Exercise 2: Aquatic carbon dynamics in UK springwaters: field and laboratory techniques

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Lesson objective

To use field data collected from upland headwaters or groundwater springs to understand how rivers export carbon from the soil to the sea, and how some of it is lost via the release of greenhouse gases to the atmosphere along the way. These processes may then be linked to changes in streamwater acidity (pH).

Setting the scene

Rivers transfer huge quantities of dissolved carbon towards the world's oceans, but not all of it gets there. This is due to the release of carbon from the water directly to the atmosphere, a process that formed the basis of the Data Exercise "*Aquatic carbon dynamics in the Amazon River Basin: inputs of CO_2 to the atmosphere*. Both these pathways can be explored easily in a combined field and laboratory class, especially if students have access to either: i) upland waters draining peatland; or ii) alkaline groundwater springs emerging from chalk or limestone aquifers.

This lesson plan is designed for both these scenarios. It is expected that access to suitable sites is feasible over transect distances of no more than 1 km and very close to the source with few tributaries. Because CO_2 is a weak acid when dissolved in water, you can try prospecting for such a site using a pH meter. If you record pH changes of about 1 unit, then you have seen an order of magnitude change in acidity, making the site ideal. Also, sites where there is turbulence (riffles, water falls) will greatly enhance the pH change because CO_2 transfer into or out of the water (known as the *gas transfer velocity* in Exercise 1) will be enhanced. Figure 1 shows an example.
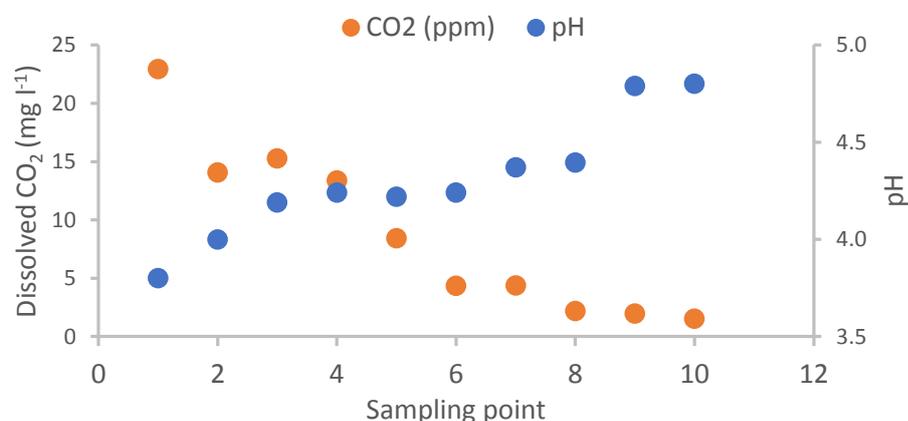

Figure 1. *Typical downstream changes in pH and CO_2 content of an acidic upland stream (Lady Canning's Plantation, at 53°20.35N and 1°34.84W). The distance covered between sampling points was ca. 1 km.*

Water samples can be analysed using simple titration and pH change (or a pH indicator). This means expensive CO_2 analysers are not necessary. Titration ideally requires volumetric glassware (50 mL burette, 25 mL pipette, 150 mL conical flask) and an appropriate titrant (e.g. weak solution of HCl). However, it can be achieved using a beaker and a syringe.

By combining measurements of water discharge with concentrations of carbon, through basic equations, students can learn how to estimate the masses of carbon released to the atmosphere, or exported towards the sea in dissolved form. However, if such measurements are not possible, then a carefully chosen site with no tributaries can allow immediate estimation of the proportions (rather than actual quantities) of total inorganic carbon exported this way.

Theory
Dissolved CO_2 can escape from rivers and lakes after entering them in some form of Dissolved Inorganic Carbon. This is because:

