Soil Carbon Pools and Fluxes: Dissolved organic carbon transport in California forest and grassland soil

Marie McKenzie and Michelle Lazaro

NREM 680

Book Information & Chapter Reading (Ch. 7)

- Decomposition consists of abiotic and biotic processes that transform litter into CO_2, **DOC**, and/or SOM.

- Decomposition results from three different types of processes:
    - Ø Leaching
    - Ø Fragmentation
    - Ø Chemical alteration

Book Information & Chapter Reading Cont.

- Most carbon enters the ecosystem as gross primary production (GPP) and leaves through several processes, including plant and heterotrophic respiration, **leaching of DOC** and DIC, emission of volatile organic compounds, methane flux, and disturbance.

- **Leaching** (water) transfers soluble materials away from decomposing organic matter into the environment. Then they are either absorbed by organisms, react with the mineral phase of soil or sediments, or are lost from the system in solution.

Book Information & Chapter Reading Cont.

- **Leaching of litter**

Physical process by which mineral ions and small water-soluble organic compounds dissolve in water and flow out of the detritus.

Carbon at the soil surface originating from litterfall can be incorporated into the mineral horizon by (1) leaching of DOC and/or (2) biological and physical mixing, with root turnover and exudation representing direct inputs of C.

Book Information & Chapter Reading Cont.

- Most decomposition occurs near the soil surface, where litter inputs are concentrated

Deep roots and soil mixing occurring by animals, especially termites and earthworms, as well as leaching of dissolved organic matter to depth.

About half of the soil organic carbon therefore is typically below
20 cm depth, while a third of roots is below that.

On average, deep-soil carbon is older, more recalcitrant, and more tightly bound to soil minerals than is surface carbon, but a small fraction of the deep soil carbon is modern, coming mostly
from turnover of deep roots.

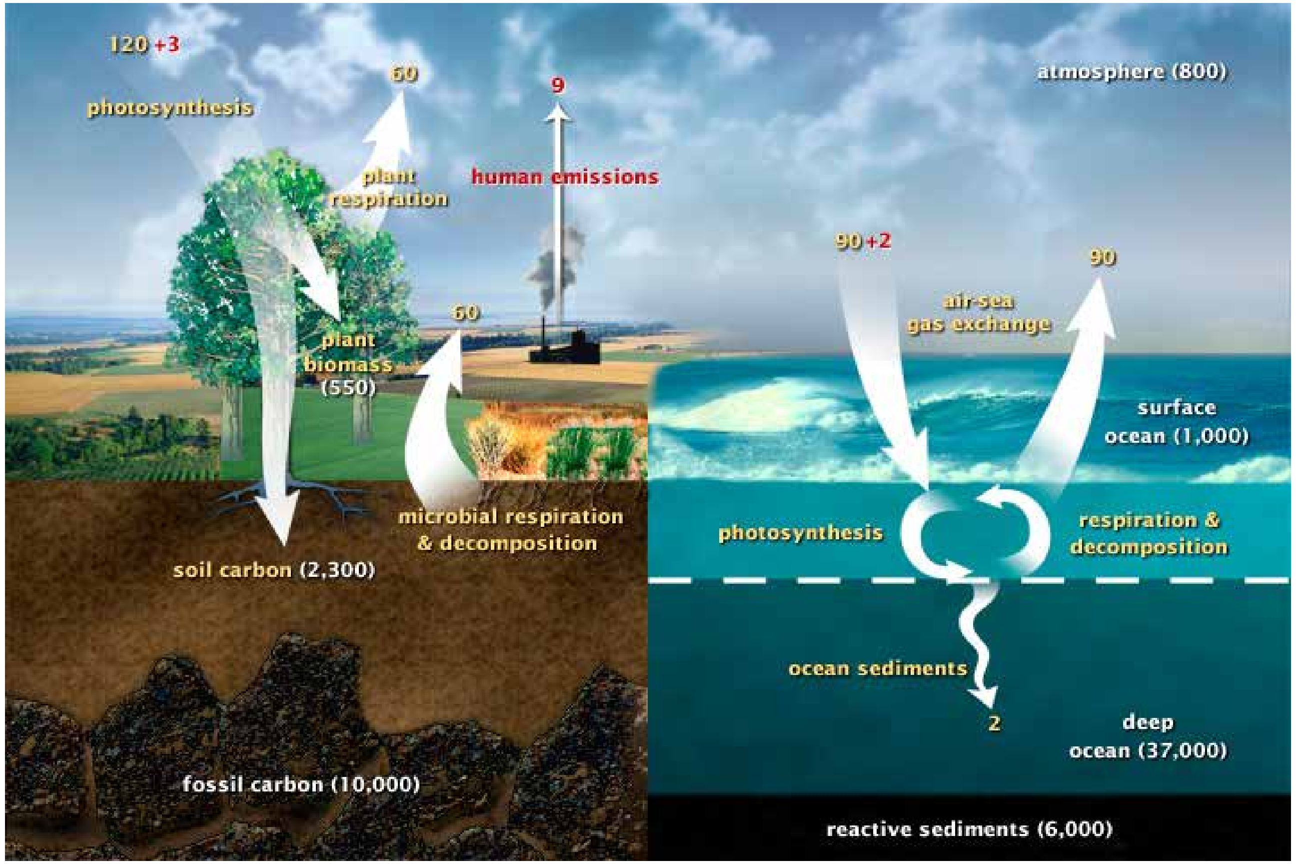
Book Information & Chapter Reading Cont.

