Title: Acidification Environmental Standards			**Paper Number:** FTT017
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Purpose: This paper presents new standards for the evaluation of anthropogenic acidification.			

Background.

UKTAG requested FTT to develop acidification environmental standards based on new biological methods and additional evidence that has become available since the last round of standard setting in 2006. This paper describes the proposed standards and the process followed for their derivation.

The original pH standards were based on expert judgement from published pressure response relationships. In this round the standards have been established to protect the biological conditions set through the UK's Inter-calibrated procedure, and recent publications which explore the range of pressures that arise from acidification.

The process followed is outlined below:

- Devise a relevant typology.
- Establish biological class boundaries- achieved through inter-calibration.
- Gather supporting evidence from the literature.
- Establish pressure response relationships
- Derive standards
- Assess implications of changes

Acid Based Chemical Determinands.

Acidification is the total outcome of a complex set of chemical processes and there are a number of critical determinands commonly used in the literature to describe this pressure:

pH- Routinely measured and uncontroversial but reflects acidity rather than acidification. pH is strongly correlated with Labile Aluminium, and is consequently a good proxy for this variable which presents a number of analytical challenges- see below.

Labile Aluminium (L-Al)- Is thought to be the primary toxic control on biological communities in acidified systems. It has been suggested that the presence of L-Al is a definitive indicator of acidification (rather than simply low pH or ANC which could be associated with natural acidity) and provides by far the best relationships with salmonid population status.

However L-Al is difficult and time consuming to determine and is therefore not suitable for assessment through the automated laboratory batch processing currently undertaken by the UK environment agencies.

Organic Carbon- Typically measured as either Total (TOC) or Dissolved (DOC). The solubility of this determinand is affected by acid deposition. However, this determinand also mediates the biological effects of acidity by binding to, and reducing the toxicity of L-Al. Areas with high organic carbon tend to have a specialised community that is adapted to low pH, but not to high L-Al. This is reflected both in UK river and lake methods that have been developed to describe acidification pressures.

- Lake Macro-invertebrates- LAMM (DOC humic/clear boundary @ 5mg/l)
- River Macro-invertebrates- WFD-AWIC (DOC Scot humic/clear boundary @ 10mg/l) and
- River Diatoms- DAM (TOC included in DAM predictive variables)

Acid Neutralising Capacity (ANC)- ANC is typically taken as a measure of available buffering capacity in aquatic systems and can be measured in a number of ways. While pH could be considered as a measure of acidity, ANC is a direct measure of anthropogenic acidification and is commonly used for managing acidification at the national and international level, where the consequences of changing acid deposition can be directly assessed in terms of changing ANC. Two measures of ANC are typically used- the Cantrell, and the Ion Balance methods, and it is proposed that the Cantrell method- excluding labile aluminium is used as it can be readily derived by the UK environment agencies.

On the basis of the above it is proposed that the following determinands are used for setting environmental standards:

- pH- as a surrogate for labile Aluminium
- ANC- measuring losses in buffering capacity arising from anthropogenic acidification.

Typology Derivation

Dissolved Organic Carbon plays an important role in determining the level of damage that arises in low pH waters because DOC binds inorganic (toxic) labile aluminium. Thus it is generally accepted that it should be a key feature of a typology that is used to categorise sensitivity to acid pressures. The current WFD-AWICS procedure uses a 10mg/l cut off to categorise clear and humic waters and it is proposed that this value be used to set the typology for pH and ANC standards. This approach has been introduced to provide a more accurate classification of naturally acidified waters using the Environmental Standards in the absence of data on toxic L-Al.

Biological Methods and Calibration to Impact.

This section describes the derivation of pH and ANC environmental standards from biological methods in clear and humic river types.

Clear Waters

Biological Boundaries

Two biological methods were used to derive clear water acid based standards:

1. **WFD-AWICS:** Developed by McFarland (2010), this is the UK's WFD-compliant invertebrate acidification index. 3 Typologies are recognised: Wales, Scotland, and Scotland (Humic (DOC>10mg/l)).

2. **Salmonid fish (Malcolm et al (in press))** This study developed ES boundaries based on the probability of finding brown trout fry in 1,2 or 3 electro fished reaches using Acid Waters Monitoring Network data (all UK), and provided boundaries and confidence limits for Cantrell & Ion Balance ANC, Labile-Al & pH.

Tables 1&2 below describe the biological class boundaries that have been used to set the proposed environmental standards. The WFD AWICS class boundaries have been set through Inter-calibration, and the fish boundaries are based on expert views of the pressure response relationship described in Appendix 2.

Table 1. Inter-calibrated EQR Boundary Values for the WFD AWICS Procedure

	Wales- Clear	Scotland- Clear	Scotland- Humic
H/G	1	0.91	0.93
G/M	0.88	0.83	0.83
M/P	0.78	0.72	0.77
P/B	0.67	0.66	0.73

Table 2. Break Points in Fish Populations Used to Set Acid Based Environmental Standards- 90% confidence (90% two sided confidence limit – equates to 95% one sided confidence limit) of an 80% probability of observing brown trout in at least 1, 2 or 3 sampling reaches, where 3 fifty metre reaches are fished using 3 pass electro-fishing. (Malcolm et al (in press))

	90% confidence of having an 80% probability of observing brown trout fry in 50m sampling reaches
H/G	3 reaches
G/M	2 reaches
M/P	1 reach

Environmental Standard Setting

Tables 3 & 4 describe the pH and ANC class boundary values that have been derived from the macro-invertebrate and fish relationships that are outlined in Appendices 1 & 2 respectively.