$$DIC = CO_{2\ (aq)} + H_2CO_{3\ (aq)} + HCO_{3\ (aq)}^- + CO_{3\ (aq)}^{2-}$$ **(Eq1)**
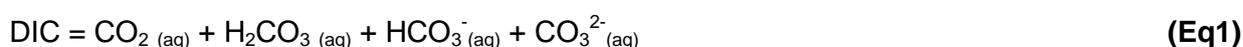
Where H_2CO_3 is called carbonic acid, HCO_3^- is bicarbonate and CO_3^{2-} is carbonate. In reality, it is best to "lump" together $CO_2(aq)$ and H_2CO_3 because they both effectively represent the same entity: dissolved Carbon Dioxide. The other forms represent what CO_2 would become if the pH of the stream increased, for example after groundwaters enter the river further downstream. The relationship between the different forms of DIC and pH is shown in Figure 2. Remember: headwaters tend to be acidic (left hand side) and groundwaters tend to be alkaline. Therefore alkaline groundwaters are less likely to release CO_2 than headwaters. In fact they can even absorb CO_2 following emergence.
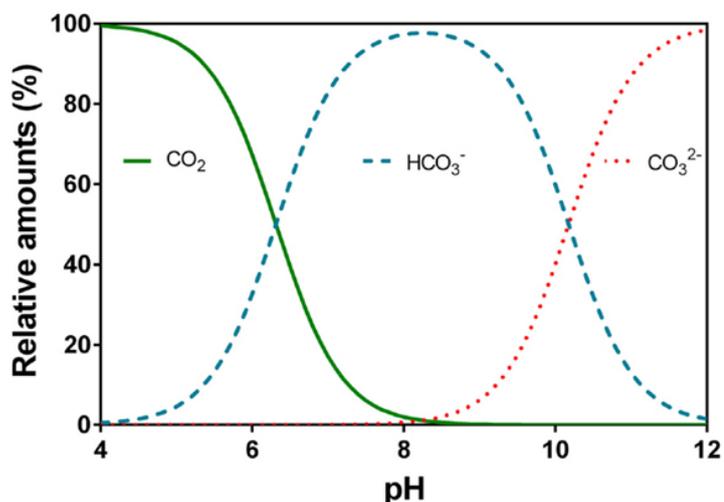
Figure 2. The distribution of Dissolved Inorganic Carbon with pH (Sourced from Freeware: http://www.iq.usp.br/gutz/Curtipot.html)

Task 1. Field work: downstream sampling and measurement of pH

Find the source of your spring and plan your sampling points. You should ideally record the downstream changes with between five and ten points. Expect the rate of change to be greatest at the start, because the water that first emerges is furthest from equilibrium with the atmosphere (Le Chatelier's Principle). Therefore, the readings of pH should become more stable as you head downstream.

At each sampling point, collect a pH reading using a calibrated meter, take a water sample (50 – 200 mL volume best) by filling a bottle up to the brim and putting the lid on underwater if possible (i.e. no air in the bottle) and describe the site and any relevant upstream features such as obvious places where soil waters can or cannot enter the stream). Turbulent water will equilibrate more rapidly than gently flowing water, so describe the channel.

If you do not have many pH meters, make it the responsibility of one group to measure it carefully at each site, whilst other groups can be tasked with the sampling, description/map orientation and discharge measurements. An alternative is that you measure the pH in the lab on the sample bottle, but this is really only recommended if you can keep them in a fridge.

The first thing to do after the field sampling is to appraise the downstream pH changes. A quick plot of location number (1 is upstream, successive numbers downstream) against pH should be examined. Also, make sure all the samples are well-labelled (write it twice on the bottle, before you use it), and keep them in a bucket of water to prevent warming. Warming up your samples is a disaster! Think about a fizzy drink going flat: it's much quicker once taken out of the fridge and opened.

To establish the downstream changes in inorganic carbon content, refer to the laboratory section below.

Note: if you are keen to teach the use of GPS, then this is another important task. Recording the position in UTM units is advised, since the positions can be imported straight into a spreadsheet and the units are metres. This can facilitate putting distance on the X axis of your graphs.

Task 2. Laboratory analysis of dissolved inorganic carbon using titration

We seek to estimate the total dissolved inorganic carbon (DIC) of your water sample. The proportion of DIC that is CO_2 is worked out afterwards. The readily available techniques are:

a) Estimation of inorganic carbon by direct acidimetric titration because the pH is 5 or above in all your samples

b) Estimation of inorganic carbon by acidimetric titration after addition of alkalinity, because the pH of your samples is below 5.

c) Use of a gas or total carbon analyser;

Most schools are without analysers (cost: ca. £4000 - £30000) and so the recommendation is to follow Procedure A) for groundwater springs (especially draining limestone rocks) and B) for acidic peatland waters (e.g. Figure 1). Procedure c) is therefore absent below, but instructions are available from the author.

If your samples range from below pH 5 to 6 or more, the recommendation is to follow Procedure A. However, if most sample pH values lie below 5 but a few are above, use Procedure B. Stick to one method if at all possible.