- **Factors controlling Decomposition**
  - **Substrate quality**
  - **Characteristics of the microbial community**
  - **Physical environment**

- 75% of terrestrial organic carbon is dead organic matter in soils.

Soil C Pool and Fluxes – additional information

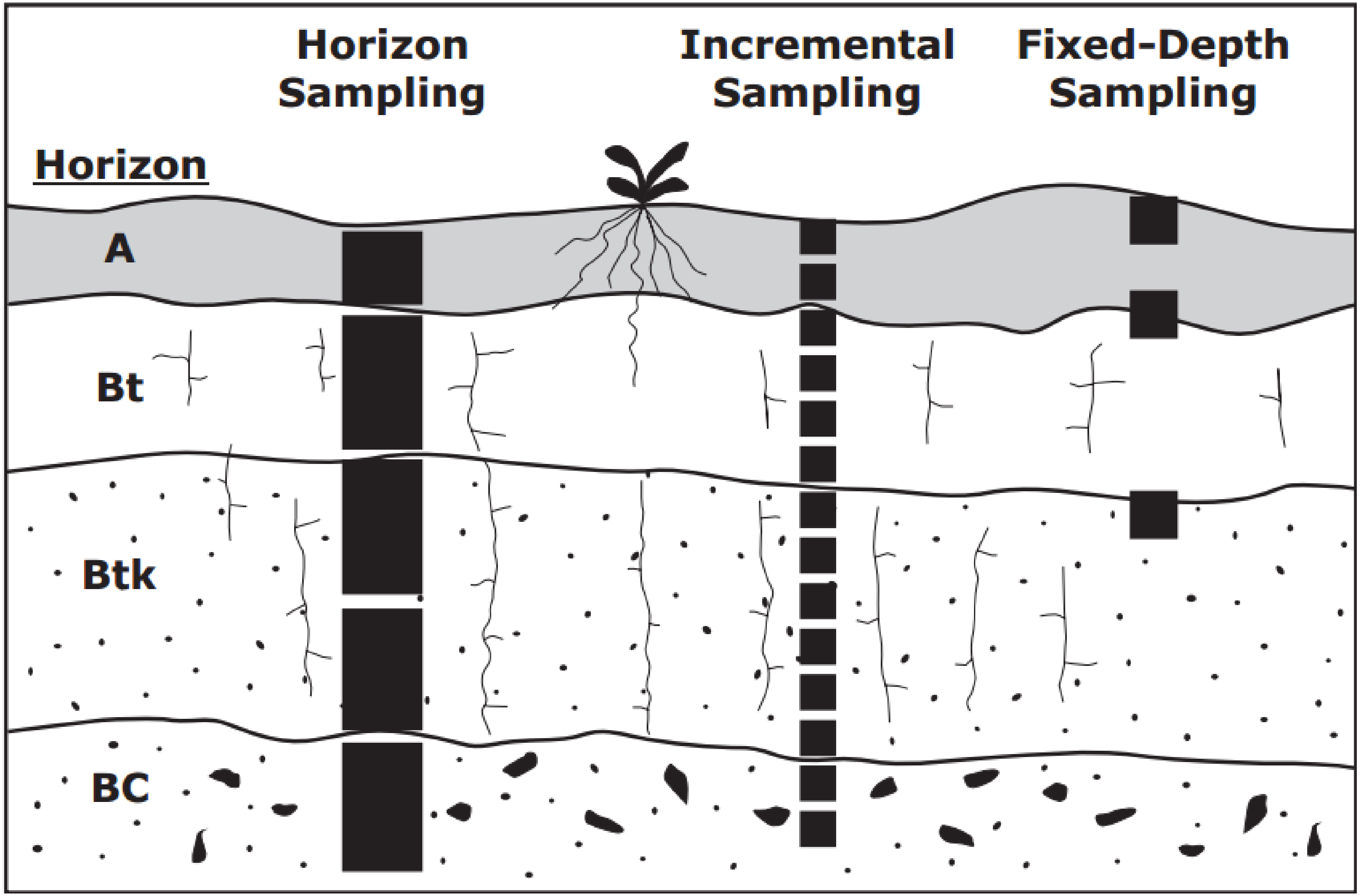
- Soils retain large quantities of carbon (C), thereby slowing its return to the atmosphere.
- More C stored within soil than within the atmospheric and vegetative pool combined
- However, the mechanisms governing organic carbon sequestration in soil remain poorly understood, yet are integral to understanding soil-climate feed- backs



