1. Field collection and transportation to the laboratory

1.1. Samples are labelled in a clear manner that is durable and given an identifier that records the site, date and time that the sample was collected.
1.2. Samples are protected, sealed and kept at 4^{o}C in the dark in cool boxes for transportation to the laboratory.
1.3. A 'chain of custody' is established that records the sample handler, sample collection time, number of samples taken and time delivered to the lab. The count of sample containers received in the lab is verified against the chain of custody.

2. Quality Assurance

Procedures are in place to monitor the effectiveness of sampling methodology, demonstrate sampling errors have been controlled adequately and to give an indication of the error encountered as a result of the variability of the sampling. This is done by regular collection of replicate samples as a check on the precision of sampling, the use of field blank samples to monitor sources of sample contamination and the use of spiked samples as quality controls to assess sample stability during transport and storage.

3. Sample handling, filtration and analysis procedures

3.1. Each sample is booked and given a lab identifier for use in all procedures.
3.2. Samples are tightly sealed and stored at 4^{o}C in the dark before analysis.
3.3. The maximum storage time for a sample before analysis is stated in the Standard Operating Procedure for each analytical method. These are as follows:
   a. All samples are filtered on arrival at the laboratory according to the methods outlined in 3.5 below.
   b. All samples for inorganic nutrient analysis are first filtered, then analysed within 24 hours of collection. For soluble reactive phosphorus (PO4-P), analyses are only completed on samples which are less than 24 hours old on collection as this fraction is unstable.
   c. All samples for DOC (NPOC) analysis are filtered and acidified to pH 2, stored at 4^{o}C in the dark until analysis, with all analyses completed within 7 days of sample collection
   d. All samples for particulate and organic nutrient analysis are digested and analysed within 7 days of collection.
   e. All repeat digests and analysis identified within the QA process are re-digested within 7 days of collection, with analysis repeated within a further 3 days.
3.4. All samples are brought to room temperature before analysis.
3.5. Samples are collected in a 500 ml bottle. On arrival in the laboratory:
3.6. 400 ml of each sample is filtered through a pre-washed, dried (105^{o}C, 24 hours) and weighed, 0.45 μm cellulose membrane filter, with the filter paper dried at 105^{o}C for 24 hours before being re-weighed to determine suspended sediment concentration.
3.7. The filtrate on all samples is analysed within 24 hours of collection to determine all inorganic N (TON, NH_4-N) fractions.
3.8. The filtrate on the 7th sample (collected fresh on the day of the weekly field visit) is analysed within 24 hours of collection to determine the soluble reactive P (PO_4-P) concentration.
3.9. The remainder of the filtrate is set aside for digestion using persulphate oxidation to determine the total dissolved N (TDN) and total dissolved P (TDP) concentration in each sample. A duplicate digestion and analysis is conducted on every tenth sample.

3.10. 50 ml of the original 500 ml sample is filtered within 24 hours of collection through a 0.7 μm Whatman GFF filter and acidified to pH 2 for subsequent determination of DOC concentration by the NPOC method. with a duplicate analysis on every tenth sample

3.11. The remaining 50 ml unfiltered subsample is set to one side for subsequent digestion using persulphate oxidation under high temperature and pressure to determine the Total N (TN) and Total P (TP) concentration in that sample. A duplicate digestion and analysis is conducted on every tenth sample.

3.12. The difference between the TN and TDN sample gives the particulate organic N (PON concentration). The difference between TP and TDP gives particulate P (PP). The difference between TDN and the sum of the inorganic N species (TON, NH_4-N) gives the dissolved organic N (DON) concentration, while the difference between the SRP and TDP concentration gives the soluble unreactive P (primarily dissolved organic P or DOP) concentration. Where the calculated fraction concentrations lie between zero and the limit of detection for the analytical instrument and procedure, the concentration is recorded as zero. Where the calculated fraction concentration is negative, the digestion and analysis steps are repeated for all fractions.

4 Reagents and standards

4.1 All glassware and plastic ware is soaked for 24 hours in 10% HCl then rinsed at least 3 times with Milli-Q water and air dried before use.

4.2 Analytical grade reagents are used to make up standards.

4.3 Fresh standards are made according to the Standard Operating Procedure for each analytical method.

4.4 Where probes are used they are rinsed with Milli-Q in between measurements.

4.5 Field sensors are cleaned weekly with a toothbrush to remove biofilms

5. Precision and Accuracy

5.1 Each method is tested with a series of blank measurements to determine the limit of detection due to noise on the signal etc. The standard deviation of the data is multiplied by 3 to give the 3 Sigma limit of detection.

5.2 Multiple analysis of a bulk sample of river water is used to ascertain the ratio of standard deviation (r.s.d.).Here r.s.d. should be < 2%. However for methods involving highly corrosive digests running through analytical instruments we accept a r.s.d of < 10%. These values are quoted in the appropriate Standard Operating Procedure.

5.3 Reference materials are used in every run of each instrument to check the calibration and to provide a record of analytical performance. For known values this would be expressed as:

- *(Measured value-Known value)/ Known value* 100*
- Within a run the tolerance allowed would be 5%.
- For agreement between different batches of Analyte we would expect better than 10 %.

5.4 QA controls use the reference recoveries to pass the instrument ready for analysis. Only results from passed criteria are quoted. These values are quoted in the appropriate Precision and Accuracy section of the Standard Operating Procedure.