Table 3. Inferred (Mean) pH Boundaries from WFD-AWIC/ Salmonid Fish in Clear Waters

Boundary	WFD-A (Wales)	WFD-A (Scot-C)	WFD-A (Scot-H)	Fish (Fry)
H/G	6.54	6.06	5.1	6.6
G/M	5.95	5.58	4.55	5.9
M/P	5.44	4.90	4.22	5.3
P/B	4.89	4.50	4.03	-

Table 4. Inferred (Mean) ANC Boundaries from WFD-AWIC/Salmonid Fish in Clear Waters

Boundary	WFD-A (Wales)	WFD-A (Scot-C)	WFD-A (Scot-H)	Fish (Fry)
H/G	80	80	80	69
G/M	40	50	50	38
M/P	5	10	10	15
P/B	-30	-10	5	-

The values highlighted in red have been selected for use as the environmental standards and they are presented along with their derivation in Table 5 below.

Table 5. Proposed Environmental Standard Boundaries and their Derivation in Clear Waters

Boundary	pH	Derivation	C-ANC	Derivation
H/G	6.6	Fish (inverts)	80	Inverts
G/M	5.95	Inverts (Fish)	40	Inverts (Fish)
M/P	5.44	Inverts	15	Fish
P/B	4.89	Inverts	-10	Inverts

Humic Waters

Biological Boundaries

Humic water standards have been derived solely from the WFD AWIC classification procedure, and the inter-calibrated class boundary EQR values are provided in Table 1.

Environmental Standard Setting

Table 6 describes the pH and ANC class boundary values that have been derived from the macro-invertebrate pressure response relationships that are outlined in Appendix 1.

Table 6. Proposed Environmental Standard Boundaries for Humic Water Sites

Boundary	pH	ANC
H/G	5.1	80
G/M	4.55	50
M/P	4.22	10
P/B	4.03	5

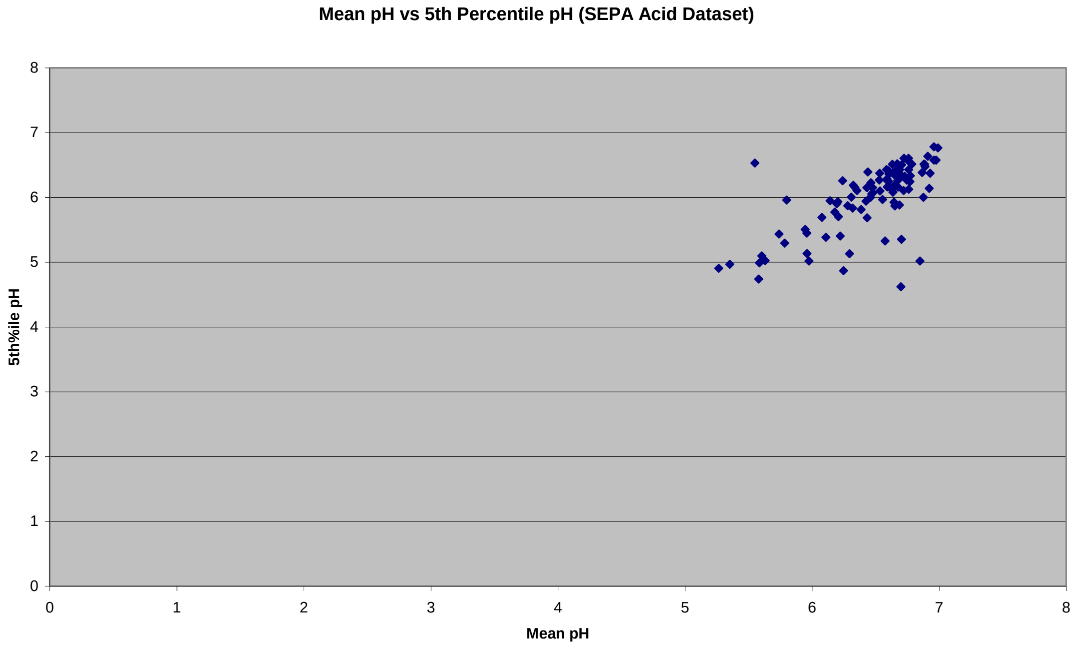
Mean and %ile Relationship

Historically pH environmental standards have been set using values which protect against extreme events- 5-10%ile for acidification and the 95%ile for alkalinity. However, the recent studies that have been used to underpin this review have demonstrated that there is a stronger relationship between mean pH and ANC and biological communities than there is for measured minimum values. Consequently, it is proposed that the new standards are based on the mean values rather than extreme events that have been used in the past. This has the benefit of making use of the most recent science in this area.