Soil orders

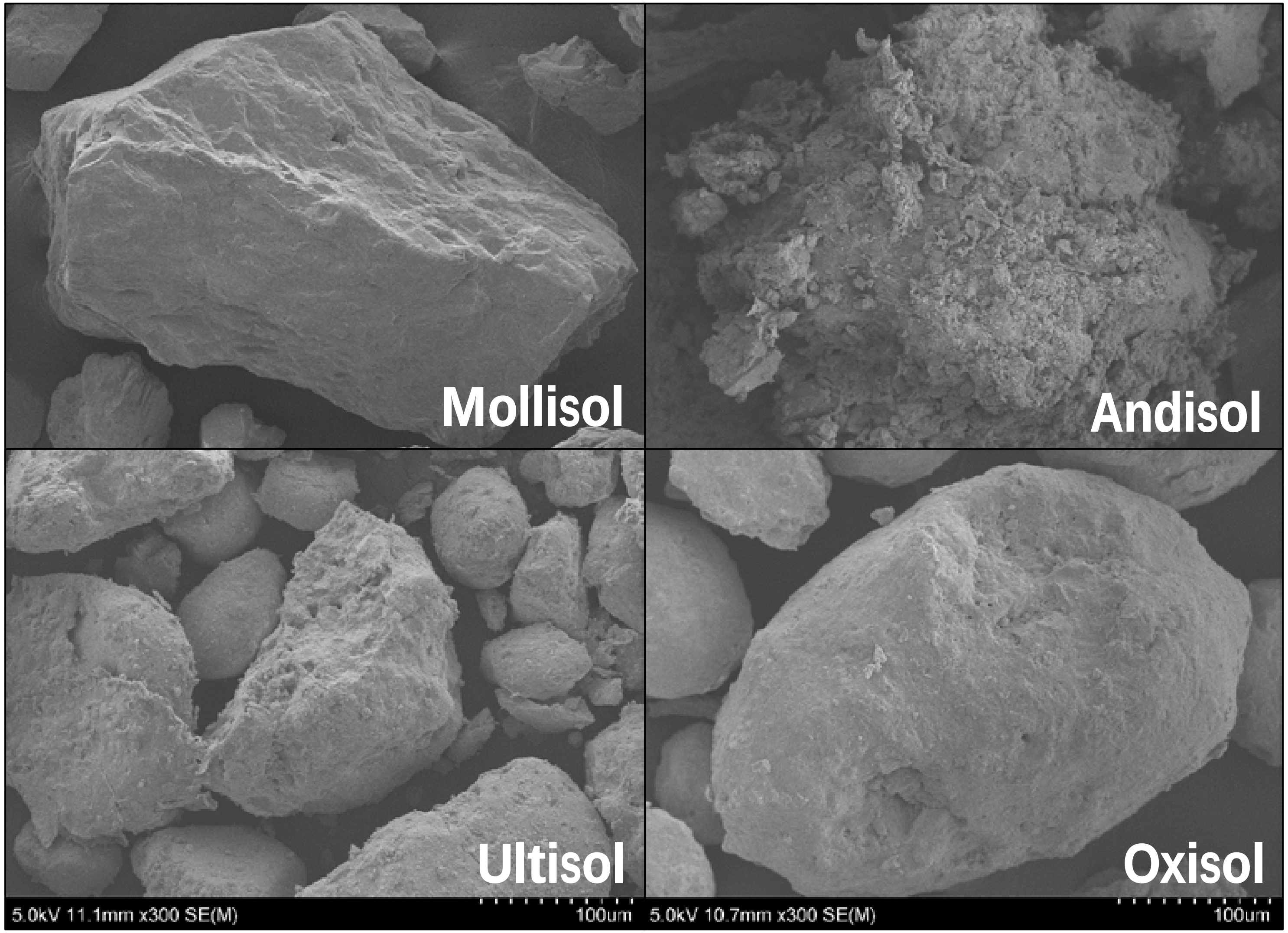
- Soils are largely spatially and temporally variable due to differences in climate, formation factors, and land management techniques
- Variations in soil properties occur within horizons, but distinct differences generally occur between horizons

