The impact of sampling techniques on soil pore water carbon measurements of an Icelandic Histic Andosol

Bergur Sigfusson [a],*, Graeme I. Paton [b], Sigurdur R. Gislason [a]

[a] *Institute of Earth Sciences, University of Iceland, Sturlugata 3, 101 Reykjavik, Iceland*
[b] *School of Biological Sciences, University of Aberdeen, Cruickshank Building, St Machar Drive, Aberdeen AB243UU, United Kingdom*

Abstract

The carbon in soil pore water from a Histic Andosol from Western Iceland was studied at three different scales; in the field, in undisturbed outdoor mesocosms and in laboratory repacked microcosms. Pore water was extracted using suction cup lysimeters and hollow-fibre tube sampler devices (Rhizon samplers). There were significant differences in all measured variables, dissolved inorganic carbon (DIC), dissolved organic carbon (DOC) and pH values between the scales of the experiment. Gaseous constituents of soil solution and pH were more susceptible to changes in scale and the type of sampling devices used. Dissolved inorganic carbon concentrations did not differ significantly between field and mesocosm solutions but where up to 14 times lower in microcosms compared to mesocosms solutions. Rhizon samplers yielded solutions with up to 4.7 times higher DIC concentrations than porous cup lysimeters. Mesocosm surface horizon DOC concentrations were 20 and 2 times higher than in field and microcosms respectively. There was difference in DOC concentration between sampling methods (up to 8 times higher in suction cups than rhizon samplers) above 50 cm depth. Soil solution pH values did not differ between field and mesocosms and mesocosms and microcosms respectively down to 80 cm depth. Direct comparison between field and microcosms was not possible due to the nature of sampling devices. Soil solutions sampled with Rhizon samplers yielded lower pH values (up to 1.3 pH units) than those sampled with suction cups. Twenty percent of annually bound organic carbon at the soils surface under field conditions was lost by leaching of DOC and through decomposition to DIC in disturbed non-vegetated microcosms. This percentage increased to 38% in undisturbed vegetated mesocosms highlighting the importance of surface vegetation in importing carbon to soils. Increased influx of nutrients will increase growth and photosynthesis but decrease carbon sequestration in near surface horizons. Although field studies considering long-term anthropogenic changes in pedogenesis require considerable experimental duration, more rapid experiments can be conducted with confidence in micro- and mesocosms as in this research.
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1. Introduction

The response of soils to elevated concentrations of CO_2 and global warming has been the subject of consi-derable research in recent years. Soils at higher latitudes which store significant amounts of organic carbon may respond most dramatically to such changes (Lal, 2004). Iceland is a 103,000 km^2 volcanic island in the North Atlantic situated on the active spreading zone between the North American and Eurasian tectonic plates. The volcanic activity of the island drives the soil-forming

* Corresponding author. Tel.: +354 525 4275; fax: +354 525 4499.
  E-mail address: bergur@raunvis.hi.is (B. Sigfusson).

processes. Approximately 48% of the country, is covered by Andosols, with the rest covered by Leptosols (~40%), Histosols (~1%) and glaciers and lakes (~11%) (Arnalds and Gretarsson, 2001; Arnalds, 2004). Of those Icelandic soils, Histosols have the highest soil organic carbon (SOC) content (over 20%), followed by Histic, Gleyic and Brown Andosols (17.5%, 7.5% and 3.3%, respectively) (Arnalds, 2004; Oskarsson et al., 2004). Rates of chemical weathering of Andosols are much higher than for soils derived from other parent materials, hence further accelerating this process may significantly impact on global chemical weathering rates and subsequent carbon fixation (Gislason et al., 1996; Louvat and Allegre, 1997; Wolff-Boenisch et al., 2004). Andosols cover around 1.9% of the Earth but contain 4.9% of soil stored carbon (Eswaran et al., 1993). Allophane, a characteristic mineral of Andosols, is known to form at pH values of between 5 and 7 (Parfitt and Kimble, 1989) by a process-driven leaching regime, the organic cycle and the soil pH which control silicic acid concentration and availability of Al species (Parfitt, 1990). Free aluminium in soil solution can preferentially form Al–humus complexes instead of combining with Si to form allophanes and this may in turn render the organic carbon recalcitrant to degradation (Nanzyo et al., 1993). This process has been termed the anti-allophanic effect and occurs intensively at $pH_{H_2O} < 5$.

In terms of pedogenesis, soils of Iceland have been classified based on two drivers: deposition of aeolian-andic materials and soil hydrological characteristics (Arnalds, 2004). Areas where poor drainage coexists with low inputs of aeolian deposition have the highest contents of organic carbon, which may exceed 20% (Arnalds, 2004). In this study, the field site was selected because of its relative tectonic stability and low (~0.1 mm year^{-1} or 115 g m^{-2} year^{-1}) influx of aeolian deposition. The soil is a fair representative of the significant group of Histic Andosols that may accumulate organic carbon to considerable depths and are associated with strongly sequestering this material. The soil at the site is a poorly drained Histic Andosol situated 200 m inland receiving considerable input from marine-derived sources. As with most Icelandic Andosols, typical allophane content is 2–5% and the soil meets the $(Al+1/2Fe)_{ox}$ criteria for Andosols (FAO, 1998; Arnalds, 2004).

Comprehensive studies of the changes in soil solution chemistry will provide information on current pedogenic mechanisms and will allow predictions of the impacts of global changes to be made (van Hees et al., 2001). Soil pore water responds more rapidly to changes in temperature and to the influx of dissolved matter than

bulk soil. Many methods have been proposed for the collection of in situ soil solutions including zero tension closed lysimeters (Giesler et al., 1996), tension plate lysimeters (Cole et al., 1961), porous cup lysimeters (Wagner, 1962; Grossmann and Udluft, 1991; Patterson et al., 2000), inert soil moisture samplers (Cabrera, 1998; Knight et al., 1998) and 'passive lysimeters' collecting soil capillary water without any suction applied (Holder et al., 1991).

For this study, inert soil moisture samplers (Rhizon samplers) were selected to sample the disturbed microcosm experiments. Porous cup lysimeters were selected for the extraction of solutions from the field. To allow a comparison of the efficacy of sample technique, both sampling methods were used for the undisturbed mesocosms. Rhizon samplers, which are not robust enough for field application, conserve CO_2 when used in combination with closed headspace, hence the calculation of DIC in soil solution is possible from the equilibrated CO_2 measurement in the headspace (Kling et al., 1991). Suction cups, although ideal for field application (Grossmann and Udluft, 1991), are prone to causing degassing of CO_2 and elevating solution pH. This problem has been overcome by using gas-tight syringes (Straub et al., 1988) and by collecting soil solution in a funnel using the sampling system as a buffer against $CO_2(aq)$ loss and measuring $CO_2(aq)$ in a system isolated from the atmosphere (Takkar et al., 1987).

The aim of this study was to assess the importance of sampling techniques and the significance of different scales on soil solution carbon chemistry. To this end, carbon fluxes in soil solutions extracted during weathering of a Histic Andosol were studied. The sampling devices used were inert soil moisture samplers (Rhizon samplers) and porous cup lysimeters. The soil water was studied at three different scales. The scales were (a) undisturbed soil profile in the field, (b) disturbed microcosms and (c) undisturbed mesocosms. The efficacy of the methodology was evaluated by comparing extraction methods at different scales. Validation of this scale approach may enable confidence in long-term studies to be made.

2. Materials and methods

2.1. Sampling site and soil characteristics

The soil (which has been developing for an estimated 10,000 years) was sampled at Klafastadir in Hvalfjordur, Western Iceland (Fig. 1). The area is characterised by low current input of aeolian materials with each tephra layer being shallower than 1 cm in
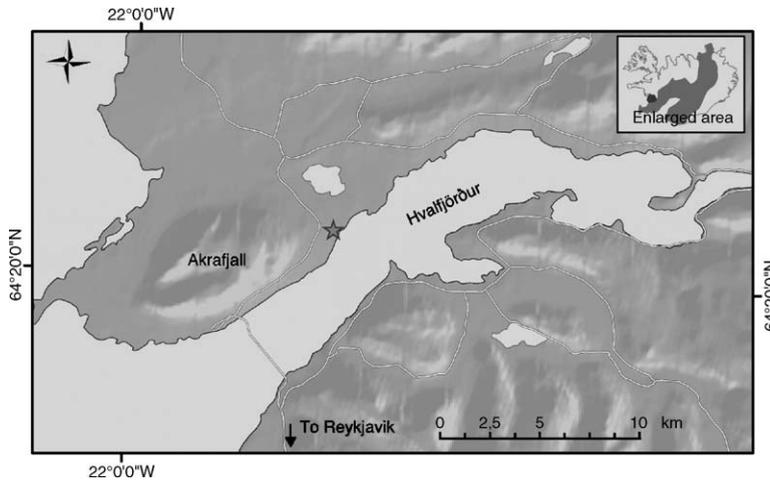
Fig. 1. Location of sampling site is depicted by a star. Shaded area on inset figure represents active volcanic rift zones (modified from Johannesson and Saemundsson, 1998). Areas of most active volcanism during the Holocene are situated in eastern zones rather than the western zone which lies nearest to the sampling site.

depth. The soil has developed from basaltic glacial till and has horizons associated with a previously forested landscape at 170 cm and 80 cm depth (Fig. 2 and Table 1). There are identifiable ash layers including "The Landnam layer", ~1 cm thick (from 870 AD) (Gronvold et al., 1995; Zielinski et al., 1997) at 50 cm depth. The rate of profile deepening for the uppermost 50 cm is estimated at 0.4 mm/year. Above "The Landnam layer" was a B_w horizon, which has the lowest carbon content (11%) in the profile. Other horizons have between 22% and 42% organic carbon (Table 1). Mean present annual precipitation was 870 mm while the 7-month precipitation (reflecting the season of active soil processes) from May to November was 540 mm (The Icelandic Meteorological Office, unpublished data 2002). Little precipitation leached through the frozen soil profile between December and April. Key pedogenic and physicochemical data are tabulated in Table 1.

