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Modelling carbon fluxes in a constructed wetland

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Abstract

Research at the University of Leeds on the Pelenna wetland situated at Tomawr (north east of Port Talbot in the Pelenna catchment) is seeking to develop a carbon budget model of the wetland using carbon isotope data from a two-year field study. Measurements are made of the concentration and $\delta^{13}C$ *of the total dissolved inorganic carbon (TDIC) inlet, outlet, and surface waters from the wetland, and the* $\delta^{13}C$ *of the carbon-bearing solid phases in the wetland (limestone and organic matter). Values can be used to calculate the rates of organic matter consumption and gaseous* CO_2 *flux, and the carbon budget model uses these to estimate the life time of the wetland.*

This paper presents the carbon model and details the calculations for the separate carbon fluxes. The model is then validated using data taken in July 1999 and calculates the carbon mineralisation rate and net diffusion fluxes which were compared to direct CO_2 *flux measurements taken in April 2002. The data show that the model calculated flux had a range of 500 to 1250 g of C/day compared to the* CO_2 *field measured flux. Therefore the model gives a realistic estimate of the* CO_2 *flux to the atmosphere, and other fluxes in the system.*

Key words: acid mine drainage, budget, carbon, constructed wetland, flux, isotopes

INTRODUCTION

The use of constructed wetlands as a biogeochemical system for the treatment of acid mine drainage has developed rapidly over the last few decades in North America and worldwide (Hammer 1989). However, wetland studies have primarily concentrated on input/output analysis, and the processes occurring within wetlands are largely unknown (although probably dominated by microbes) and unquantified. These microbial processes require an organic matter substrate as their energy source and the long-term sustainability of the wetland will depend on the resupply of the metabolisable organic matter.

Unlike many dissolved species which remain in solution or are retained in the wetland, carbon can potentially be lost from the wetland system as CO_2 to the atmosphere. This paper seeks to produce a full carbon mass balance for a wetland system in order to evaluate its long term sustainability.

Carbon isotopic compositions can be used to identify sources of carbon and this is valuable in distinguishing between carbon derived from organic matter (isotopically light) and carbon derived from carbonate sources (isotopically heavy) (Drever 1997). In general, wetlands contain two primary sources of carbon:

1. dissolution of calcite, aragonite or dolomite from limestone, which introduces relative heavy carbon into the system;
2. oxidation of organic matter, which introduces relatively light carbon.

SITE DESCRIPTION

The Pelenna wetland system is situated in the River Pelenna catchment, north east of Port Talbot in west Glamorgan, south Wales. The area has a long history of coal mining which ceased in the early 1960s. The Environment Agency estimated that in the 1990s approximately 17 km of the water courses in the Pelenna catchment had been adversely affected by acid mine drainage. As a result of this, West Glamorgan County Council and the National Rivers Authority constructed the wetland system. One part of the system is

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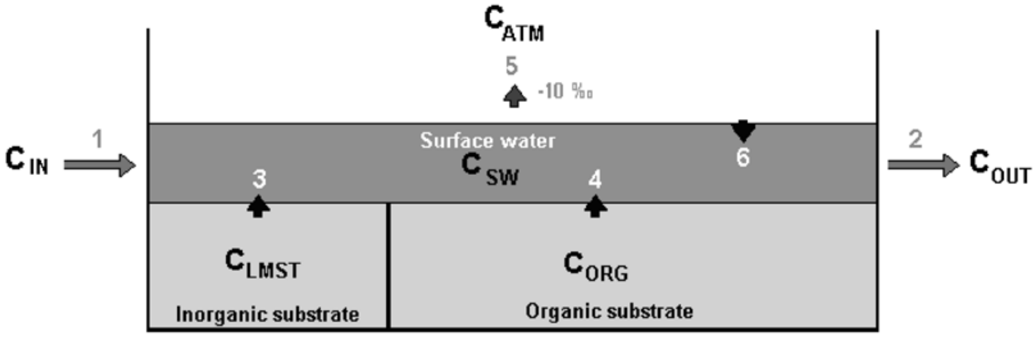