Procedure "A" for sample pH values greater than 5

Theory: This method involves the neutralisation of alkalinity in a fixed sample volume by an acid solution of known concentration. Thus the more acidity required, the greater the alkalinity present. The alkalinity is assumed to be entirely due to inorganic carbon (HCO_3- and CO_3^{2-}), which is a reasonable assumption in most dilute surface waters. We will neutralise the sample pH to a value of 4.5 (at which HCO_3 is no longer present) by using BDH Mixed Indicator solution or a pH meter. Thus the solution will change colour from dark blue/grey to colourless. If your solution becomes an orangey-pink colour, you have added too much acid.

Equipment: 100 ml conical flask
                50ml burette and retort stand
                25 ml safety pipette
                pipette dropper
                pH meter (or use indicator solution)

Reagents: 0.01 M HCl (Use safety glasses and gloves)
                BDH mixed indicator solution.

Procedure with indicator

- Use clean glassware and then rinse 25 ml pipette with sample water.

- Pipette 25 ml of sample into clean conical flask

- Add two or three drops of BDH mixed indicator and swirl gently

- Position conical flask under the burette containing the acid solution and note the initial volume of acid in the burette. Decant the acid solution slowly into the conical flask, swirling gently and trying to control the flow of acid and to avoid spillage.

- When the indicator begins to change colour, reduce the burette flow to drop-by-drop. When the indicator goes clear, stop titrating (if the indicator goes pink, you have passed the endpoint – start again!)

- Note the final volume in the burette.

Procedure with pH meter

- Rinse 25 ml pipette with sample water.

- Rinse conical flask once with deionised water and once with sample

- Pipette 25 ml of sample into conical flask

- Record the pH after allowing to stablilise

- Position conical flask under the burette containing the acid solution and note the initial volume of acid in the burette. Decant the acid solution slowly into the conical flask, swirling gently and trying to control the flow of acid and to avoid spillage.

- Record the volume of acid required to produce a stable pH of 4.5.

You can optimise the process by using more or less sample

Calculations:

First we calculate Dissolved Inorganic Carbon or "DIC" and then we establish the proportion of that would have been present as dissolved CO_2. The concentration of acid (C_{acid}) used to titrate the samples, the volume used (V_{acid}) and the volume of the sample (V_s) are all that is required:

DIC = (C_{acid}.V_{acid})/V_s   **(Eq2)**

Using the volume measurements in mL and concentrations in millimoles per litre (mM) given above means:

DIC = (10 x V_{acid})/25   **(Eq3)**

Which means the DIC concentration unit is millimoles per litre (or "mM").

With more concentrated samples, a small correction is required for the volume of acid added and the fact that the end point of 4.5 is not entirely accurate. Don't do this if it results in negative numbers:

final DIC = concentration derived above in mM – 0.0316 - (0.0316 x V_a/25)   (Eq4)

Finally, if you don't like mM units, then convert to mgC/L by multiplying the result by 12.

Procedure "B" for sample pH values lower than 5

Theory: This method involves titration using NaOH up to an end-point pH of 8.3. The end point can be determined by a different indicator solution or by a pH meter once more. Some caution is required in order to prevent CO_2 from the atmosphere entering the solution. Therefore use of fresh, boiled lab water to make the NaOH immediately before titration is recommended. Fixing a soda-lime scrubber on top of the burette then helps avoid CO_2 from the atmosphere interfering during the analysis, but you could also use a syringe to add the NaOH to the sample instead, making this much simpler (though less accurate volumetrically). Also make sure all sample bottles are filled underwater during sampling, so that no air space is present - and don't let the sample warm up (cool them down if you like by using a fridge or cold water bath).

Equipment: 100 ml conical flask
                          50ml burette and retort stand (or you can use a graduated 50 mL syringe)
                          25 ml safety pipette
                          pipette dropper
                          pH meter (or use indicator solution)
                          Parafilm or similar
                          Old 20 mL syringe (without plunger) filled with Soda Lime

Reagents: 0.01 M NaOH. Prepare this fresh using boiled lab water that was poured into a gas-tight plastic or glass bottle and filled to the top.
                          Phenolpthalein indicator (turns from clear to pink at pH endpoint of 8.3)

- Make a CO_2 scrubber by taking a syringe and discarding the plunger. Add some cotton wool (about 5 mL) and then add ca. 20 mL of soda lime. The put in more cotton wool and put a film over the top. Perforate the film a couple of times.

- Clean a 50 mL burette and fill with NaOH solution and add the CO_2 scrubber to the top. Seal with the film (or tape) so that as the solution is drawn down, all air coming into the burette goes through the scrubber.