2.2. Field soil solution sampling

Soil solution was sampled in the field with Prenart soil solution samplers (Denmark) made of PTFE (Teflon) and quartz. Four holes were excavated at sampling depths of 15, 35, 50, 80, 115, 150 and 205 cm with a stainless steel auger, 2.5 cm in diameter, inserted into the soil at a 60° angle (Fig. 2). Those holes where filled with a slurry of sieved soil and de-ionised (DI) water (4 : 1 w/w). Each sampler was then pressed into the slurry with a polyethylene coated aluminium pipe. All tubing from the soil solution samplers to the sampling bottles was made of high-density polyethylene (HDPE). After installation, the porous cup samplers
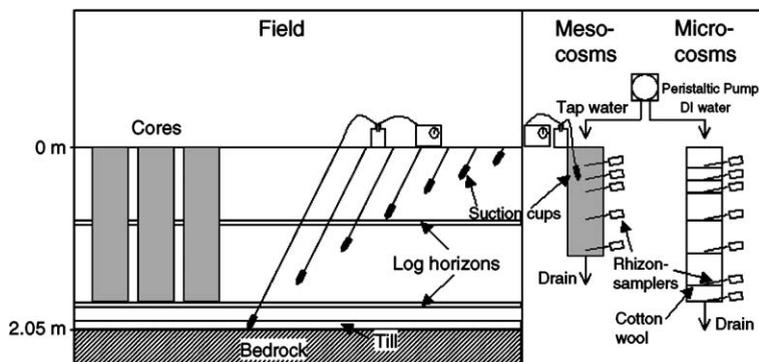

Fig. 2. Sampling and experimental setup. Cores for mesocosm- and microcosm experiments were taken 3 m downhill from field sampling site after solution sampling had been carried out. Mesocosm was undisturbed but microcosms were repacked from sieved soil. Actual height of microcosms was 3 times less than showed in the figure.

Table 1
Key pedogenic and physicochemical data of the soil[a]

Horizon[b]	Depth (cm)	pH_{H_2O}	pH_{CaCl_2}	ρ_s[c] (g cm^{-3})	Total C[d] (%)	Total N (%)	C/N ratio[e]	Allophane (%)	Ferrihydrate (%)
A/O/Bw	0–15	5.17	4.62	0.30	22.5	1.49	17.6	3.8	2.5
2O	15–35	5.06	4.53	0.22	24.5	1.52	18.8	1.7	2.5
3Bw	35–50	4.97	4.71	0.76	11.1	0.67	19.2	23	3.8
3O	50–80	4.82	4.45	0.25	22.0	1.18	21.8	8.9	5.3
4O/Tephra	80–115	3.93	3.88	0.38	25.2	1.21	24.2	3.8	2.4
5O	115–150	4.59	4.48	0.26	33.4	1.62	24.0	3.6	0.6
5O	150–170	4.53	4.45	0.25	41.8	1.84	26.9	2.5	0.8

[a] See description in Section 2.4.
[b] Horizons according to FAO (1998).
[c] ρ_s = dry bulk density.
[d] All % values are wt.%.
[e] Molar ratio.

were allowed to settle for 2 weeks prior to sampling of first batch. Soil solution was sampled three times at 3-week intervals during the summer of 2002. A 700 mbar suction was applied to an acid washed and DI rinsed air tight Pyrex bottle and maintained through the sampling procedure with automatic vacuum pumps. The sampling system was first rinsed with 200–500 ml of soil solution that was then discarded. Then soil solution was sampled for 12–20 h until at least 1 l of soil solution was collected in each bottle. All sampling bottles were maintained in the dark and under constant vacuum during sampling and transfer to the laboratory.

2.3. Field soil solution preparation and analysis in the laboratory

All soil solution samples from the field were treated immediately after sampling at the University of Iceland in an Ar-purged and filled glove box. Oxygen concentration in the glove box was measured by equilibrating DI water to the atmosphere in the glove box and the oxygen concentration in that water was then measured colorimetrically with CHEMets ampoules from CHE-Metrics. All bottles and glasses were aired in the inflow of Ar to the glove box (Sigfusson, 2004).

On opening each sample bottle, the following procedure was followed. 50 ml were pipetted into a beaker and the pH was measured immediately. Dissolved inorganic carbon (DIC) was measured by back titration (Arnorsson et al., 2000) by adding 0.1 M NaOH solution into the beaker to increase the pH to above 8.3 and the solution titrated to pH 3 for the HCO_3^- (DIC) analysis in the water. Finally, 30 ml of sample were filtered through 0.2-µm cellulose acetate membrane into acid washed (1 M HCl) polypropylene (PP) bottle and acidified with 0.4 ml of 1.2 M HCl for analysis of dissolved organic carbon (DOC). DOC concentration was measured by

high temperature oxidation using a Shimadzu 5000 Total Organic Carbon Analyser.

2.4. Soil sampling and analysis

Soil was sampled as intact soil cores 3 m from the sampling point of soil solutions after all soil solutions had been sampled (Fig. 2). Three 50-cm-diameter black HDPE pipes were pushed into the soil with the aid of a backhoe loader. All pipes were pushed down to 170 cm depth, which was the maximum depth that the backhoe loader could accomplish. An excavation (0.6 m × 1.9 m and 1.7 m deep) was then dug around each pipe, which was then laid down horizontal and finally lifted up, sealed with a HDPE lid and silicone and transported to Aberdeen, Scotland. The cores were stored upright outdoors in Aberdeen under a transparent roof allowing sunlight to reach the vegetation on top of the soil cores. One of the cores was destructively sampled and split into constituent horizons. The soil from this core was used for the repacked microcosm experiment (Fig. 2) and for determining physical and chemical characteristics of the soil (Table 1). The remaining two cores were left intact for the mesocosm experiment and irrigated by Aberdeen tap water, at pH 6.9 with DOC below detection limit (8.3 µM), every 2 weeks to avoid excess drying.

Soil pH values were measured in H_2O and 0.01 M $CaCl_2$ (Soil Survey Staff, 1996; Table 1) using a glass/calomel electrode (HI 8424 microcomputer pH meter). Bulk density was determined by the Core Method (Blake, 1965; Table 1). Total carbon and nitrogen were analysed by a Fisons NA1500 NCS analyser (Table 1). Al, Si and Fe were extracted from soil with ammonium oxalate (Blakemore et al., 1987) and analysed by flame atomic absorption (Perkin Elmer AAnalyst 100). Allophane contents were calculated by multiplying oxalate extractable Si by 6 (Parfitt, 1990) (Table 1).

Ferrihydrate content was calculated by multiplying oxalate extractable Fe by 1.7 (Parfitt and Childs, 1988) (Table 1).

2.5. Construction of repacked microcosms

Soil was dried to 50% water holding capacity and then sieved through a 2-mm sieve. Visible vegetative materials were removed. Soil from each horizon was mixed with HDPE beads (acid washed and DI rinsed) of 4 mm average diameter in a ratio 9:1 soil/beads (w/w). Soil was then packed to the field bulk density in a 10 cm diameter polyvinyl chloride (PVC) tube with a 1-cm layer of pre-washed (acid and deionised water) non-absorbent cotton wool between all of the horizons (Fig. 2). The topsoil was covered with Whatman no. 1 filter paper and a 3-cm layer of HDPE beads. There was no surface vegetation in the microcosm experiments, which were conducted in triplicate.

Precipitation from May to November (540 mm) in the field was used to simulate annual precipitation (1414 ml of DI water). During the microcosm experiment 74.6 l were leached through each replicate over a period of 57.5 days simulating 52.8 years of precipitation. A peristaltic pump (Cole Parmer Masterflex L/S) was switched on for 1 h with a flow rate of 1.8 ml min^{-1} and then switched off for 1 h giving a steady outflow of 0.9 ml min^{-1} at the base of the soil columns throughout the experiment. The microcosm design was compatible with this flow rate.