It is believed that the poor relationship between biological features and minimum phyisco-chemical determinants is due to the difficulty of capturing extreme events through routine monitoring programmes where the mean value may be a better predictor of the true minimum than an observed minimum. This could be over come by using continuous monitoring equipment or by modelling using flow concentration curves (e.g. Tetzlaff et al., 2011), but the paucity of this data means that this approach is not practically feasible at this time.

A typical relationship between the mean and the 5th%ile value in a small data set is provided in Figure 1.

Figure 1. 5th%ile/ Mean pH relationship for SEPA test data.



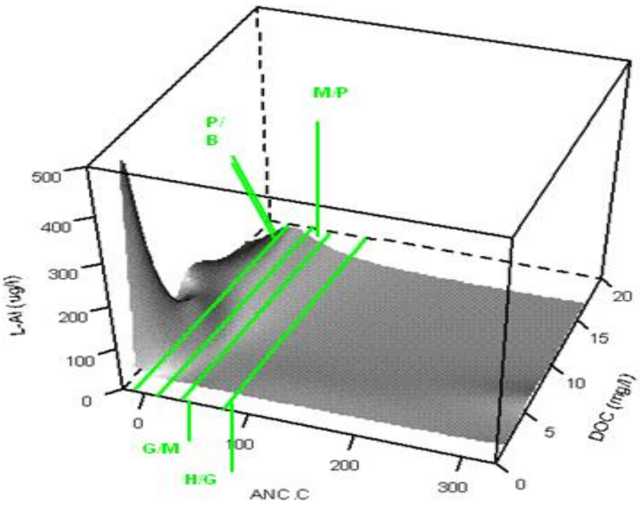
Validation of Environmental Standard Boundaries

Validation of the proposed environmental standards has been undertaken using an independent long-term data set form Loch Ard which established a series of multi-determinant models for ANC-C, DOC & L-Al and pH, DOC, & L-Al.

The proposed pH and ANC boundaries have been transposed onto the models and in both instances it is believed that they provide relevant break points to support the classification and regulation of acid pressures.

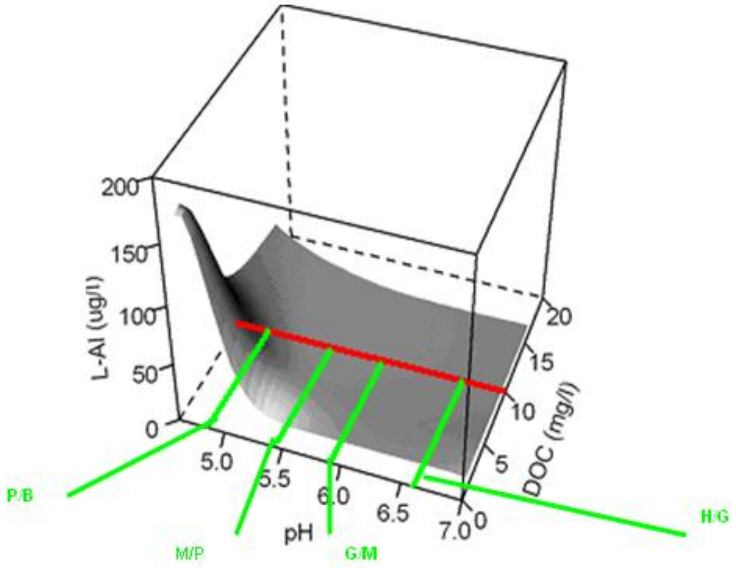
ANC In terms of the ANC model it is believed that the proposed boundaries are a good fit, see Figure2. The high boundary is above the point where L-Al levels begin to elevate. The G/M & M/P boundaries are at appropriate places on the L-AL gradient. The P/B boundary is placed at a level just below maximum L-Al concentration at most DOC concentrations.

Figure 2. Proposed ANC boundaries superimposed on Malcolm et al (2012) multi-determinand model.



pH At the proposed G/M pH boundary we start to see increases in labile aluminium concentrations which a range of studies have indicated is the point at which significant damage starts to be observed in biological communities- see Figure 3

Figure 3. Proposed pH boundaries superimposed on Malcolm et al (2012) multi-determinand model from Loch Ard.



Comparison of Current and Proposed Acid Environmental Standards

The proposed pH boundaries might seem slightly higher compared to the current (Phase 1) figures. However, it is important to note that the new boundaries are based on means rather than the pre-existing ones which typically use a low-percentile value of the distribution. It is also important to note that existing standards are not always in good agreement with observed biological status (particularly for fish). It is expected that these revised standards, with an improved evidence base, will reduce these discrepancies.

Table 7 A Comparison of Current and Proposed pH Environmental Standards

	Current	**Proposed**	
	pH	**pH**	**ANC**
High	pH 6 as a 5-percentile value; pH 9 as a 95-percentile value	6.6, as mean pH 9 as a 95-percentile value	80, as mean
Good	pH 5.2 as a 10-percentile value	5.95, as mean	40, as mean
Moderate	pH 4.7 as a 10-percentile value	5.44, as mean	15, as mean
Poor	pH 4.2 as a 10-percentile value	4.89, as mean	-10, as mean

At present high status has a test set to protect against alkaline events, and no change is proposed for this standard.