Additional soil information – sampling methods



- Soil sampling is typically done using one of three methods
- Each method has pros and cons
- Depends on methods and project goals

Sand sized particles



- Differences in soil orders cause drastic differences in the soil surfaces
- Stage of weathering affects the amount of surface area on the particle surface

Why dissolved organic C (DOC) is important in soil C pools and fluxes

- Paradox in the literature, researchers recognize the importance of the dissolved phase in the decomposition of detrital material as a requirement for microbial processing of SOM
  - However, models of soil C cycling almost exclusively ignore DOC
- It is commonly observed that DOC concentrations are highest in soil solutions leaching out of the O horizons and that concentrations typically drop as water percolates through the mineral soil
- Actual mechanisms by which this occurs is poorly understood
  - Most current literature on soil DOC explains this trend as production of DOC in the organic-rich surface layers and subsequent loss by adsorption and microbial mineralization

A comparative study of dissolved organic carbon transport and stabilization in California forest and grassland soils – Sanderman and Amundson (2009)

- Ronald Amundson, PhD Professor of pedology and chair, department of environmental science, policy and management at University of California Berkeley

- Jonathan Sanderman, PhD senior research scientist in CSIRO Land and Water's Soil and Landscape Science Program – Waite Campus, Australia

Terminology

Carbon sequestration

Transferring atmospheric CO_2 into long-lived pools and storing it securely so it is not immediately reemitted.

Soil organic matter

Organic matter component of soil, consisting of plant and animal residue at various stages of decomposition, cells and tissues of soil organisms, and substances synthesized by soil organism.

Radiocarbon

Radioactive C.