Figure 1. Schematic model of fluxes occurring in the wetland system (terms in brackets refers to the equations below)

Whitworth No. 1 wetland which is a constructed wetland consisting of four cells. Cells 1 and 4 contain bark mulch as substrate and cells 2 and 3 contain mushroom compost. Cells 1 and 3 were planted with *Typha* species and cells 2 and 4 with *Juncus* species. Average inlet mine water concentrations (from 1995 to 2002) into Whitworth No. 1 wetland were 6.9 pH, 65 mg/L alkalinity and 3.8 mg/L total Fe. Each cell was designed to treat flows in the range 510 m^3/day.

MODELLING OF CARBON FLUXES

A schematic model of the fluxes occurring in a wetland cell was constructed (Figure 1):

Where flux 1 = DIC in the inflow (C_{IN})
2 = DIC in outflow (C_{OUT})
3 = DIC from limestone dissolution (C_{LMST})
4 = DIC from mineralisation of organic substrate (C_{MIN})
5 = exsolution of CO_2 to atmosphere (C_{EXS})
6 = dissolution of CO_2 to surface water to form HCO_3^- (C_{DIS})

Dissolved inorganic carbon (DIC) enters the wetlands in the inflow (C_{IN}). DIC is generated by limestone dissolution (C_{LST}) within the bed and mineralisation of organic substrate (C_{MIN}). Inflow DIC are balanced by outflow of DIC (C_{OUT}) and any net loss (by exsolution) of CO_2 to the atmosphere (C_{EXS}). Since P_{CO2} is higher in the surface waters, ~ $10^{-1.6}$, than the atmosphere at $10^{-3.5}$ the flux will be from the water surface to the atmosphere. This gives:

$$C_{MIN} = C_{OUT} + C_{ATM} - C_{IN} - C_{LST} \qquad (1)$$

C_{IN} and C_{OUT} are measured directly (from water samples taken in the field) and C_{LST} can be calculated from the increase in Ca concentration between the influent and outflow waters. If C_{ATM} can be estimated therefore, C_{MIN} can be calculated. A further mass balance constraint is available if the isotopic compositions of the different carbon fluxes are considered.

$$C_{MIN} \cdot \delta_{MIN} = C_{OUT} \cdot \delta_{OUT} + C_{EXS} \cdot \delta_{EXS} - C_{DIS} \cdot \delta DIS - C_{IN} \cdot \delta_{IN} - C_{IN} \cdot \delta_{IN} - C_{LST} \cdot \delta_{LST} \qquad (2)$$

The net flux of CO_2 to the atmosphere can be considered as the sum of the exsolution (C_{EXS}) and dissolution (C_{DIS}) of CO_2, since they are associated with opposite isotopic effects and compositions. Dissolution of CO_2 into water to form HCO_3^- (the dominant species present) carries a –10‰ fractionation (e.g. Cerling 1984), so δ_{DIS} is 10‰ enriched relative to atmospheric CO_2 at –8‰, so $\delta_{DIS} = +2$‰. Exsolution of CO_2 carries the opposite fractionation,

$$\text{so:} \quad \delta_{EXS} = \delta_{TDIC} - 10 \qquad (3)$$

Surface water TDIC (δ_{TDIC}) is calculated as the mean of the measured input (δ_{IN}) and output (δ_{OUT}) values (Table 1).

There is no fractionation between the carbon isotopes during dissolution of limestone or mineralisation of organic matter; δ_{MIN} and δ_{LST} are taken as the means of the organic carbon and limestone $\delta\ ^{13}C$ values from the wetland core samples. The carbon mass balance and isotopic mass balance equations can be plotted in terms of the two unknowns (C_{MIN} and C_{AIR}) and their intersection defines these two carbon fluxes at the time of measurement.

Field samples were taken to test the validity of the model.