Classification Impact.

Class distributions for 304 sites using the current and proposed Environmental Standards are shown in Table 8.

Table 8 A Comparison of the Classification Results from the Current and Proposed Environmental Standards

	Current	Proposed
High	86	89
Good	10	9
Moderate	3	2
Poor	1	0
Bad	0	0

Tables 8 & 9 shows that there is a very slight upgrading of sites following the application of the new standards, and it is believed that this is largely due to the reclassification of the humic sites with low pH which would previously been classed as less than good.

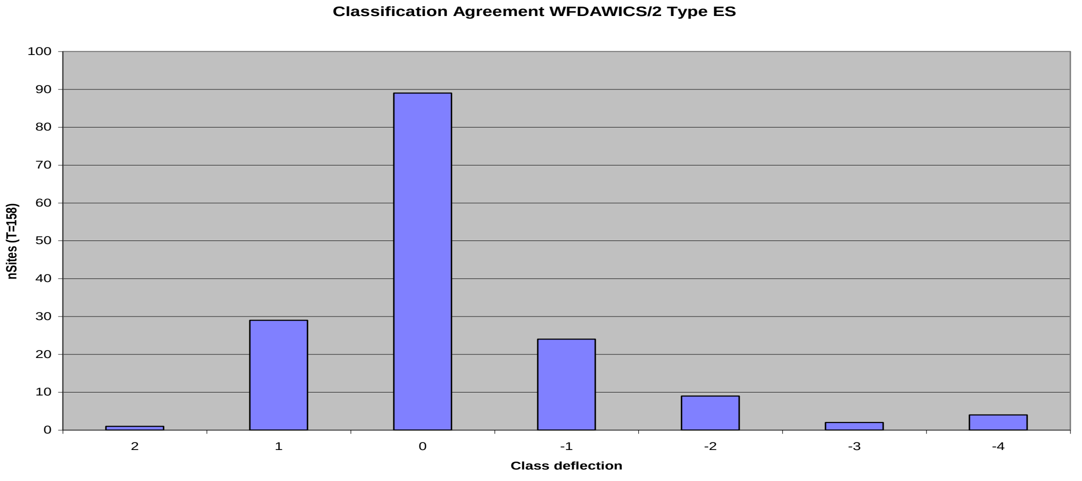
Table 9 Environmental Standard Class Comparison between Current and Proposed (2xDOC Type)

		New (2x DOC)						
		H	G	M	P	B	n	%
Current	H	249	13	1			263	86
	G	15	12	2			29	10
	M	6	1	2			9	3
	P	1	1	1	0		3	1
	B						0	0
	n	271	27	6			304	
	%	89	9	2	0	0		100

Alignment between Biological and Environmental Standards

Figure 4 demonstrates that under most instances WFD AWIC and the proposed environmental standards provide the same classification, and where there is a class disagreement it is most commonly by one class. There is a slight bias towards WFD-AWIC producing a lower class than the ES- as indicated by the RHS tail on the graph. However, this might be expected as the biological data provides a continuous record of conditions, and the chemical records only describe the conditions at the time of sampling- ie. the invertebrate fauna will be shaped by extreme events not detected by chemistry sampling. In areas subject to acidification therefore we can be confident that a mixture of biological and chemical sampling will adequately reflect environmental status, and that the two methods are in broad alignment

Figure 4. A Comparison of WFD AWICS and the 2 Type Environmental Standard Classifications