2.6. Microcosms and mesocosms solution sampling

Samples of soil solution were taken from the base of each horizon (Fig. 2) with inert hollow fibre soil moisture samplers (Rhizon samplers, Eijkelkamp, The Netherlands). The samplers were cleaned by drawing 60 ml of 5% HNO$_3$ solution through the samplers and rinsed five times in the same way with DI water prior to finally allowing the sampler to stand in DI water. A small hole (4 mm) was drilled into the PVC tube and kept closed between sampling batches. During sampling, the Rhizon devices were inserted through this hole and into the soil. The samplers were then connected with a 3-way valve to a 60-ml Luer lock polypropylene (PP) syringe that had previously been filled with 20 ml of nitrogen gas as a headspace. The syringe was then kept fully open and soil solution flowed into the syringe overnight yielding 40 ml of sample. Furthermore, using the previously described method, suction cups were used to sample soil solutions from the mesocosms for direct comparison to field solutions. Suction cup-sam-

pled solutions were treated in a similar manner to the field solutions described above.

2.7. Microcosms and mesocosms gas and aqueous solution sample preparation

After sampling, the solution was sealed inside the syringe without introducing atmosphere to the sample. A known amount of gas, 5 ml for microcosms and 2–5 ml for mesocosms, from the equilibrated headspace in the syringe were transferred to a 20-ml gas-tight nylon syringe and diluted to 20 ml with nitrogen gas at ambient pressure. Then 15 ml of soil solution was transferred directly through a 25-mm-diameter filter holder with 0.2-μm cellulose acetate filter into a 15-ml PP vial and the pH was measured and recorded. This sample was also used for the analysis of DOC. 10 ml were then injected into another PP vial for the analyses of aluminium. The sample was acidified with 0.1 ml of concentrated HNO$_3$ prior to analysis (Gislason et al., 2002). Finally, 10 ml were injected into PP vial for analysis of fluoride and sulphate.

2.8. Microcosms and mesocosms gas and aqueous solution measurements

Analysis of soil water from microcosms and mesocosms were conducted at the University of Aberdeen. Soil solution DIC was determined by headspace analysis (Hope et al., 1996). All sample handling was carried out at ambient temperature and pressure to enable the use of Henry's law to calculate amount of DIC equilibrated with headspace (McDonald and Gulliver, 1990). Samples were injected using a flow injection loop (250 μl) system with a nitrogen carrier gas onto a Porapak Q column. Before entering the injection loop, they were passed through anhydrous calcium sulphate. The oven temperature of the gas chromatograph (Chrompack 9001) remained constant at 50 °C and a flame ionisation detector set at 250 °C determined CO$_2$ concentrations after calibration with standard gas mixtures (Linde Gases, Aberdeen) (Dawson et al., 2001). Concentrations of diluted samples were within the range of 0.5–10 mmol mol^{-1} CO$_2$. The concentration headspace CO$_2$ was used to determine the concentration in the soil solution:

$$[X]_{(aq)} = [X]_{(g)} \times P \times \left(K_h + \left(\frac{V_{headspace}}{V_{sample}} \times \frac{1}{R \times T} \right) \right)$$

(Kling et al., 1991)Where $[X]_{(aq)}$ represented the concentration of DIC in the soil solution (μM), $[X]_{(g)}$

the concentration of DIC in the headspace (μmol mol^{-1}), P as pressure (atm), K_h the Henry's law constant (Plummer and Busenberg, 1982) at given temperature for CO_2, $V_{headspace}$ and V_{sample} the volumes of headspace and sample in syringe, respectively (L), R was the universal gas constant (atm m^3 mol^{-1} K^{-1}) and T was the absolute temperature (K).

Dissolved organic carbon (DOC) was measured in a Labtoc instrument (Pollution and Process monitoring). Results of DOC measurements have been shown to be within analytical error between the Labtoc instrument and Shimadzu instrument used for the DOC analysis of the field samples (Chaudri, personal communication) Aluminium was analysed by GFAAS (Perkin Elmer Atomic Absorption Spectrometer 3300) with $Mg(NO_3)_2$ as matrix modifier. Fluoride and sulphate were analysed by IC (Dionex 4500i).

2.9. Carbon fluxes

Annual net carbon sequestration of the soil profile was calculated as (kmol ha^{-1} year^{-1}) using soil physical data and published accumulation rates from tephrachronology (Larsen, 1993). DIC and DOC measured values were used to calculate and interpolate total carbon output from the microcosms (Fig. 7a and b). Mean annual flux was calculated by dividing total output with land surface area. Steady state fluxes of DOC (kmol ha^{-1} year^{-1}) were calculated according to Duan et al. (2002).

2.10. Speciation of soil solution

Speciation of DOC was estimated using the geochemical model PHREEQC version 2.8 (Parkhurst and Appelo, 1999). Oxalate ($C_2O_4^{2-}$), a strong complexing organic ligand for cations represented DOC in soil solution (Chadwick and Chorover, 2001). The speciation of aluminium with oxalate, fluoride and sulphate were calculated, and the partition between the different species studied.

2.11. Statistical analysis

The statistical software package Sigmastat 3.0 (SPSS Scientific) was used to carry out all analysis. If a normality test was passed, a general linear model was employed. If the normality test failed, a Kruskal–Wallis one-way ANOVA on ranked data was carried out. All values of each variable at each depth were compared to all other depths. Mean values of each variable in each treatment were compared to other treatments. A t-test was carried out to confirm if a steady state flux of carbon

had been reached between sampling points at all depths. All levels of significance are expressed as $p \leq 0.05$.

3. Results

3.1. Dissolved inorganic carbon (DIC)

At the pH values of most of the soil solutions in this study the predominant aqueous DIC species was CO_2(aq). There was no significant difference in the DIC value when suction cups were used in either the field or the mesocosm experiment (Fig. 3). However, when the Rhizon samplers were used, the measured DIC levels were where up to 20 times higher in the mesocosm study when compared with the microcosm experiment (Fig. 3). The mesocosm, which was sampled using both techniques, had up to 4.7 times higher DIC solution concentrations from Rhizon samplers when compared with suction cups.

There was a significant increase in DIC content down the profile for the microcosms (which had been thoroughly homogenised through sieving and repacking) but this was not observed for the mesocosm despite both experiments being sampled with Rhizon samplers. In the mesocosm and field experiments (both using "pristine profiles"), the DIC content increased significantly at 115 cm depth when sampled with suction cups.

3.2. Dissolved organic carbon (DOC)

Mean concentration of DOC differed significantly between the microcosm, mesocosm and field scales of the experiment (Fig. 4). Solutions sampled with suction cups had up to 20 times higher DOC concentrations present in the mesocosms than in the field experiment. This difference was not significant between 80 and 115 cm depths. Solutions sampled with Rhizon samplers had up to twice the measured concentrations in mesocosms when compared with microcosms for surface horizons but this difference was not significant at 80 and 115 cm depths (Fig. 4). The solutions sampled with suction cups had up to 8 times higher DOC than solutions sampled with Rhizon samplers at 50 cm depth (Fig. 4). In the microcosm and mesocosm treatments, the mean concentrations of DOC were greatest at 0–35 cm profile depth (Figs. 4 and 6b, e). Such corresponding levels of DOC were not measured in the field samples (Figs. 4 and 6b, e).

3.3. pH

There was no significant difference for the pH value of the pore waters sampled at 80 cm between the

microcosms and mesocosm when using the Rhizon samplers (Fig. 5). The pH values from the microcosms were 1.4 pH units lower than the mesocosm at 115 cm depth. There was also no significant difference between pH values of the solution extracted with suction cups from either the field or the mesocosms regardless of depth. For the mesoscosm samples, suction cup extracts had higher pH values (by 0.3 to 1.3 units) than Rhizon-sampled solutions. In general, suction cup-sampled soil solution in the field and in the mesocosms had pH values that followed the trend reported for the total carbon content of the bulk soil. This observation did not hold for the pH of soil
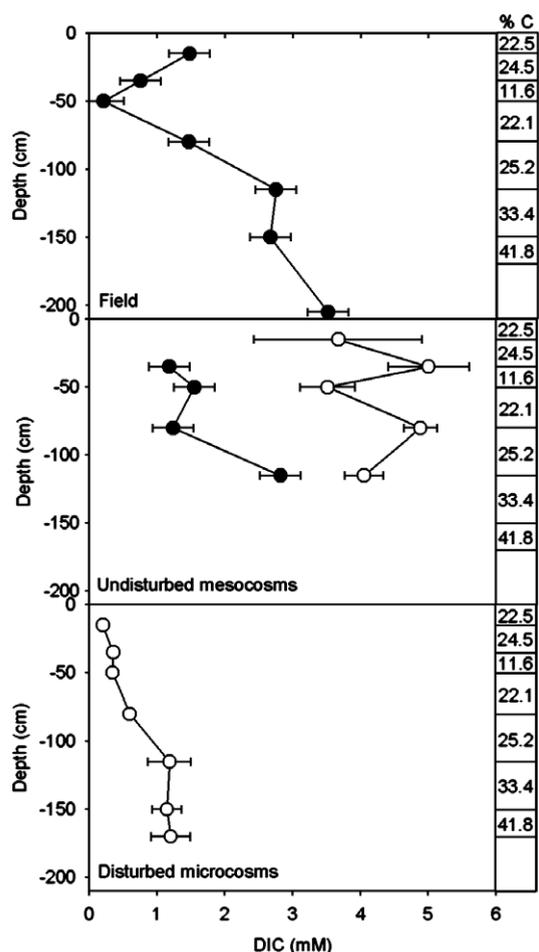

Fig. 3. Concentration of dissolved inorganic carbon (DIC) in individual treatments vs. depth: (●) samples taken with suction cups; (○) samples taken with Rhizon samplers. First sampling batch in microcosms not included. Error bars are standard errors of means ($n=3$, 2, 4 and 15 for field, mesocosm with suction, mesocosm with Rhizon and microcosm with Rhizon samples, respectively). Percentage of soil carbon is showed on the right-hand side of the figures for comparison.

solution extracted with suction cups at 80 cm (total $C>20\%$) relative to 50 cm depth (total C 11%) where the pH value had dropped (Fig. 5).

