine ecosystem down stream? How reversible is the effect?

A review of literature on liming as a remedial measure for acidification is currently being prepared along with estimates for carrying out the work recommended above.

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Appendix 1 Field Sampling Details