Alignment with Lake Standards

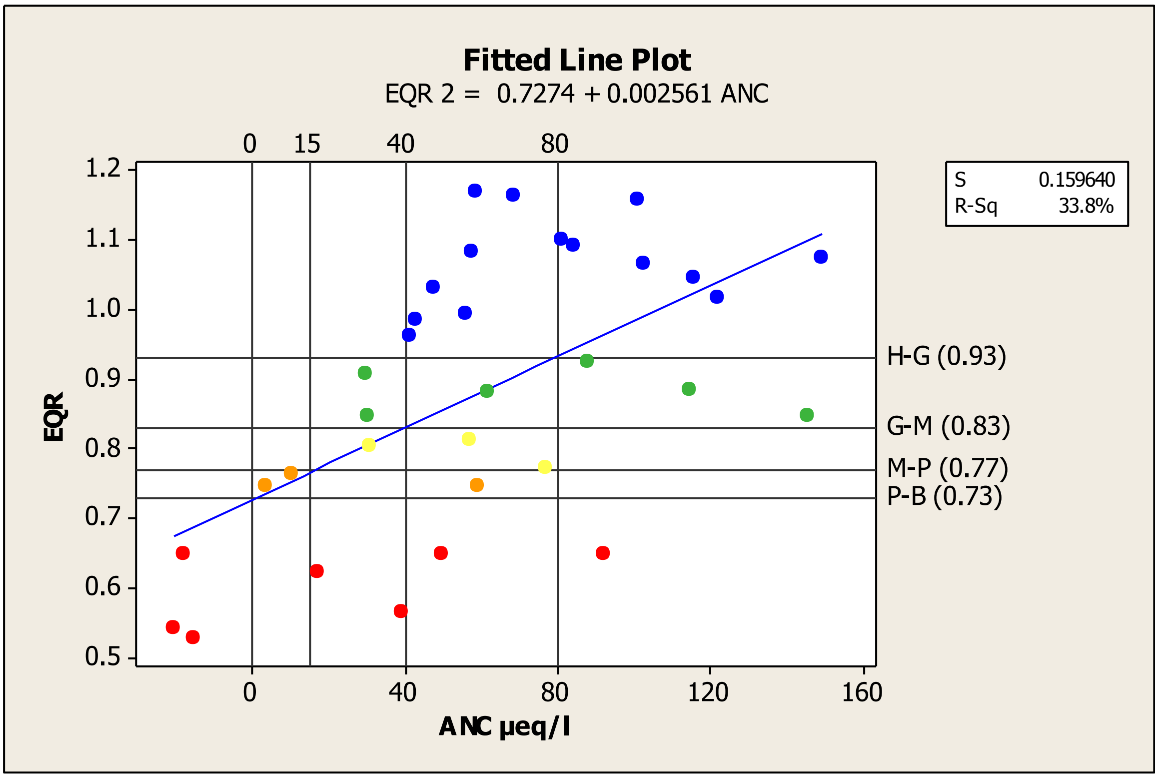
The proposed ANC standards for rivers are more precautionary than the comparable lake standards reflecting the greater temporal variability in the chemistry of running waters (Bridcutt et al., 2004), and the analysis undertaken through this work indicates that river fauna is more sensitive to acid events.

Use of the Environmental Standards

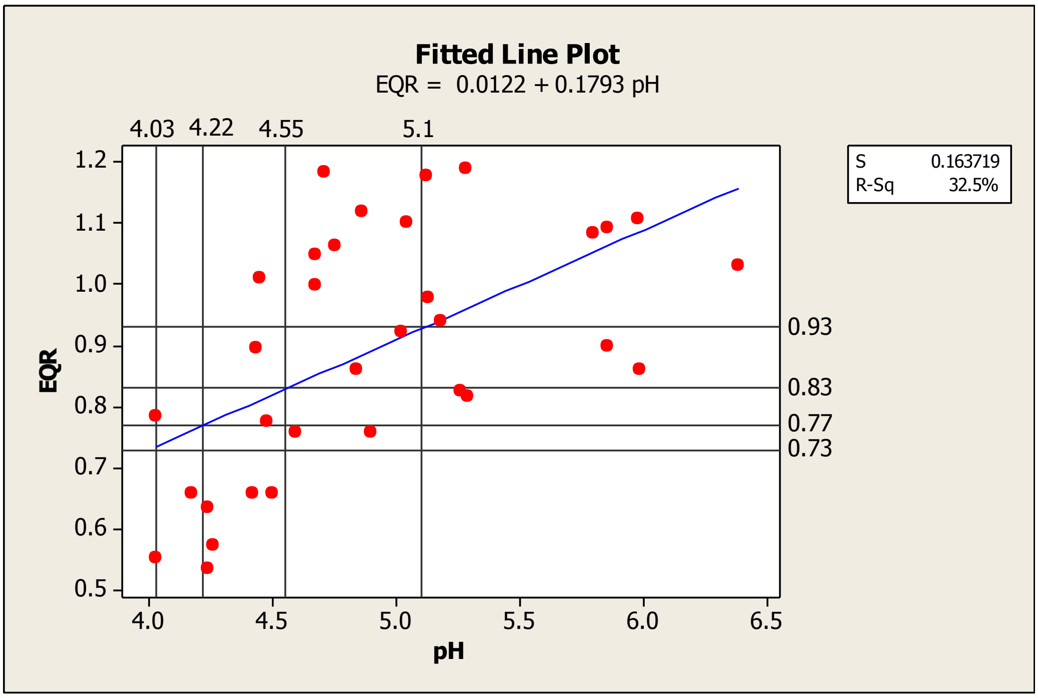
As described earlier in the paper ANC and pH fulfil 2 different roles in describing the impact of acidification. ANC provides an indication of buffering capacity that is useful in the context of national and international management of acid deposition because it forms the basis of critical loads approaches. pH is a measure of overall acidity (natural and anthropogenic), which is strongly correlated with labile Aluminium concentration once variability in DOC has been accounted for. Consequently it proposed that the UK environment agencies be given the opportunity to select one or both of these determinants depending upon the site monitoring objectives. The assessments included in this paper are based on the application of both ANC & pH at all of the sites.