The lowest pH values were recorded at 80 cm depth in the field sampled with suction cups and in mesocosms sampled with Rhizon samplers. The pH values increased significantly from 80 to 115 cm after being in contact with an 8 cm horizon, characterised as being rich in volcanic glass. This increase in pH value was not observed in the mesocosms sampled with suction cups, where the pH varied less down the soil profile. In the microcosm, there was a decrease in the pH value from 4.2 at 80 cm depth to below pH 4 at 115 cm depth but no further significant decrease was observed. In the microcosm soil, there was a significant increase in pH_{H_2O} (Table 1 and Fig. 5) below 115 cm depth and a corresponding increase in soil pore water pH.

3.4. Time

The concentration of DIC in the microcosm experiments decreased rapidly during leaching reaching a steady state at nearly all depths when 26 l of water (the equivalent of 18.3 years) had leached through (Fig. 6a). A strong pulse of DOC was observed at the beginning of the microcosm experiment but both the DOC and DIC concentrations declined until there was no significant difference between the concentrations measured in the microcosm or the field (Fig. 6). The pH values did not change significantly at soil depths of between 0 and 80 cm during the microcosm experiment, after 75 l of water (the equivalent of 52.8 years) had leached through (Fig. 6c). At depths below 80 cm, the pH values had dropped significantly when compared to field values. The DIC in the mesocosm experiment did not reach steady concentrations between sampling batches (Fig. 6d). In the mesocosms experiment, the DOC of surface horizons increased at the commencement of leaching and these values remained higher than DOC sampled at between 50 and 115 cm (Fig. 6e). The pH value did not change significantly over the period of the mesocosm experiment (Fig. 6f). 440 l of water (the equivalent of 4.2 years of precipitation) were leached through the mesocosm during the experiment.

3.5. Speciation of soil solution

Partitioning of Al between Al^{3+}, $C_2O_4^{2-}$, F^- and SO_4^{2-} in soil solution is shown in Table 2. Hydroxide speciated aluminium is also shown but was most frequently only a minor fraction in the soil solution.

4. Discussion

4.1. Dissolved inorganic carbon (DIC)

The concentrations of DIC measured in the soil solution varied according to the sampling techniques used. In the mesocosm experiment, soil solution sampled with suction cups consistently yielded lower DIC concentrations than the Rhizon samplers. This may be because suction cups caused a continuous degassing of the samples. Most of the soil solution C content was in the form of H_2CO_3* ($H_2CO_3* = H_2CO°$ and $CO_2(aq)$) or HCO_3^- depending on the solution pH values (Kern, 1960). As pH lowers, the H_2CO_3* concentration increases and hence degassing rate increases. Therefore,

measurements of DIC in soil solutions sampled with suction cups as described in the current research do not represent the actual DIC levels in the field profile and that the lower concentrations of DIC at 50 cm are due to the fast degassing of CO_2 from the water. Lower DIC concentrations at 50 cm than at 80 cm was due to higher moisture content at 80 cm depth and a commensurate difference in vacuum efficiency from the selected pump. Furthermore, Hope et al. (1996) reported up to 4.5 and 1.7 times higher pCO_2 values in river waters when using headspace analysis compared values calculated from alkalinity titration and field and laboratory determined pH values respectively. These data show that there was a degassing of CO_2 in Hope et al.'s study between sampling and measurement, a process probably not
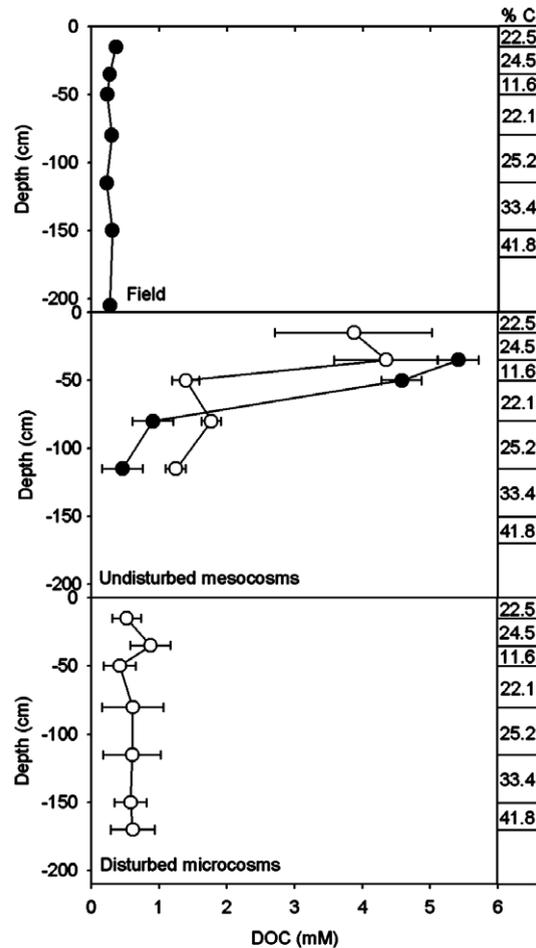

Fig. 4. Concentration of dissolved organic carbon (DOC) in individual treatments vs. depth: (●) samples taken with suction cups; (○) samples taken with Rhizon samplers. First sampling batch in microcosms not included. Error bars are standard errors of means ($n=3$, 2, 4 and 15 for field, mesocosm with suction, mesocosm with Rhizon and microcosm with Rhizon samples, respectively). Percentage of soil carbon is showed on the right-hand side of the figures for comparison.

Fig. 5. pH values in individual treatments vs. depth: (●) samples taken with suction cups; (○) samples taken with Rhizon samplers; (□) soil pH$_{H_2O}$ in air-dried soil for comparison. First sampling batch in microcosms not included. Error bars are standard errors of means ($n=3, 2, 4$ and 15 for field, mesocosm with suction, mesocosm with Rhizon and microcosm with Rhizon samples, respectively). Percentage of soil carbon is showed on the right-hand side of the figures for comparison.
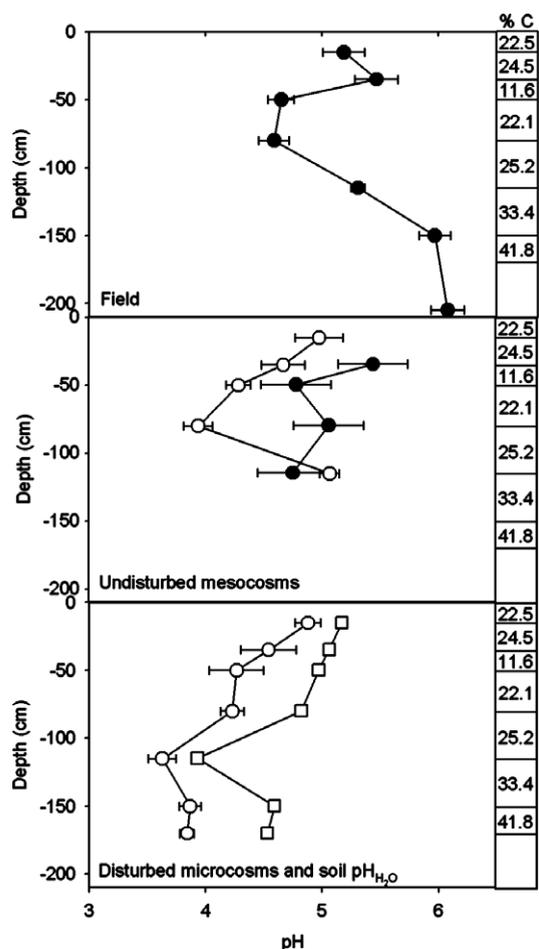
occurring in this research as samples maintained at constant vacuum from sampling to measurement. The difference in DIC may therefore be an artefact more of sampling procedure and measurement than of the actual field conditions.

Solutions sampled from mesocosm with suction cups were not titrated in an Ar controlled environment and as a consequence, this may have led to faster degassing of CO_2 in field samples. Takkar et al. (1987) had reported that 20% to 40% of $H_2CO_3^*$ was lost from soil solution resulting in increased pH after equilibrating with the laboratory atmosphere. However, there was no significant difference between values from field solutions and mesocosm solutions sampled with suction cups (Fig. 3).