SAMPLING AND FIELD MEASUREMENTS FOR CARBON MASS BALANCE EXPERIMENT

500 mL air tight plastic bottles were acid washed (with concentrated KNO_3 and HCl solution) and dried. Fifty mL of alkaline $SrCl_2$ solution was added to each bottle, acting as a fixing agent for the removal of dissolved HCO_3^- and CO_2 as solid $SrCO_3$ (Bishop 1990). Water samples for isotope analysis were taken from the inlet and outlet of cell 3, as well as for ICP and Dionex analysis to measure for the major cations and anions. The pH, conductivity and alkalinity were also measured in the field. Flow rates were measured at the inlet to cell 3 by timing the length of time to fill a 10 L bucket. This was repeated three times with an average flow (L/sec) calculated. Flow rate could not be measured at the outlet, due to over engineering of the outlet channels.

Direct measurements of CO_2 fluxes

CO_2 was measured in the field using a CO_2 measuring device originally tested in the laboratory. Using scaffolding poles, two plastic boxes (dimensions: 1 m × 0.8 m × 0.35 high) were suspended over the top right hand corner of cell 3, Whitworth No. 1 wetland, on a sledge system. Plastic piping connected the plastic boxes to the CO_2 measuring device. The boxes were connected to glass sparging apparatus containing NaOH as a CO_2 trapping solution, and the pump was connected to the flow meters. The flow meters were then connected to the inlets on both boxes. The two boxes were flushed out with N_2 gas via the measuring device for ten minutes to flush out accumulating CO_2 so its concentration could be measured. The boxes were then left to settle for one and a half hours in order to accumulate CO_2 with the start time noted. After one and a half hours, the box's height above the water was noted and the pump started. N_2 was pumped through the flow meter for one and a half hours at 0.8 L/min. After this time period, contents from the sample tubes were poured into separate acid washed plastic bottles containing 10 g of $SrCl_2$ powder and taken back to the laboratory. The experiment was repeated in the bottom left hand corner of cell 3.

Laboratory procedure

In the laboratory, samples were reweighed (this was used later to calculate the concentration of TDIC in the sample), then suction filtered through a pre-weighed Whatman 47 μM filter paper. Precipitates were thoroughly washed with distilled water (to minimise contamination by the fixation of atmospheric CO_2), then dried in a drying oven at 60°C for 24 hours. Dried precipitates were allowed to cool before reweighing. Using the determined mass of precipitate and volume of collected sample, TDIC concentrations in the sample were calculated.

Approximately 20–30 mg of precipitate was weighed out and run on the carbon isotope line. Phosphoric acid (McCrea 1950) was first added to the sample to liberate CO_2 gas, and then the gas was cryogenically purified. The purified CO_2 gas sample was then analysed on a V G Sira-10 gas source mass spectrometer. Using standard procedures (Craig 1957), data were corrected giving a value of $\delta^{13}C$ in ‰ relative to the Vienna Pee Dee Belemnite standard.

RESULTS

TDIC concentrations and isotopic compositions from five replicate samplings of cell 3 are given in Table 1.

Carbon and isotopic mass balance calculations

Values obtained from field sampling for: $\delta^{13}C$ (inflow and outflow), TDIC (inflow and outflow), inlet flow, Ca concentrations and alkalinity were entered into the model. Graphs were plotted at three different mineralisation rates of 700, 1500, 3000 g of C/day and compared to the net diffusion flux (g of carbon as CO_2 from the wetland). Mineralisation rate and net diffusion flux lines were calculated from the model's simultaneous equations, therefore when the two lines crossed then exsolution of CO_2 from the wetland occurred. Graphs are presented here from data obtained in July 1999 (Figure 2) and solutions derived from five separate measurements presented in Table 2.