Appendix 1. Invertebrate/Stressor Relationships (from McFarland (2010))

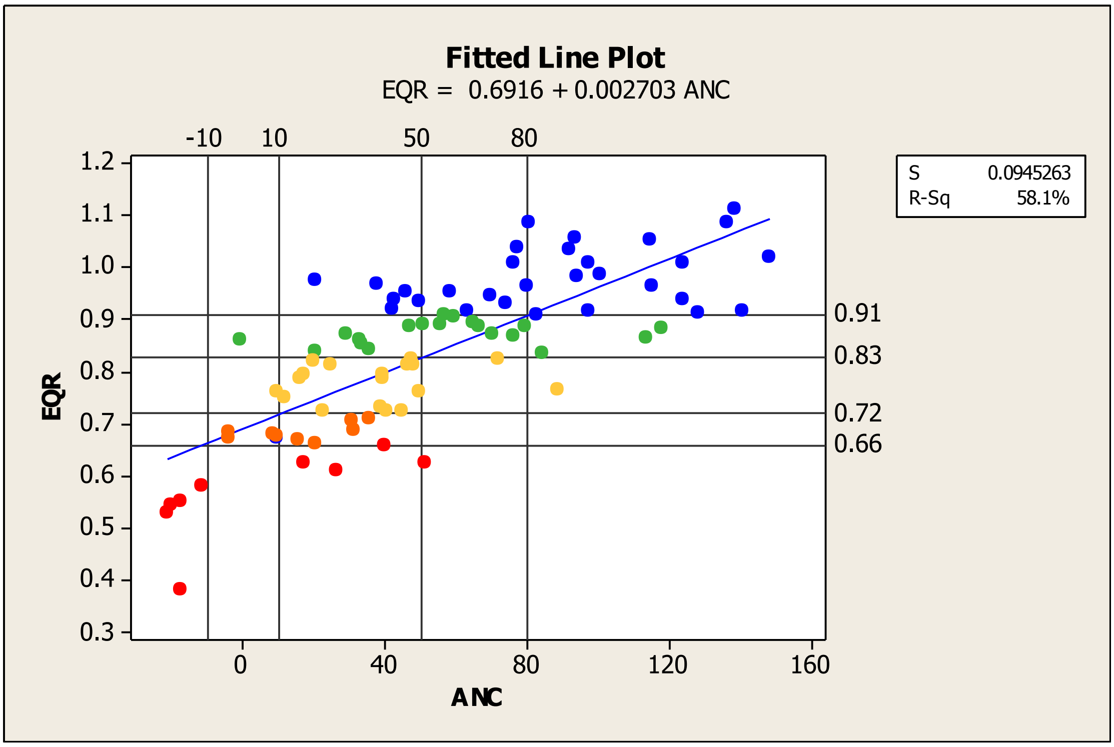
Linear regression of WFD-AWICsp EQRs verses ANC at Scottish humic sites. References lines are derived from Figure 14 and are used to predict EQR boundaries on the y-axis (● = High, ● = Good, ● = Moderate, ● = Poor, ● = Bad).



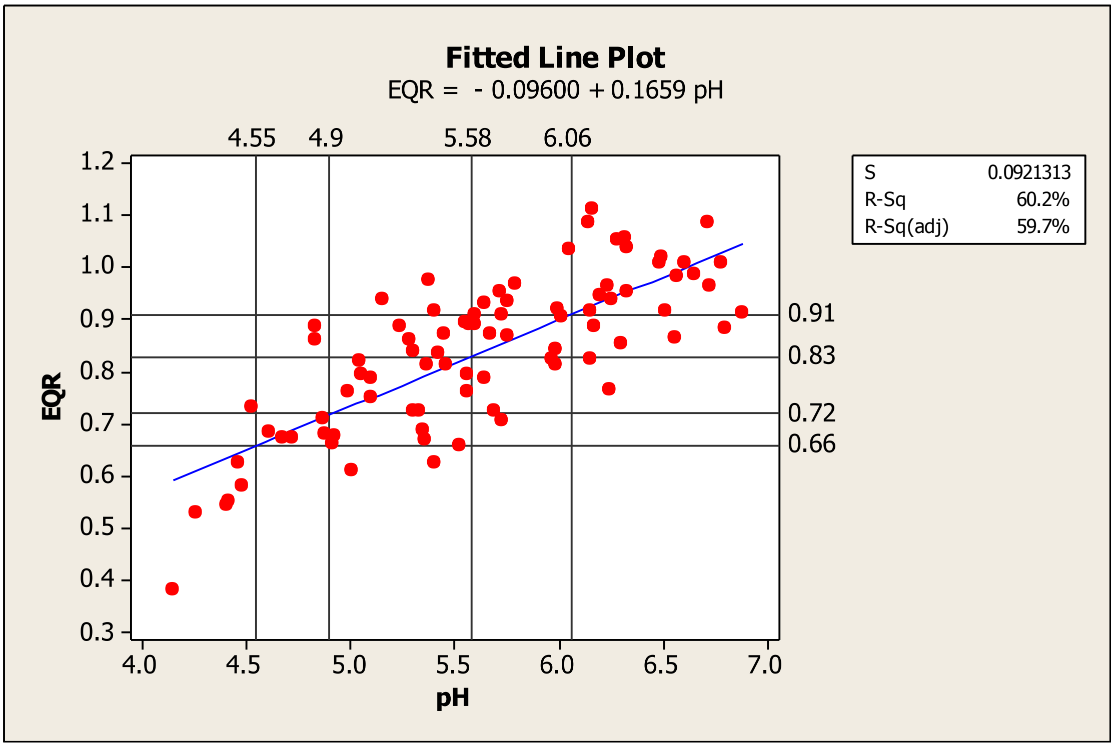
Linear regression of WFD-AWICsp verses pH at Scottish humic sites. Reference lines from the y-axis of Figure 15 are used to predict pH values.