In the microcosm experiment, initial DIC levels were elevated (Fig. 6a) relative to the levels measured for the remaining duration of the experiment. This elevation in DIC is likely to be related to the increase in microbial activity, a consequence of the physical disruption and homogenisation of the sample (Fig. 6b). Ladd et al. (1993) acknowledged that following such disruption of aggregates there was a commensurate stimulation of microbial activity. Six et al. (2000) reported that soil aggregates contained a higher proportion of labile carbon in the form of less altered plant material than the bulk soil and this would further enhance the response of the microbial population. After the initial high DIC in the microcosms, the system settled and reached a steady state. At this point, the measured levels of DIC were lower than those in the mesocosm and the field samples. This result was despite the fact that the microcosm was carried out at a higher temperature and under a more intense management regime (Fig. 3). In the case of the mesocosm and the field, however, the presence of photosynthetic activity and a mature rhizosphere ensured the continual input of carbon to the system. This steady input of carbon was not the case for the microcosm, where the initial zymogenous activity associated by labile carbon was depleted and this was replaced by the autochthonous component of the biomass degrading the more refractory carbon sources.

4.2. Dissolved organic carbon (DOC)

Different behaviour of DOC in the laboratory and field is widely reported (Kalbitz et al., 2000). High DOC adsorbance capacities of clay minerals and sesquioxides are often overestimated in microcosms because of macropore fluxes and hydrological conditions that are poorly translated from field to laboratory (Jardine et al., 1989). Rhizon-sampled solutions from the mesocosm contained higher concentrations than those measured in the microcosm-derived solutions. Suction cup-sampled solutions from mesocosms had higher concentrations than Rhizon-sampled solutions from mesocosms. This is in agreement with findings of Jones and Edwards (1993) that reported polysulphone rhizon samplers had a relatively low molecular weight rejection levels (100,000 MW). The lowest and the highest DOC concentrations recorded were sampled with suction cups from the field and mesocosm profiles, respectively. These elevated concentrations of DOC in mesocosms compared to field (with suction cups) and microcosms (with rhizon samplers) respectively may have been the surface vegetation's response in adapting to environmental change and to the physical disruption and
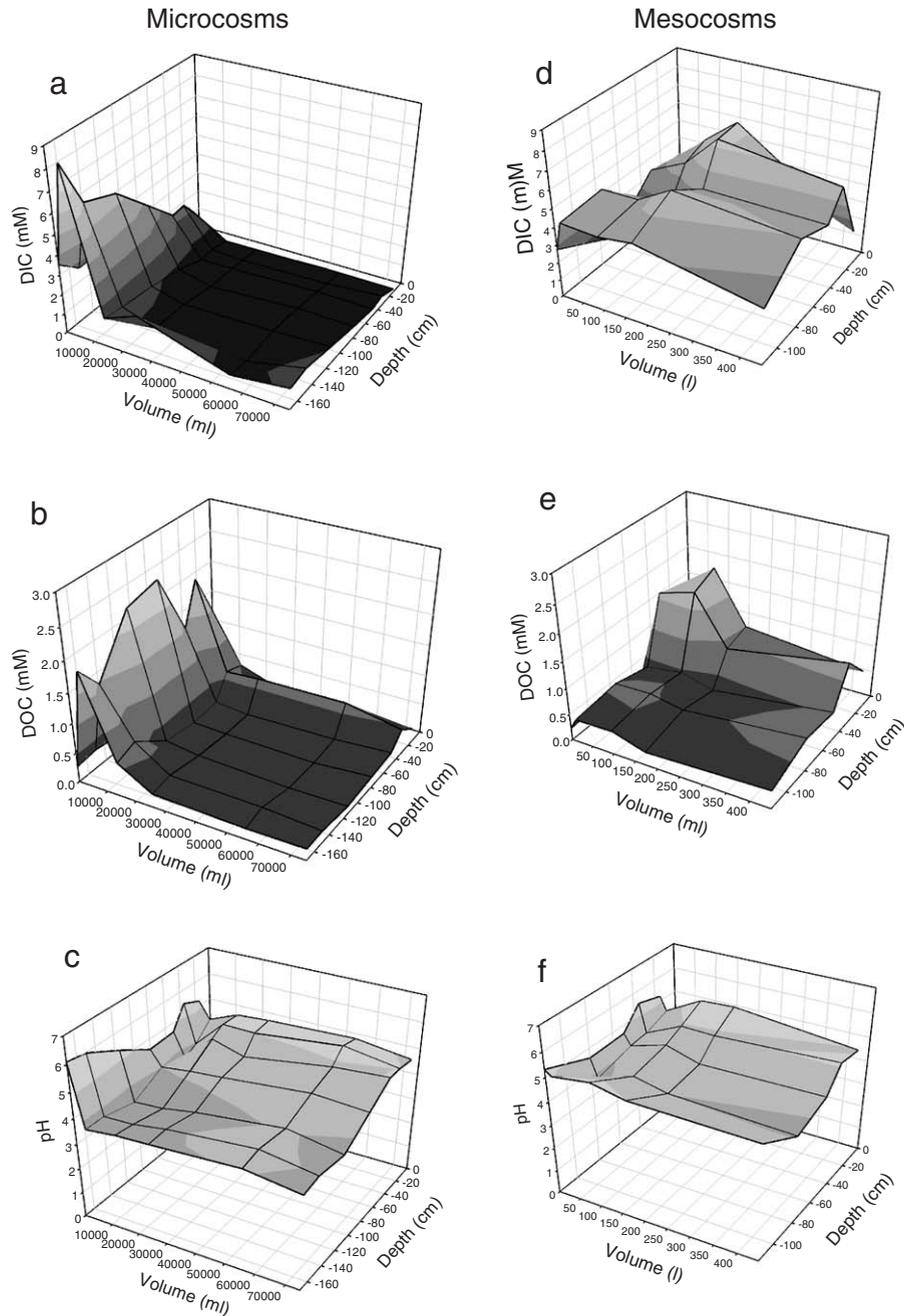
Fig. 6. Figures of changes in carbon content and pH of the soil solutions during the experiments: (a–c) from microcosm experiments; (d–f) from mesocosm experiment. Values from field solutions sampled with suction cups are included in the figures at zero volume, but all experimental data are from samples obtained with Rhizon samplers.

rhizosphere damage associated with sampling (Singh et al., 2004). The mesocosms after all were transplanted from Iceland to Aberdeen and this would be likely to have a bearing on the response of carbon in the soil system.

Kalbitz et al. (2000) highlighted the difficulties in distinguishing the source of dissolved organic matter

and whether it was derived from recent litter deposition or from the degradation of more stable organic matter. In this study, the concentrations of DOC in field solutions did not increase down the soil profile indicating sufficient decomposition of DOC by the soil biomass. The relative stability of DOC concentrations down the

Table 2
Mean, minimum and maximum percentage of predicted aluminium species in soil solution from leaching experiments

	pH	Al^{3+} species	Al–F species	Al–oxalate species	Al–sulfate species	Al–(OH) species
Mean	4.03	6.6	0.0	81.6	7.3	0.7
Minimum	3.32	0.0	0.0	0.0	0.0	0.0
Maximum	5.70	87.2	0.3	100	68.0	22.8

soil profile could be a response of the dynamic equilibrium between sorption and desorption from the soil solid components.

The concentration of DOC increased significantly at all depths at the commencement of the microcosm leaching but then reduced to values similar to those observed in the field as the microcosm experiment progressed. As with the elevated DIC, the initial increase was the consequence of disturbance in the soil which impacted on the key biological, chemical and physical processes of this Andosol. There would be a release of cations and anions into the soil solution and a corresponding drop in soil solution pH (Fig. 6b). Lundquist et al. (1999) reported an increased concentration in DOC during rewetting cycles as a consequence of recovery of microbial activity from dry periods and an enhanced availability and subsequent mineralisation and transformation of this carbon associated with soil physical changes. Dissolved organic carbon that was leached from SOM in elevated concentrations from the surface horizons after 50 years (75 l) of simulated rainfall was mineralised or biologically transformed in soil solutions with depth (Fig. 6b). This resulted in stable DOC concentrations below 50 cm suggesting a dynamic equilibrium between sorption/desorption mechanisms of DOC at the soil exchange complex had been reached.

It is widely acknowledged in Andosols that Al has a key association with DOC (Dahlgren et al., 1993). However, high concentrations of F^- and SO_4^{2-} are likely to complex Al^{3+} rendering it unavailable to form stable complexes with humus at the soil surface. Calculation in PHREEQC showed that F^-, SO_4^{2-} and $C_2O_4^{2-}$ competed for the aluminium in the experimental soil solution (Table 2). When fluorine and sulphate were in elevated concentrations, the aluminium was complexed as Al–fluorine and Al–sulphate species instead of Al–oxalate, leaving the carbon-bearing species susceptible to leaching or decomposition. This competition for free aluminium is the controlling factor for which secondary phases will be formed in the soil (Dahlgren et al., 1993).

Mean temperatures during sampling were 9.6 °C and 14.9 °C for field and mesocosm, respectively. Mean DOC concentrations were 0.28 mM DOC and 2.84 mM for field and mesocosms solutions, respectively. Temperature differences could account for some of the variations in DOC concentrations as could the actual experimental design and the issue of edge effects caused by the cores. Cronan and Aiken (1985) reported that seasonal differences in DOC concentrations were mainly observed near the surface and this translated to the elevated DOC concentrations of the uppermost horizons in the mesocosms when compared to field measured values. There was not a significant difference in DOC concentrations between the mesocosm and field scales for deeper horizons (80–115 cm) where these impacts and edge effects may have been less prominent.

