Nitrogen in water

Introduction

Nitrogen, usually in the form of nitrate, is one of the key elements required for plant growth. In water, high nitrate levels are one of the main reasons for eutrophication – the blooming of phytoplankton (small free-floating plants) and algae. Eutrophication results in a depletion of oxygen in water and can lead to death of fish and other aquatic animals.

Nitrogen is introduced to water usually as ammonia (from sewage) or nitrate (from agricultural fertilizer). Where there is ammonia in water, the ammonia is broken down to nitrate and nitrate by bacteria[1]. CRAG measures nitrogen in water using the following methods:

- Ammonia – test strips
- Nitrate – Hanna nitrate meter
- Nitrate and Nitrite – test strips

Standards for nitrogen in water – units of measurement

The Ammonia test strips that CRAG use actually measure the combination of ammonia (NH3) and ammonium (NH4+) in water. Ammonia (NH3) is the compound that is most detrimental to fish.

In water, ammonia and ammonium exist in a balance. The balance between ammonia and ammonium is determined by the pH, the salinity and the temperature of the water. pH has the largest impact on this balance, temperature and salinity have a relatively small impact. In the Coquet (fresh water and estuary), because the pH is generally high (between 7 – 9) and the temperature generally low (5 – 15 degrees centigrade), the level of ammonia is likely to be between 2%-3% and the level of ammonium between 97% - 98%. Therefore, for our purposes, we can assume we are measuring ammonium. When we mention ammonium below, we are referring to ammonium + ammonia.

Ammonium, nitrate (NO3) and nitrite (NO4) are measured using the above test strips and meter as mg/L (milligrams per litre, which is the same as ppm (parts per million)). The standards against which these measurements should be tested are either ammonium or ammonium as N, nitrate or nitrate as N and nitrite or nitrite as N. The difference between these descriptions is that the former descriptions are for the whole compound (i.e. ammonium, nitrate and nitrite are all chemical compounds) or just for the nitrogen within that compound. There are simple conversion equations between the compounds and the nitrogen in the compound:

- Convert ammonium to ammonium as N – multiply ammonium value by 0.78
- Convert nitrate to nitrate as N - multiply nitrate value by 0.226
- Convert nitrite to nitrite as N - multiply nitrite value by 0.304

Some standards are described as Dissolved Inorganic Nitrogen (DIN). This is the sum of ammonium as N +nitrate as N + nitrite as N.

[1] USA EPA – Nitrification (https://www.epa.gov/sites/default/files/2015-09/documents/nitrification_1.pdf)

Standards for nitrogen in water – impact of salinity

We have seen above that salinity has a small impact on the balance between ammonia and ammonium in water. However, salinity does have two larger impact that we need to consider:

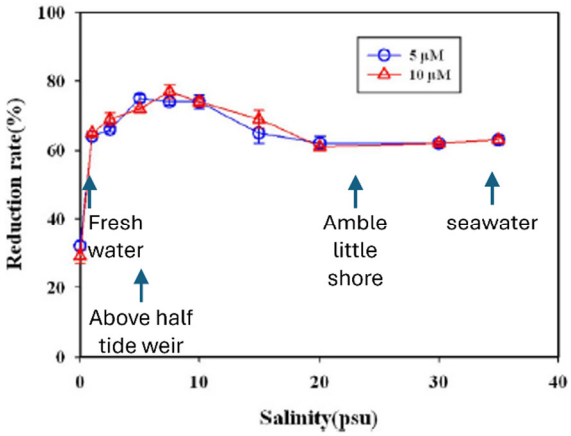
- Fish are affected by a lower level of nitrogen in saline water compared with fresh water. This is reflected by the lower standards set for nitrogen in saline water (see next section)
- Salinity has an impact on the readings from the Hanne nitrate meter that we use.

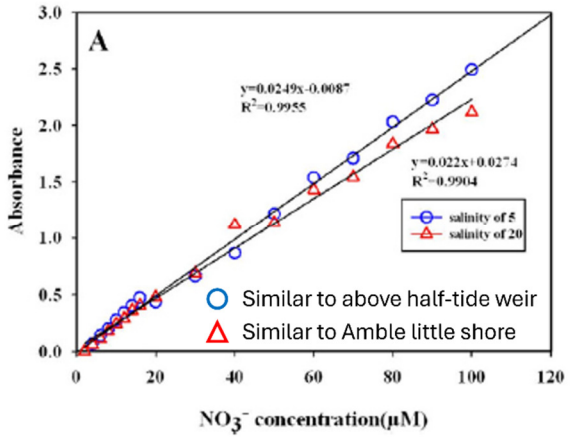
The Hanne nitrate meter that CRAG uses is specifically adapted for marine conditions. This means that the meter will measure the nitrate level correctly in seawater. When we measure nitrate levels in an estuary or in fresh water, the measurement will be less accurate.