Dissolved organic carbon

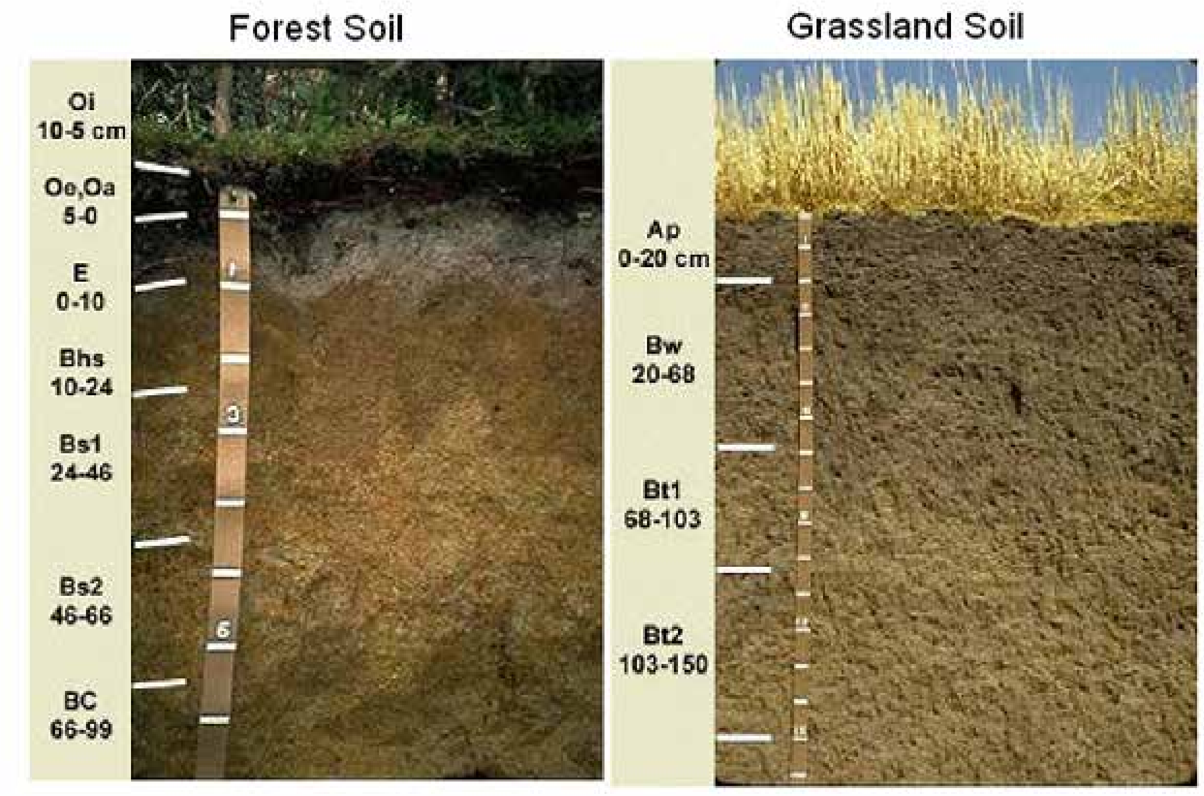
water-soluble organic C.

Mean residence time (MRT)

Calculated as the total mass divided by the flux into or out of the atmosphere over a given time period.

Purpose of the study

- Examine the importance of DOC in transporting and sequestering C in the mineral soil in two strongly contrasting ecosystems
- In order for C to be effectively sequestered beyond a timescale of a few decades, C must become physically stabilized, commonly by association with clay surfaces and in subsurface mineral horizons
  - Yet the rates of this process are poorly known



Site description – forest location

- Casper creek located in the coastal redwood zone of Mendocino County, CA
- Dominated by 100 year-old second growth redwood-Douglas fir forest
- Soils are well-weathered derived from greywacke sandstone
- Classified as a Typic Haplohumults

Site description – prairie site

- Tennessee valley located in coastal Marin county California
- Dominated by European grasses, various forbs, and to a lesser extent native perennial grasses
- Soils classified as a Typic Haplustolls
- A horizon mixed by gophers and ground squirrels




Methods

Field sampling and monitoring

Probes and dataloggers used to investigate DOC fluxes.

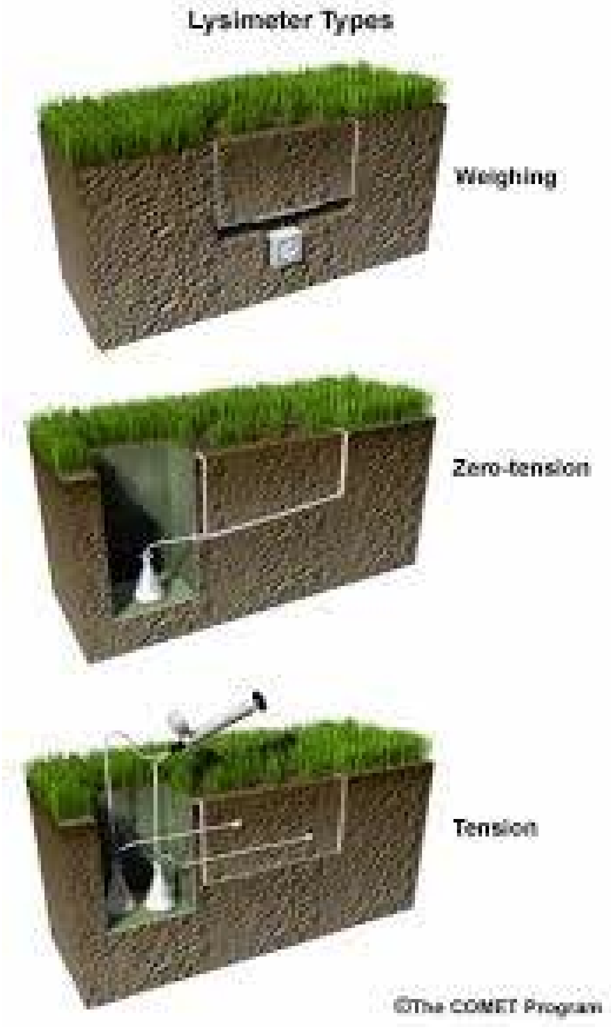
Decagon echo probes: volumetric water content. Dug holes, monitoered continuously at 10, 20 and 50 cm.