The chemical composition of the eluent was different between the field (rain) and mesocosm (tap water) but the DOC was below detection limits (8.3 μM) for each of these treatments. The mean concentration of calcium was 10 times higher in the water used to irrigate mesocosms when compared to field precipitation.

4.3. pH

A comparison of the pH values between sampling methods cannot be done because of the significant role of CO_2 degassing when sampling with suction cups. Mesocosm solutions taken with suction cups were 0.7 pH units higher than solutions extracted with the Rhizon samplers. The pH values differed significantly between disturbed and undisturbed treatments. The pH values were lowest at 115 cm in the disturbed treatment (microcosms) while the lowest measured values for the undisturbed cores (mesocosms) were measured at 80 cm. This low mean pH value (3.94) was followed by a significant increase in pH values at 115 cm depth to 5.06. This change in pH was also observed for the microcosm experiment, which, after dropping initially at all depths, increased to match the field pH in horizons above 80 cm. This recovery in pH value was not observed in horizons deeper than 80 cm where organic matter content was greater while ferrihydrate was in low concentrations (Table 1). Cation exchange sites were disrupted during the drying and rewetting of the repacked microcosms. Johnson (2002) suggested oxyhydroxides could bind DOC on their surface resulting in increased cation exchange capacity. This process would, to some extent, alter the CEC (particularly the mineral/organic interface) and change the physicochemical properties of the soils. The DOC was flushed out initially but as the experiment progressed there became a tendency to retain the carbon on the mineral surface. Over time, this resulted in a degree of recovery of the
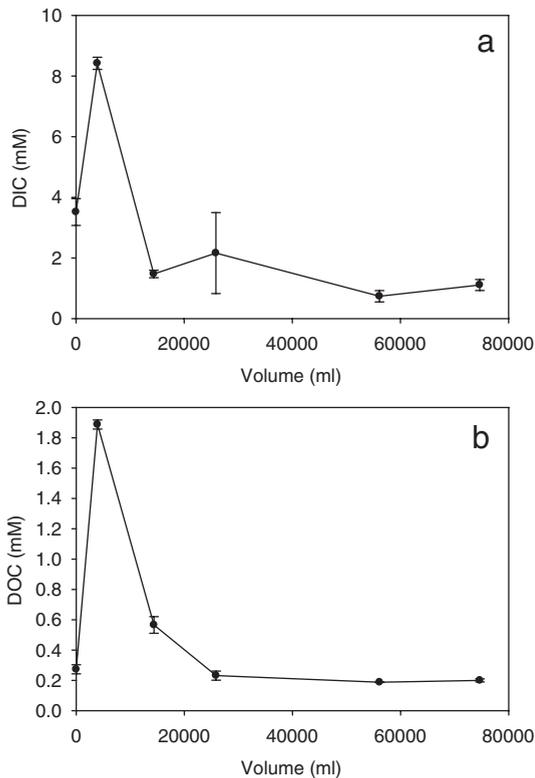
Fig. 7. Concentrations of DIC (a) and DOC (b) during sampling of microcosm experiment at 170 cm depth. Field concentration is included at zero volume for comparison. Area under line that connects data points represents total amount of each variable leached out from the experiment. Error bars represent standard errors of replicates ($n=3$).

CEC and there was a commensurate rise in pH in the shallow horizons where ferrihydrate became detectable as opposed to deep horizons where organic matter was the dominant component of the soil exchange capacity and ferrihydrate was rarely detectable.

The lower pH values did not have a significant influence on DIC or DOC concentration in the undisturbed samples. DIC increased as the pH values reduced in the microcosm experiment but this may be related to factors such as nutrient availability and the location of the sample collection in the soil profile. The lowest pH values were observed either at the commencement of leaching (when sample preparation and the subsequent lack of equilibration would have been significant factors) or deep in the profile where horizons were acquiring elevated DIC from above.

4.4. Fluxes of DIC and DOC through the soil profile

The total amount of DIC leached from the microcosm experiment was 118 mmol (Fig. 7a). This equated

to a mean annual flux of 8.5 kmol ha^{-1} year^{-1} (Table 3). The experiment did not reach a steady state flux for DIC (Fig. 7a). Similarly, the total amount of DOC leached from the microcosm experiment was 32 mmol (Fig. 7b). This was equivalent to a mean annual flux of 2.3 kmol ha^{-1} year^{-1}. The steady state flux of DOC from microcosms at 170 cm depth at the end of experiment was 1.1 kmol ha^{-1} year^{-1} (Fig. 7b and Table 3). The total amount of carbon stored initially in the microcosm soil was 29.4 mol. Therefore, an estimated 0.4% of the initial pool of C was leached in the form of DIC and 0.1% as DOC over the equivalent of a 52-year period.

A steady state flux of DIC was not reached in the mesocosm experiment at 115 cm depth but the net flux from the soil profile at a depth of 115 cm was 1770 mmol. This equated to a mean annual flux of 21.5 kmol ha^{-1} year^{-1} compared to a calculated mean annual flux of 5.6 kmol ha^{-1} year^{-1} at 115 cm depth from the microcosm results (Table 3). The steady state flux of DOC from mesocosms at 115 cm was 2.0 kmol ha^{-1} year^{-1} compared to the steady state flux of 1.1 kmol ha^{-1} year^{-1} from microcosms (Table 3).

Annual net sequestration of carbon to the surface soil horizon was estimated at 39.4 kmol ha^{-1} year^{-1} (Table 3). To place this in a wider temporal context, annual carbon sequestration between 870 AD and 1500 AD (50 cm and 35 cm depths, Bw horizon) was 16.7 kmol ha^{-1} year^{-1}. Annual inflow of carbon in the form of DIC dissolved in precipitation was 0.1 kmol ha^{-1} year^{-1}. Total dissolved carbon (DIC and DOC) leached annually from the soil profile in microcosms was 8.5(DIC)+1.1(DOC) =9.6 kmol ha^{-1} year^{-1} by the end of experimental duration. Therefore, the equivalent of 19.6% of annual photosynthetically fixed carbon that accumulated on the soil's surface was leached from the microcosm soil's base in the form of DIC (17.3%) and DOC (2.3%).

The mesocosms had natural vegetation from the field site on their surface (grass and mosses) and as a consequence, carbon was continuously cycled near the soil surface by photosynthesis and respiration. This resulted in a higher flux of carbon at the base of the soil profile than in the microcosms. The mean annual flux of DIC at 115 cm depth was 21.9 kmol ha^{-1} year^{-1} and a steady state flux of DOC was 2.0 kmol ha^{-1} year^{-1}. Therefore, the equivalent of 37.8% of carbon that annually accumulated by photosynthesis on the soil's surface was leached from the mesocosm soil's base in the form of DIC (34.5%) and DOC (3.1%).

The difference between the mean flux of DOC from the microcosm experiment and the steady state flux values for the "pristine profiles" was that the microcosms

Table 3
Carbon fluxes in various surface environments in Iceland

Location	Depth (cm)	Activity	Precipitation (mm year^{-1})	Fluxes			
				(kmol ha^{-1} year^{-1})	(g C m^{-2} year^{-1})	(kmol ha^{-1} year^{-1})	(g C m^{-2} year^{-1})
Field (870 AD–1500 AD)	0	Sequestration of organic C	n.d.	16.7	20.0		
(1500 AD – 2003 AD)	0	Sequestration of organic C	n.d	39.4	47.3		
				DIC		DOC	
Microcosms	15	Flux C through base of horizon	540 [a]	1.0 [b, c]	1.2	1.2 [b]	1.5
	35	Flux C through base of horizon	540 [a]	1.8 [b, c]	2.1	3.1 [b]	3.8
	50	Flux C through base of horizon	540 [a]	2.0 [b, c]	2.4	1.0 [b, c]	1.2
	80	Flux C through base of horizon	540 [a]	3.3 [b, c]	4.0	0.9 [b]	1.0
	115	Flux C through base of horizon	540 [a]	4.8 [b]	5.7	1.0 [b]	1.2
	150	Flux C through base of horizon	540 [a]	4.8 [b, c]	5.7	1.0 [b]	1.2
	170	Flux C through base of horizon	540 [a]	6.1 [b, c]	7.3	1.1 [b]	1.3
Mesocosms	115	Mean flux C through base of horizon	540 [a]	5.6 [d]	6.7	2.0 [d]	2.5
	170	Mean flux C through base of horizon	540 [a]	8.5 [d]	10.2	2.3 [d]	2.8
	15	Flux C through base of horizon	540 [a]	19.8 [d]	23.8	6.3 [b]	7.5
	35	Flux C through base of horizon	540 [a]	27.0 [d]	32.4	7.0 [b]	8.4
	50	Flux C through base of horizon	540 [a]	19.0 [d]	22.8	2.3 [b]	2.7
	80	Flux C through base of horizon	540 [a]	26.4 [d]	31.7	2.9 [b]	3.4
	115	Flux C through base of horizon	540 [a]	21.9 [d]	26.2	2.0 [b]	2.4
Other studies:							
Active soil conservation area [e] (fertilizer applied)		Sequestration of organic C in soil	–	62.5	75.0	–	–
Wetland soils from W-Iceland [e]		Sequestration of organic C in soil	–	56.7	68.0	–	–
Lake Myvatn [f]		Sequestration of C by diatoms	–	183.3	220.0	–	–
River catchment studies:			Runoff (mm year^{-1})				
Bare soil [g]		C-fixation by chemical weathering	1000–1500	0.4	0.4	–	–
Soil covered with birch [g]		C-fixation by chemical weathering	1000–1500	0.9	1.1	–	–
Soil covered with conifers [g]		C-fixation by chemical	1000–1500	1.0	1.2	–	–