The Hanna nitrate meter measures the reduction (removal of oxygen) as the nitrate (NO3) is converted to nitrite (NO2) using the zinc reduction method. This conversion results in a change in colour of a dye. It is this change in colour that is detected by the meter, and the amount of colour change is then converted to a nitrate measurement.

A scientific paper[2] illustrates (see graphs below) that the measurement of nitrate by the zinc reduction method in seawater and freshwater is about the same (reduction rate in first graph is about the same for seawater and freshwater). However, the measurement in estuarine water is about 20% higher. Thus, the Hanna meter that CRAG use might show a reading of 4 mg/L in a seawater sample, but a sample with the same amount of nitrate taken above the half-tide weir would read 5 mg/L. The graph on the right illustrates that this difference in the reading in estuary waters is consistent regardless of the actual nitrate concentration.

CRAG has been informed by the National Rivers Trust that the citizen science group on the River Kennet asked a local university to check the impact of salinity on readings from the Hanna nitrate meter. Their conclusions were similar. They found that readings in low salinity water was about 13% higher than in seawater.





[2] https://www.nature.com/articles/srep20165

Standards for nitrogen in water – national standards

So, given the variety of measurements that can be made and the various influences on measurement described above, what should CRAG used as the standards to indicate the level of nitrogen in the Coquet?

Various documents indicate standards that we should consider:

Ammonia as N (mg/L) in freshwater

- The Water Framework Directive[3] sets levels of High < 0.2 mg/L, Good 0.2-0.3 mg/L, Moderate 0.3-0.75 mg/L, Poor 0.75-1.10 mg/L, Bad >1.10 mg/L for freshwater rivers with low alkalinity (tributaries upstream of Felton, excluding those that are SSSI). And High < 0.3 mg/L, Good 0.3-0.6 mg/L, Moderate 0.6-1.10 mg/L, Poor 1.10-2.25 mg/L, Bad >2.25 mg/L for tributaries downstream of Felton.
- Standards for SSSI stretches of the river (main river down to the Warkworth dam, Alwin burn and parts of the Wreigh burn) are Good < 0.25 mg/L, Bad > 0.25 mg/L[4]
- The US Environmental Protection Agency sets a standard for ammonia based on toxicity of ammonia to fish. A University of Dundee scientist has used this standard to calculate pH-dependent standards that can be used for the UK salmonid waters[5]. This is not depended on temperature or salinity (i.e. this standard is suitable for freshwater, estuaries and seawater) but is dependent on pH (only the range of pH we expect to find in the Coquet are shown here, standards for lower pH are shown in the paper). The standards are:
    - pH = 8: Good < 0.67 mg/L, Bad > 0.67 mg/L
    - pH = 7.5: Good < 2.0 mg/L, Bad > 2.0 mg/L
    - pH = 7.0: Good < 6.56 mg/L, Bad > 6.56 mg/L

Dissolved inorganic nitrogen (DIN) as N (mg/L)

- The Irish Environmental Protection Agency[6] sets standards for DIN (ammonia and ammonium as N + Nitrate as N + Nitrite as N) for:
    - Fresh water: Good < 2.6 mg/L, Bad > 2.6 mg/L
    - Estuaries: Good < 1.4 mg/L, Bad > 1.4 mg/L
    - Seawater: Good < 0.25 mg/L, Bad > 0.25 mg/L
- The Water Framework Directive[3] sets standards for DIN in transitional (estuary) and coastal waters. Their standards depend on the turbidity of the water. Assuming that the water at Amble is not turbid, the standards for DIN are: High < 0.74 mg/L, Good 0.74-1.12 mg/L, Moderate 1.12-1.67 mg/L, Poor 1.67-2.51 mg/L, Bad >2.51 mg/L[7]

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[3] Water Framework Directive (https://www.legislation.gov.uk/uksi/2017/407/contents)
[4] Common Standards Monitoring Guidance for Rivers (https://jncc.gov.uk/our-work/common-standards-monitoring-guidance/)
[5] Ammonia toxicity in fish (https://www.noaa.gov/sites/default/files/legacy/document/2020/Oct/07354626285.pdf)
[6] Irish EPA – Water quality in 2023 (https://www.epa.ie/publications/monitoring--assessment/freshwater--marine/water-quality-in-2023.php)
[7] These standards are derived using an equation of the relationship between salinity and DIN, and assume that estuarine waters have a salinity of 25-35 ppt. If the salinity of the estuary at our test points are lower than 25ppt, we should consider recalculating these standard values.