Table 1. TDIC values (inlet, outlet and surface) for cell 3

Sample	TDIC IN (mg/L)	$\delta^{13}C$ in ‰ VPDB TDIC IN	TDIC OUT (mg/L)	$\delta^{13}C$ in ‰ VPDB TDIC OUT	TDIC SURF (mg/L)	$\delta^{13}C$ in ‰ VPDB TDIC SURF
07.07.99	21.5	–5.5	33.1	–5.8	27.3	–5.65
08.07.99	25.3	–5.7	33.7	–8.5	29.5	–7.10
09.07.99	21.5	–5.0	32.4	–8.3	26.95	–6.65
10.07.99	19.8	–5.4	32.6	–7.8	26.2	–6.60
11.07.99	21.2	–6.8	27.4	–6.7	24.3	–6.75

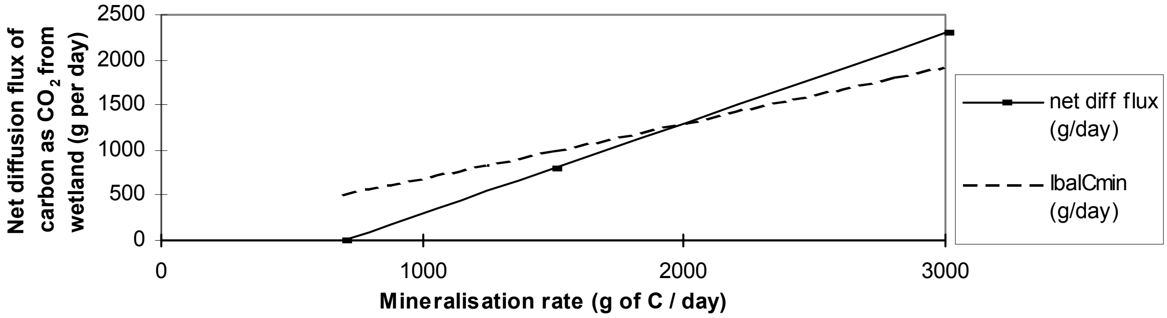

Figure 2a. C mass balance graphs for mineralisation rate versus net diffusion flux of carbon as CO_2 from the wetland on cell 3, Whitworth No. 1 wetland (07.07.99)

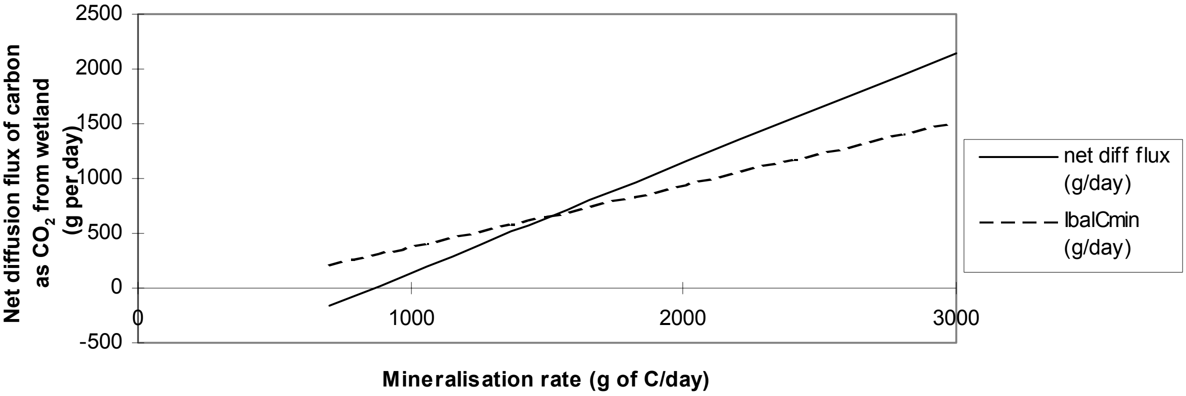

Figure 2b. C mass balance graphs for mineralisation rate versus net diffusion flux of carbon as CO_2 from the wetland on cell 3, Whitworth No. 1 wetland (09.07.99)

An example of carbon mass balance graphs calculated from the carbon mass balance model.