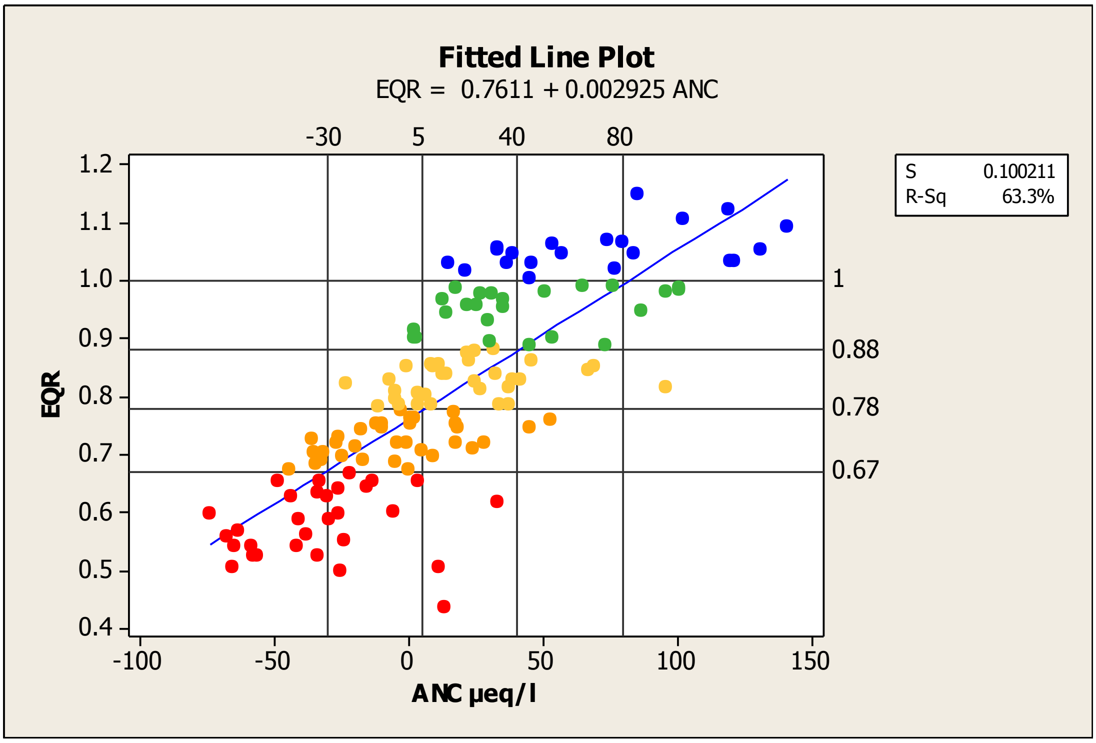
Linear regression of WFD-AWICsp EQRs verses ANC at Scottish clear-water sites (DOC <10 mg/l). Reference lines are derived from Figure 21 and are used to predict EQR boundaries on the y-axis. (● = High, ● = Good, ● = Moderate, ● = Poor, ● = Bad).



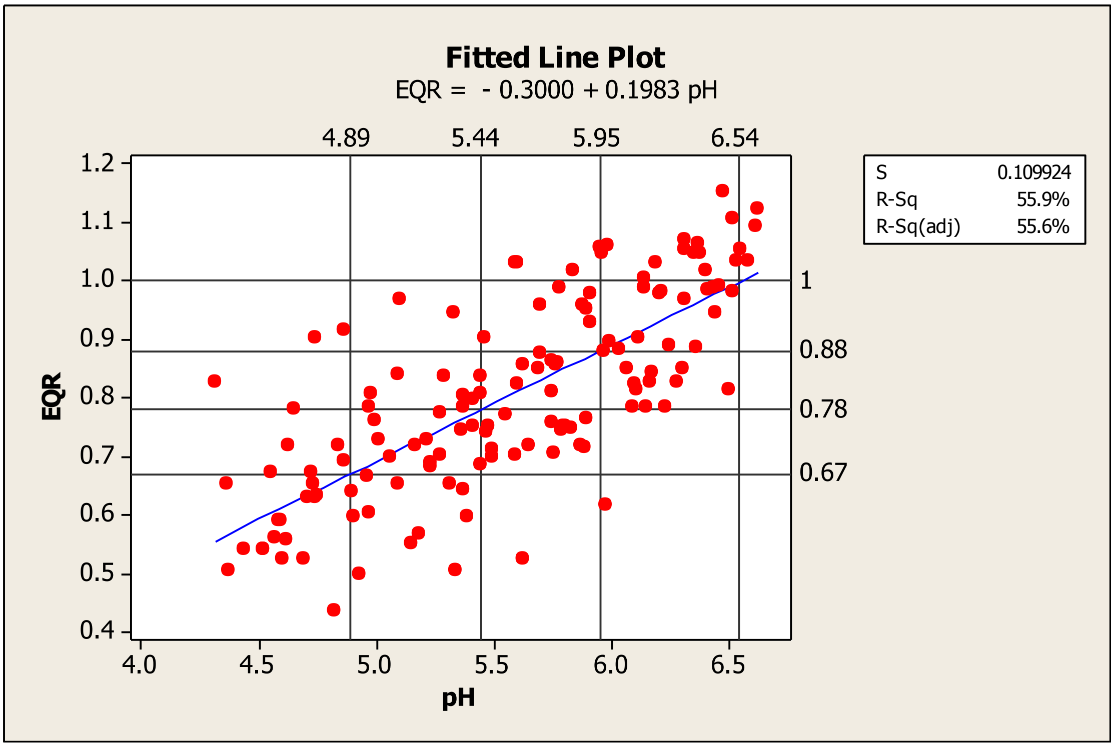
Linear regression of WFD-AWICsp verses pH at Scottish clear-water sites (<10 mg/l DOC). Reference lines from the y-axis of Figure 22 are used to predict pH values.