- Rinse 25 ml pipette with sample and decant into a clean conical flask. Take sample straight from fridge and add 25 mL to the flask using the pipette. If you like, use a syringe.

- Add several drops (up to 10) of phenolpthalein indicator. It should not turn pink – if it does, use the method described as "Procedure A" above.

- Position conical flask under the burette containing the Sodium Hydroxide solution and note the initial volume in the burette. Decant the solution slowly into the conical flask, swirling gently and avoiding spillage.

- When the indicator begins to change colour, reduce the burette flow to drop-by-drop. When the indicator goes pink, stop titrating and note the final volume in the burette.

    You can optimise the process by using more or less sample

Calculations:
First we calculate Dissolved Inorganic Carbon or "DIC" and then we establish the proportion of that would have been present as dissolved CO_2. The concentration of alkali (C_{alk}) used to titrate the samples, the volume used (V_{alk}) and the volume of the sample (V_s) are all that is required:

DIC = ($C_{alk}.V_{alk}$)/V_s   **(Eq5)**

Using volume measurements in mL and concentrations in millimoles per litre (mM), then:

DIC = (10 x V_{alk})/25   **(Eq6)**

Which means the DIC concentration unit is millimoles per litre (or "mM").

If you don't like mM units, then convert to mgC/L by multiplying the result by 12.

Health and Safety notice:
(COSHH ASSESSMENT OF ASSOCIATED HEALTH RISKS SHOULD BE UNDERTAKEN)

SUBSTANCES INVOLVED:	PRECAUTIONS TO BE TAKEN:
Phenolpthalein Indicator	Wear safety glasses, lab. coat and gloves. Avoid breathing vapour.
NaOH	Wear safety glasses, lab. coat and gloves
Soda lime	Wear safety glasses, lab. coat and gloves

Calculating the proportion of DIC that is CO_2

Figure 2 shows that pH can control the distribution of DIC among the various forms that include CO_2. Temperature also exerts an effect, not least because gases are typically more soluble at low temperature. Both the pH and the temperature are therefore required to calculate the proportion of DIC that is CO_2 (and H_2CO_3).

To avoid complex thermodynamic calculations with the students, open the Excel spreadsheet 'Dissolved CO2 calculator'. Enter a sample name, the pH, temperature and DIC (in mM) concentration. The results will be displayed on the right hand side in mM, mgC/L and as a percentage of the total DIC. Note that the coefficients are temperature dependent, and so a look-up table is provided.

Task 3. Combining concentration and river flow measurements to estimate fluxes

Fluxes of CO_2 and DIC transported by the river may be calculated directly by multiplying the river discharge (usually in L/s for small streams) and concentration (it is best to use mgC/L). The resultant units are mgC/s transported by the river.

Note that if you have studied a reach of river with no tributaries or appreciable inputs from soil or ground water (an assumption that is usually best during low flow conditions), then changes in the CO_2 and DIC fluxes between the start and end of your transect can most likely be attributed to exchange across the air-water interface (i.e. outgassing or drawdown of CO_2). Note that in slow moving lowland streams, internal biological processes might also contribute (such as photosynthesis). The exact quantity transferred across the water-air interface can be estimated by

subtracting the up and downstream fluxes and then multiplying the difference by the time taken for water to flow between them.

Web-based resources

An excellent web resource for calculating carbonate alkalinity from a range of pH and acid volume additions is available at:

http://or.water.usgs.gov/alk/

This site allows you to input several pH and acid volume additions and use more complex calculations to estimate HCO_3^- and CO_3^{2-} (the latter being significant at high pH levels). It is therefore a potential replacement for Procedure A.

Tips for using web alkalinity calculator:

- Record the initial pH of the sample and then add acid until you have a pH of 5.5, then 4.5. The latter enables a fixed endpoint calculation (rather like using the indicator, which should turn at the same pH of 4.5). The former stage (pH 5.5) will help you use a range of other methods (e.g. Gran method) in the Web Alkalinity Calculator.

- Then add acid in order to depress the pH by three (or more is better) successive increments of, say, 0.3 pH units. This is to get a few data points around the point of inflection of the buffering curve (ie the pH – volume of acid added curve). You should stop when the pH has dropped to about 3.4, even sooner (say pH 4) if you are using just the inflection point method.

- The above procedure is slow, so, for a large sample batch save time by simply recording the acid required to depress the pH to 4.5. The relationship between this quick method and the more protracted one can be deduced later and an empirical correction applied if necessary.