Table 2. Solutions to carbon mass balance curves for cell 3, Whitworth No. 1 wetland obtained in July 1999

Date	Mineralisation rate (g of C/day)	Net diffusion flux of C as CO_2 from wtld (g of C/day)
7.07.1999	1900	1250
8.07.1999	1900	1250
9.07.1999	1500	800
10.07.1999	2100	1000
11.07.1999	900	500

Direct flux measurements

Direct flux measurements calculated from field data from cell 3 in April 2002 are given in Table 3.

DISCUSSION

Figure 2 and data in Table 1 taken in July 1999 indicate a mineralisation rate of 1500 to 2000 g of C/day and net diffusion flux of 800 to 1250 g of C as CO_2 per day, apart from 11.07.1999 which had lower fluxes of 900 g of C/day mineralisation rate and 500 g of C as CO_2 per day net diffusion flux. Although the 11.07.1999 data generated lower fluxes than the previous four days, it still showed that more than 50% of the mineralisation flux was lost as CO_2 from the surface of the wetland to the atmosphere as in the previous four days' data. Looking at the carbon fluxes (Table 1), TDIC was greater in the outlet to cell 3 compared to the inlet demonstrating that carbon was also being lost from the wetland as HCO_3^-. Possible sources are from limestone

Table 3. Net diffusion flux of carbon for cell 3, Whitworth No. 1 wetland calculated from field data in April 2002

Sample location	Box number	Net diffusion flux (g of C/wtld/day)
Cell 3, far right corner	1	395
Cell 3, far right corner	2	660
Cell 3, near right corner	1	700
Cell 3, near right corner	2	360

dissolution and from organic mineralisation.

Net diffusion flux was also calculated for the wetland area in g/day/wetland from the CO_2 accumulating experiments to compare with 07.1999 data.

Table 4. Carbon per wetland area on cell 3, Whitworth No. 1 wetland

Calculation	C per wetland area (g/day/wtld)
From model (07.1999 data)	1.20
CO_2 experiment (04.2002 data)	1.65

The flux calculated from the model is closely similar to the field measurement flux (Table 4). Although the measurements were made on different occasions, the close correspondence of model and measured fluxes gives confidence that the model is a realistic representation of the wetland system.

The net aqueous flux of TDIC is given by the difference in concentration and flow rate. Using July 1999 data (Table 5), the net aqueous flux was greatest on 10.07.1999 at 820 g of C/day followed by 7.07.1999 and 9.07.1999 at 730 g of C/day. Net fluxes were lower on 8.07.1999 and 11.07.1999 at 530 and 370 g of C/day respectively. Change in net flux over the five-day period may be due to temperature change, weather conditions or other variables.

Table 5. Net flux of TDIC from the wetland calculated from the model for July 1999 data

Sample	Flow rate (L/sec)	TDIC (IN-OUT) mg/L	Net flux aqueous flux (g of C/day)
07.07.1999	0.73	11.6	730
08.07.1999	0.78	8.4	570
09.07.1999	0.67	12.6	730
10.07.1999	0.74	12.8	820
11.07.1999	0.69	6.2	370

Aqueous fluxes of carbon from the wetland are subordinate to the diffusive loss of CO_2 gas from the wetland surface. Therefore any realistic carbon budget for these systems *must* take CO_2 gas losses into account.

CONCLUSION

A carbon model has been devised to represent the fluxes from the inlet and outlet of the wetland, as well as the fluxes from limestone dissolution, organic mineralisation and exsolution (net diffusion flux) to the atmosphere as CO_2. Using field data from July 1999, the calculated diffusion flux from the model ranged from 500 to 1250 g of C/day over the five days and was closely similar in magnitude to an experimentally measured flux (in April 2002). Therefore the model gives a realistic estimate of the fluxes occurring from the wetland. The model also showed that organic mineralisation and CO_2 exsolution to the atmosphere are important fluxes which need to be accounted for.

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