Ceramic cup tensiometers installed 10, 25, 50, 75 and 100 cm – monitored using a needle pressure transducer.

Zero-tension lysimeter, used for collecting water and contaminants that are mobile in the soil. Installed at 0, 3, 7, 15, and 30 cm at the forest site and 10 cm at the grassland site

Prenart super-quartz tension lysimeter installed at 40, 70 and 120 cm.

After a three month quilibrium period, soil solution samples were collected approx. every 2 weeks from the tension lysimeter and after most large rain events for the zero tension samplers for 2005 and 2006 hydrologic years



Methods Cont.

CO_2 soil concentration at 10, 25, 20, 75 and 100 cm – measured in the filed by sampling soil air from stainless steel gas wells capped with silicon septa at 18 sampling dates thru out HY2005.

Analyzed on a portable Licor 6200 infrared gas analyzer

Soil inputs

Aboveground productivity of the grasses was assessed by measuring the max. standing biomass in 0.25 m^2 quadrants. Root-to-shoot ratio smaller subsamples next to quadrants used to estimate belowground productivity. Root mass was measured by washing soil from roots and then measuring dry weight samples.

Casper Creek site, litterfall, as a proxy for aboveground C inputs to the soil system, collected at approx. monthly intervals using 0.1 m^2 baskets (n=6). Baskets excluded most coarse woody debris, thus underestimating the actual productivity.

DOC flux

Multiplying the DOC concentrations for each sampling period by the water flux then summing to obtain annual values.

Methods Cont.

Laboratory & Bioavailable Experiments

Sorption isotherms

Potential for the soils to absorb or desorb C – batch adsorption experiment

Triplicated 3 g samples of dried soil, equilibriated with different DOC concentrations overnight on a shker table, centrifuged and then filtered to 0.45 µm.

Field-collected throughfall and soil water samples were incubated in the dark at lab temp. (~18C) for 2 months. The field samples were filtered to 0.7 µm. Results from bioavailability experiment were interpreted using the 2-pool 1st order decay model:

$$\%DOC_{\text{remaining}} = Ce^{k_f t} + (100 - C)e^{k_s t},$$

Study questions and experimental design

- C in the soil surface can be incorporated into mineral horizon by leaching of DOC and/or biological and physical mixing, with root turnover and exudation representing direct inputs of C
- The relative magnitude of these processes and how they vary from forests to grasslands has been difficult to determine
- DOC and CO_2 fluxes, laboratory sorption, and biomineralization rates, and soil C stocks from a coniferous forest and prairie soil were measured in order to compare the magnitude of DOC transport and retention relative to the other major C transport processes

Overview on modeling equations

Where change in C mass in a given horizon over time is equal to the net addition/loss by diffusive process minus net addition/loss by advective processes minus C loss to microbial respiration plus any input of C from plants

$$\frac{\partial C}{\partial t} = D\frac{\partial^2 C}{\partial z^2} - v\frac{\partial C}{\partial z} - kC + f_d,$$

Z = changes in C mass in a given horizon

kC = net addition/loss by diffusive processes minus net addition/loss by advective processes minus C lost to microbial respiration