Nitrate (mg/L) in freshwater

- The UK Nitrate Pollution Prevention Regulations[8] indicate that water is considered to polluted for drinking water when the level of nitrate is > 50 mg/L. This value comes from the World Health Organisation[9]
- The US Environmental Protection Agency[10] used a lower value of 44.3 mg/L (or 10 mg/L nitrate as N) as the standard for drinking water
- The Irish EPA[5] uses much lower targets for nitrate in freshwater High < 4 mg/L (<0.9 mg/L nitrate as N), Good 4-8 mg/L (0.9-1.8 mg/L nitrate as N), and unsatisfactory > 8 mg/L (> 1.8 mg/L nitrate as N)
- Martyn Kelly (who worked for many years with UKTAG) in his article 'This is not a Nitrate standard…'[11] comes up with values not too dissimilar from those of the Irish IPA. Martyn's values vary depending on the altitude and the alkalinity of the river. For our purposes, we have assumed that Rothbury is the cut-off – upstream of Rothbury the altitude is > 185m and the alkalinity is approximately 50 mg/L[12] (relatively soft water); downstream of Rothbury is low altitude and alkalinity is approximately 100 mg/L[12] (moderately hard water). The alkalinity is some parts of the Hazon and Tyelaw burns are over 200 mg/L. Using Martyn's values (for total oxidised nitrogen = nitrate as N + nitrite as N):
    - Upstream of Rothbury - High < 0.7 mg/L, Good 0.7-1.2 mg/L, Moderate 1.2-1.9 mg/L, Poor 1.9-3.0 mg/L, Bad >3.0 mg/L
    - Downstream of Rothbury (excluding estuary) - High < 1.5 mg/L, Good 1.5-2.4 mg/L, Moderate 2.4-3.7 mg/L, Poor 3.7-6.0 mg/L, Bad >6.0 mg/L

Considering these possible standards, CRAG will use the following standards[13].

Total Ammonia (As measured using the Ammonia test strips). Note: These test strips measure total ammonia – the values need to be converted to Ammonia as N for comparison with these standards.

- SSSI stretches of the river (main river down to the Warkworth dam, Alwin burn and parts of the Wreigh burn; using SSSI guidance) - Good < 0.25 mg/L, Bad > 0.25 mg/L
- Tributaries upstream of Felton, excluding those that are SSSI (using the Water Framework Directive) - High < 0.2 mg/L, Good 0.2-0.3 mg/L, Moderate 0.3-0.75 mg/L, Poor 0.75-1.10 mg/L, Bad >1.10 mg/L

[8] Nitrate Pollution Prevention Regulations (NPPR) (https://www.legislation.gov.uk/uksi/2015/668/contents)
[9] WHO fact sheet on nitrate (https://www.who.int/publications/m/item/chemical-fact-sheets--nitrate-nitrite)
[10] US EPA – Nitrification (https://www.epa.gov/sites/default/files/2015-09/documents/nitrification_1.pdf)
[11] This is not a Nitrate standard (https://microscopesandmonsters.wordpress.com/2016/12/18/this-is-not-a-nitrate-standard/)
[12] According to the Environment Agency WIMS data
[13] CRAG will test the salinity of tributaries near Warkworth and Amble (the Birling beck, The Gut and the Guilders burn before deciding whether measurements from these tributaries should be compared with the freshwater or estuary standards.

- Tributaries downstream of Felton (using the Water Framework Directive) - High < 0.3 mg/L, Good 0.3-0.6 mg/L, Moderate 0.6-1.10 mg/L, Poor 1.10-2.25 mg/L, Bad >2.25 mg/L
- The estuary (using the pH-based standards for fish toxicity from the US Environmental Protection Agency and University of Dundee):
    - pH = 8: Good < 0.67 mg/L, Bad > 0.67 mg/L
    - pH = 7.5: Good < 2.0 mg/L, Bad > 2.0 mg/L
    - pH = 7.0: Good < 6.56 mg/L, Bad > 6.56 mg/L

Nitrate in freshwater (as measured using the test strips or nitrate meter). Note: these tests measure nitrate – the values should be converted to Nitrate as N for comparison with these standards.

- Freshwater (using the Martyn Kelly's targets):
    - Upstream of Rothbury - High < 0.7 mg/L, Good 0.7-1.2 mg/L, Moderate 1.2-1.9 mg/L, Poor 1.9-3.0 mg/L, Bad >3.0 mg/L
    - Downstream of Rothbury (excluding estuary) - High < 1.5 mg/L, Good 1.5-2.4 mg/L, Moderate 2.4-3.7 mg/L, Poor 3.7-6.0 mg/L, Bad >6.0 mg/L

Dissolved inorganic nitrogen (DIN) in the Coquet estuary. Because there are no nitrate standards for estuary conditions, we recommend using a measurement of DIN and comparing these measurements against the standard set by the Irish EPA. Until we can measure the salinity and turbidity of our test sites over a season, we feel it would be unwise to use the WFD standards.

CRAG will measure DIN by adding the nitrate measurement (from nitrate meter or nitrate test strips) with the Ammonia measurement (using the Ammonia test strips). These tests measure Total Ammonia and Nitrate. The amount of Nitrite will be small and so can be ignored for our purposes. These measurements will need to be converted to Ammonia as N and Nitrate as N before the calculation of DIN and the comparison with this standard.

- Estuaries: Good < 1.4 mg/L, Bad > 1.4 mg/L

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