Linear regression of WFD-AWICsp EQRs verses ANC at Welsh sites. References lines are derived from Figure 27 and are used to predict EQR boundaries on the y-axis.

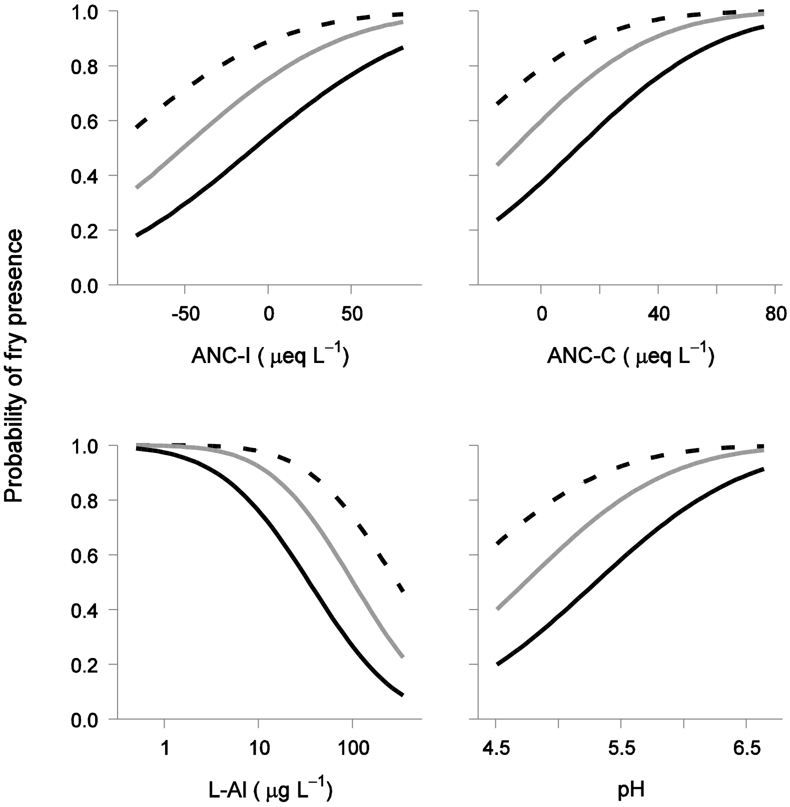


Linear regression of WFD-AWICsp verses pH at Welsh sites. Reference lines from the y-axis of Figure 28 are used to predict pH values.



Appendix 2
Probability of fry presence/Acid stressor relationships (from Malcolm et al 2012)

Probability of brown trout fry presence in at least one (dashed black line), two (grey line) or all three reaches (solid black) for a given chemical value assuming that three 50m reaches are fished using the same approaches as the AWMN.



Estimates of C80s, hydrochemical values giving an 80% probability of observing brown trout presence in at least one, two or three reaches, where three fifty metre reaches are fished using three pass electrofishing. Two-sided 90% confidence limits are given in brackets (prefixed by < or > if outside the range of the data).

	L-Al (□gL^{-1})	**pH**	**ANC-I (□eqL^{-1})**	**ANC-C (□eqL^{-1})**
Fry				
1 Reach	72 (39, 153)	5.0 (<4.5, **5.3**)	-28 (-73, 0)	1 (<-15, 15)
2 Reaches	26 (14, 48)	5.5 (5.1, **5.9**)	12 (-17, 46)	22 (7, 38)
3 Reaches	8 (3, 15)	6.1 (5.8, >**6.6**)	59 (29, >81)	46 (31, 69)
Parr				
1 Reach	always reached	always reached	always reached	always reached
2 Reaches	264 (61, >348)	4.9 (<4.5, 5.1)	-39 (<-63, -13)	-10 (<-13, 7)
3 Reaches	12 (<0.5, 48)	5.5 (5.3, 5.9)	19 (-6, 61)	28 (11, 58)