Table 3 (*continued*)

Location	Depth (cm)	Activity	Precipitation (mm year^{-1})	Fluxes			
				(kmol ha^{-1} year^{-1})	(g C m^{-2} year^{-1})	(kmol ha^{-1} year^{-1})	(g C m^{-2} year^{-1})
Laxá, Vogatunga [h]		weathering C-fixation by chemical weathering	1732	6.6	8.0	–	–
Hvítá, Kljáfoss [h]		C-fixation by chemical weathering	1769	6.9	8.3	–	–
Hvítá, Kljáfoss [i]		C-fixation by chemical weathering	1404	4.5	5.4	–	–
Bugða [j]		C-fixation by chemical weathering	4930 [k]	14.7	17.6	–	–
			6220 [k]	16.6	19.9		

[a] Precipitation from May to November.
[b] Steady-state flux.
[c] Not significant.
[d] Mean flux.
[e] Oskarsson (personal communication).
[f] Olafsson (1979).
[g] Moulton et al. (2000).
[h] Gislason et al. (1996).
[i] Louvat (1997).
[j] Stefansson and Gislason (2001).
[k] Runoff at time of sampling.

were associated with the measurement of a large initial pulse of DOC (Fig. 7b). For the microcosms, the DOC concentration, after steady state was reached at 170 cm depth, did not differ significantly from the mean concentration measured in the field (Fig. 7b). It may be interpreted that after a period of equilibration (of chemical, biological and physical parameters) the "settled" microcosms more closely reflects the "pristine profiles" (Hodson and Langan, 1999).

Four percent of the carbon stored in the microcosms leached from the soil profile at 170 cm depth in the form of DIC during the experimental duration, the equivalent of 52.8 years (Fig. 7a and Tables 1 and 2). The total percentage of carbon leached out as DOC from the microcosm experiment was 0.1% (Fig. 7b and Tables 1 and 2). Zsolnay (1996) reported that the pool of dissolved organic matter in soils was only 0.04–0.22% of the bulk soil organic carbon. Heal et al. (1978) reported that the litter that is incorporated into the surface horizons had relatively higher potential to leach out DOC than more recalcitrant organic material deeper in the soil profile. It may be assumed that the dominant DOC supply was therefore recently formed litter and plant debris (including roots) near the soil surface. The turnover rate of OM was proportional to the aeolian additions of tephra, the parent material of the soil.

Hence, an increased load of soil minerals and nutrients from the dissolution of parent material in combination with assimilable forms of organic matters enhances microbial activity, the decomposition rates of organic matter and the leaching rates of these components in soils.

The carbon fluxes interpolated from this study are in the same range that other studies have reported for similar soils (Moulton et al., 2000; Oskarsson, personal communication). Furthermore, the lowest and highest fluxes in river catchments reported in the literature also correspond to the calculated fluxes in the microcosm experiment. The lowest values reflect the surface horizons and the highest values relate to the deep horizons. Table 3 summarizes data from various chemical weathering studies in Iceland. Annual sequestration of carbon in the soil profile from 1500 AD to the present was lower (39.4 kmol ha^{-1} year^{-1}) than that of Lake Myvatn, N-Iceland (183 kmol ha^{-1} year^{-1}) (Olafsson, 1979) but higher than the calculated consumption of carbon by chemical weathering in river catchments studies. Gislason et al. (1996) reported carbon consumption of Laxa at Vogatunga at 6.6 kmol ha^{-1} year^{-1} (Table 3). Stefansson and Gislason (2001) reported carbon consumption of Bugda and Sanda river catchments (14.7 and 16.6 kmol ha^{-1} year^{-1}, respectively) by

chemical weathering (Table 3). Laxa at Vogatunga, Bugda and Sanda are all near this study site. Gislason et al. (1996) and Louvat (1997) reported carbon consumption of Hvita-W at 6.9 and 4.5 kmol ha^{-1} $year^{-1}$, respectively. Leaching of DIC from the microcosm profile was one order of magnitude more rapid than levels reported for consumption of HCO_3^- from catchment draining bare volcanic soil (Moulton et al., 2000) but the flux of DIC at 15 cm depth in the microcosms was similar (Table 3). The soil was primarily sequestering carbon in shallow horizons and therefore only small amounts of DIC were leached from the soil into drainage waters or to lower horizons. Moulton et al. (2000) reported that carbon fluxes in waters draining soil increased by a factor of 3 when vegetation was present; hence this represents both a significant input and an important factor in carbon cycling and turnover. This observation by Moulton et al. (2000) is relevant to this study, where the DIC and DOC fluxes were between twice and four times higher for the "pristine profiles" that had vegetation when compared to those reflecting sieved and repacked soils (Table 3).

5. Conclusions

Data on DIC concentrations showed up to 4.7 times higher values in solutions sampled with Rhizon samplers than suction cups. DOC concentrations were up to 8 times higher at 35 and 50 cm depth in solutions sampled with suction cups when compared with Rhizon samplers. This difference was not significant at 80–115 cm depth. Soil solution pH values were up to 1.3 pH units lower Rhizon sampler solutions than in those sampled with suction cups. Low DIC concentrations in the later stages of leaching in the microcosms were due to lack of vegetative cover and the disruption caused by repacking.

Nearly 20% of the carbon that was annually bound near the soil surface was leached from the soil profile at 170 cm depth, 17.3% as DIC and 2.3% as DOC. The carbon in vegetated mesocosm at 115 cm depth was 3- and 2-fold higher in DIC and DOC respectively than that of non-vegetated microcosm.

Carbon sequestration in Icelandic Andosols is high compared to binding of carbon by chemical weathering on river catchment scale in Iceland.

Methods applied in this research can be used to study long-term trends of carbon in Andosols. Although Rhizon samplers cannot be applied in the field due to their lack of ruggedness, they are well suitable to study long-term laboratory experiments. Suction cups should be used in conjunction with sampling funnels and the

sampling system itself used as a buffer against CO_2 loss from soil solution.

References

Arnalds O. Volcanic soils of Iceland. In: Arnalds O, Stahr K, editors. Catena, special issue: volcanic soil resources: occurrence, development and properties, vol. 36. ; 2004. p. 3-20.

Arnalds O, Gretarsson E. Soil map of Iceland. 2nd edition. Iceland: The Agricultural Research Institute; 2001. www.rala.is/desert.

Arnorsson S, Gerardo J, D'Amore F. In: Arnorsson S, editor. Isotopic and chemical techniques in geothermal exploration, development and use. International Atomic Energy Agency; 2000. p. 109–11.

Blake GR. Methods of soil analysis: Part 1. In: Black CA, editor. Physical and mineralogical properties including statistics of measurements and sampling. Madison: American Society of Agronomy; 1965. p. 374–90.

Blakemore LC, Searle PL, Daly BK. Methods for chemical analysis of soils. 1987. New Zealand soil bureau scientific report, vol. 80. ; 1987. 103 pp.

Cabrera RI. Monitoring chemical properties of container growing media with small soil solution samplers. Sci Hortic 1998;75: 113–9.

Chadwick OA, Chorover J. The chemistry of pedogenic thresholds. Geoderma 2001;100:321–53.

Chaudri AM. Personal communication. IACR Rothamsted, Agr and Environm Div, Harpenden, Herts AL5 2JQ, England.

Cole DW, Gessel SP, Held EE. Tension lysimeter studies of ion moisture movement in glacial till and coral atoll soils. Proc – Soil Sci Soc Am 1961;25:321–4.

Cronan CS, Aiken GR. Chemistry and transport of soluble humic substances in forested watersheds of the Adirondack Park, New-York. Geochim Cosmochim Acta 1985;49:1697–705.

Dahlgren R, Shoji S, Nanzyo M. Mineralogical characteristics of volcanic ash soils. In: Shoji S, Nanzyo M, Dahlgren R, editors. Volcanic ash soils – genesis, properties and utilization. Developments in soil science. Amsterdam: Elsevier; 1993. p. 101–44.

Dawson JJC, Bakewell C, Billett MF. Is in-stream processing an important control on spatial changes in carbon fluxes in headwater catchments? Sci Total Environ 2001;265:153–67.

Duan L, Hao JM, Xie SD, Zhou ZP, Ye XM. Determining weathering rates of soils in China. Geoderma 2002;110:205–25.

Eswaran H, Van Den Berg E, Reich P. Organic carbon in soils of the world. Soil Sci Soc Am J 1993;57:192–4.

FAO. World reference base for soil resources. World soil resources reports, vol. 84. Rome: FAO; 1998. 88 pp.

Giesler R, Lundstrom US, Grip H. Comparison of soil solution chemistry assessment using zero-tension lysimeters or centrifugation. Eur J Soil Sci 1996;47:395–405.

Gislason SR, Arnorsson S, Armannsson H. Chemical weathering of basalt in southwest Iceland: effects of runoff, age of rocks and vegetative/glacial cover. Am J Sci 1996;296:837–907.

Gislason SR, Snorrason A, Kristmannsdottir HK, Sveinbjornsdottir AE, Torsander P, Olafsson J, et al. Effects of volcanic eruptions on the CO_2 content of the atmosphere and the oceans: the 1996 eruption and flood within the Vatnajokull Glacier, Iceland. Chem Geol 2002;190:181–205.

Gronvold K, Oskarsson N, Johnsen SJ, Clausen HB, Hammer CU, Bond G, et al. Ash layers from Iceland in the Greenland Grip Ice Core correlated with oceanic and land sediments. Earth Planet Sci Lett 1995;135:149–55.

Grossmann J, Udluft P. The extraction of soil water by the suction-cup method: a review. J Soil Sci 1991;42:83–93.

Heal OW, Latter PM, Howson G. A study of the rates of decomposition of organic matter. In: Heal OW, Perkins DW, editors. Production ecology of British moors and Montane grasslands. New York: Springer; 1978. p. 136–59.

Hodson ME, Langan SJ. A long-term soil leaching column experiment investigating the effect of variable sulphate loads on soil solution and soil drainage chemistry. Environ Pollut 1999;104:11–9.

Holder M, Brown KW, Thomas JC, Zabcik D, Murray HE. Capillary-wick unsaturated zone soil pore water sampler. Soil Sci Soc Am J 1991;55:1195–202.

Hope D, Dawson JJC, Cresser MS, Billett MF. A method for measuring free CO_2 in upland streamwater using headspace analysis. J Hydrol 1996;166:1-14.

Jardine PM, Weber NL, McCarthy JF. Mechanisms of dissolved organic carbon adsorption on soil. Soil Sci Soc Am J 1989;53: 1378–85.

Johannesson H, Saemundsson K. Jarðfræðikort af Íslandi. 1 : 500 000. Berggrunnur. Geology map of Iceland, 1 : 500,000, bedrock (2nd edition). Icelandic Institute of National History, Reykjavik, 1998.

Johnson CE. Cation exchange properties of acid forest soils of the northeastern USA. Eur J Soil Sci 2002;53:271–82.

Jones DL, Edwards AC. Evaluation of polysulfone hollow fibres and ceramic suction samplers as devices for the in situ extraction of soil solution. Plant Soil 1993;150:157–65.

Kalbitz K, Solinger S, Park J-H, Michalzik B, Matzner E. Controls on the dynamics of dissolved organic matter in soils: a review. Soil Sci 2000;165:277–304.

Kern DM. The hydration of carbon dioxide. J Chem Educ 1960;37: 14–23.

Kling GW, Kipphut GW, Miller MC. Arctic lakes and streams as gas conduits to the atmosphere: implications for tundra carbon budgets. Science 1991;25:298–301.

Knight BP, Chaudri AM, McGrath SP, Giller KE. Determination of chemical availability of cadmium and zinc in soils using inert soil moisture samplers. Environ Pollut 1998;99:293–8.

Ladd JN, Foster RC, Skjemstad JO. Soil structure: carbon and nitrogen metabolism. Geoderma 1993;56:401–34.

Lal R. Soil carbon sequestration to mitigate climate change. Geoderma 2004;123:1–22.

Larsen G. Nokkur orð um Kötlugos og Kötlugjósku. In: Larsen G, editor. Kötlustefna, Rannsóknir á eldvirkni undir Mýrdalsjökli. Reykjavík: The Science Institute, University of Iceland; 1993. p. 6–7. [in Icelandic].

Louvat P. Étude géochimique de l'érosion fluviale dîles volcaniques a l'aide des bilans d'éléments majeurs et traces: Ph.D. thesis, University of Paris, Paris, 1997.

Louvat P, Allegre CJ. Present denudation rates on the island of Reunion determined by river geochemistry: basalt weathering and mass budget between chemical and mechanical erosions. Geochim Cosmochim Acta 1997;61:3645–69.

Lundquist EJ, Jackson LE, Scow KM. Wet–dry cycles affect dissolved organic carbon in two California agricultural soils. Soil Biol Biochem 1999;31:1031–8.

McDonald JP, Gulliver JS. Methane tracer technique for gas transfer at hydraulic structures. In: Wilhelms SC, editor. Air–water mass transfer - selected papers from the 2nd international symposium on gas transfer at water surfaces. New York, USA: American Society of Civil Engineers; 1990. p. 267–77.

Moulton KL, West J, Berner RA. Solute flux and mineral mass balance approaches to the quantification of plant effects on silicate weathering. Am J Sci 2000;300:539–70.

Nanzyo M, Dahlgren R, Shoji S. Chemical characteristics of volcanic ash soils. In: Shoji S, Nanzyo M, Dahlgren R, editors. Volcanic ash soils: genesis, properties and utilization. Amsterdam: Elsevier; 1993. p. 323–53.

Olafsson J. Chemistry of Lake Myvatn and River Laxa. Oikos 1979;32:82-112.

Oskarsson H, Arnalds O, Gudmundsson J, Gudbergsson G. Organic carbon in Icelandic Andosols: geographical variation and impact of erosion. In: Arnalds O, Stahr K, editors. Catena, special issue: volcanic soil resources: occurrence, development and properties, vol. 36; 2004. p. 225–38.

Parfitt RL. Allophane in New-Zealand – a review. Aust J Soil Res 1990;28:343–60.

Parfitt RL, Childs CW. Estimation of forms of Fe and Al: a review, and analysis of contrasting soils by dissolution and Moessbauer methods. Aust J Soil Res 1988;26:121–44.

Parfitt RL, Kimble JM. Conditions for formation of allophane in soils. Soil Sci Soc Am J 1989;53:971–7.

Parkhurst DL, Appelo CAJ. User's guide to PHREEQC (Version 2) – a computer program for speciation, batch-reaction, one-dimensional transport, and inverse geochemical calculations. Water resources investigations report 99-4259. Lakewood: US Geological Survey; 1999.

Patterson BM, Franzmann PD, Rayner JL, Davis GB. Combining coring and suction cup data to improve the monitoring of pesticides in sandy vadose zones: a field-release experiment. J Contam Hydrol 2000;46:187–204.

Plummer LN, Busenberg E. The solubilities of calcite, aragonite and vaterite in CO_2–H_2O solutions between 0 and 90 °C, and an evaluation of the aqueous model form the system CaO_3–CO_2–H_2O. Geochim Cosmochim Acta 1982;46:1011–40.

Sigfusson, B., 2004. Assessment of in-situ weathering of a, Histic Andosol – microcosm to field scale study. M.Sc. thesis. University of Iceland. 136 pp.

Singh BK, Millard P, Whitely AS, Murrell JC. Unravelling rhizosphere–micobial interactions: opportunities and limitations. Trends Microbiol 2004;12:388–93.

Six J, Elliott ET, Paustian K. Soil macroaggregate turnover and microaggregate formation: a mechanism for C sequestration under no-tillage agriculture. Soil Biol Biochem 2000;32:2099–103.

Soil Survey Staff. Soil survey laboratory methods manual. Soil survey laboratory investigations report no. 42. Washington D.C.: USDA-NRCS; 1996.

Stefansson A, Gislason SR. Chemical weathering of basalts, Southwest Iceland: effect of rock crystallinity and secondary minerals on chemical fluxes to the ocean. Am J Sci 2001;301: 513–56.

Straub H, Udluft P, Wiel L. Neues system der Sickerwassergewinnung zur Bestimmung leichtfluchtiger organischer Spurenstoffe. Z Wasser-Abwasser Forsch 1988;21:155–7.

Takkar PN, Ulrich B, Meiwes K. Method for estimation of $CO_2(aq)$ plus $H_2CO_3^0$, HCO_3^- and pH in soil solutions collected under field conditions. Z Pflanzenernahr Bodenkd 1987;150:319–26.

van Hees P, Lundström U, Danielsson R, Nyberg L. Controlling mechanisms of aluminium in soil solution – an evaluation of 180 podzolic forest soils. Chemosphere 2001;45:1091–101.

Wagner GH. Use of ceramic cups to sample soil water within the soil profile. Soil Sci 1962;94:379–86.

Wolff-Boenisch D, Gislason SR, Oelkers EH, Putnis CV. The dissolution rates of natural glasses as a function of their composition at pH 4 and 10.6, and temperatures from 25 to 74 °C. Geochim Cosmochim Acta 2004;68:4643–58.

Zielinski GA, Mayewski PA, Meeker LD, Gronvold K, Germani MS, Whitlow S, et al. Volcanic aerosol records and tephrochronology of the Summit, Greenland, ice cores. J Geophys Res-Oceans 1997;102:26625–40.

Zsolnay A. Dissolved humus in soil waters. In: Piccolo A, editor. Humic substances in terrestrial ecosystems. Amsterdam: Elsevier; 1996. p. 171–223.