Fd = any input from plants (direct input of organic via litterfall at the surface and via root turnover within the soil

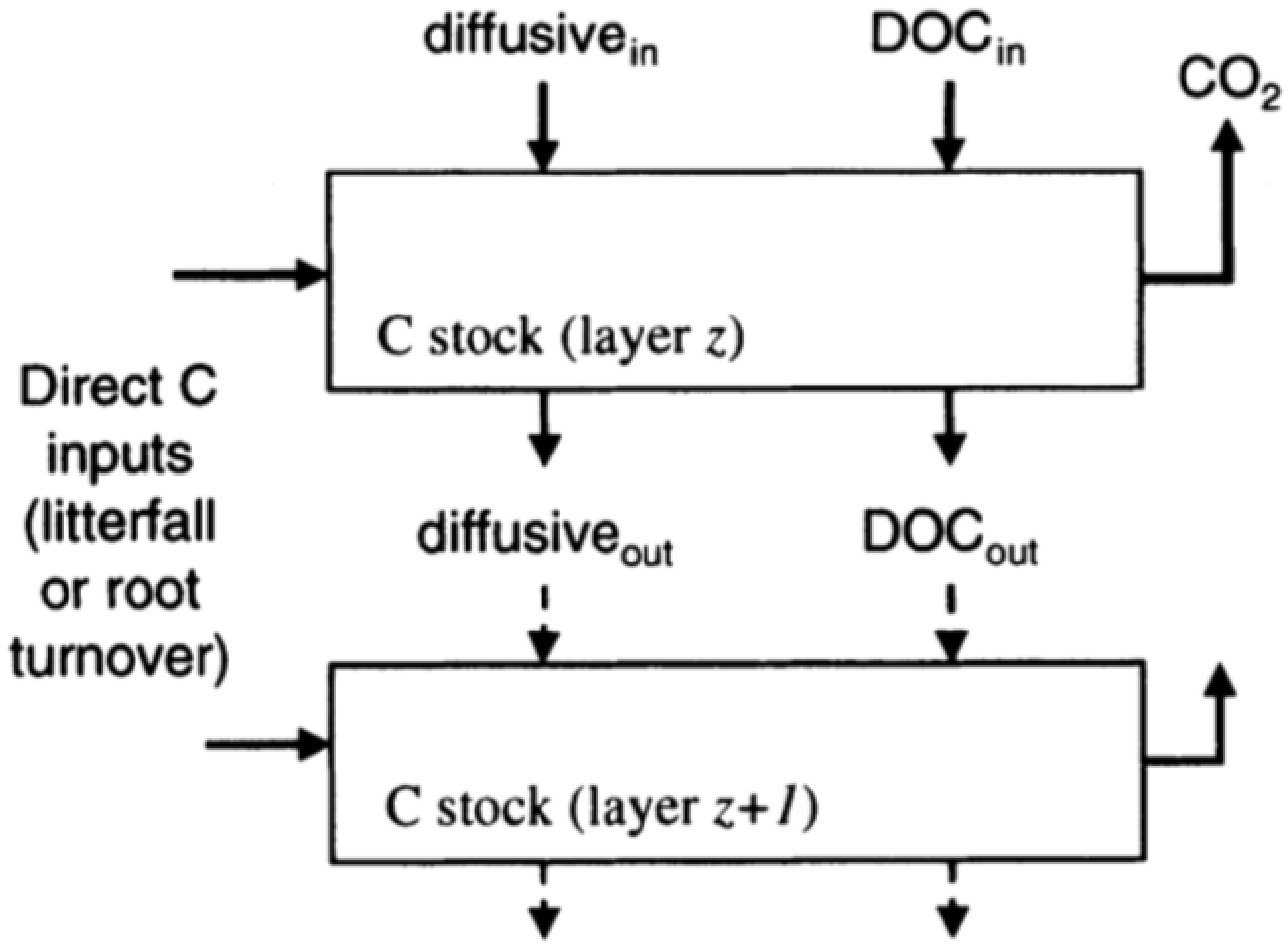
D = diffusion coefficient ($mm^2 year^{-1}$)

v = advective transport coefficient ($mm\ year^{-1}$)

k = decomposition constant ($year^{-1}$)

Overview of modeling equations – C transport model

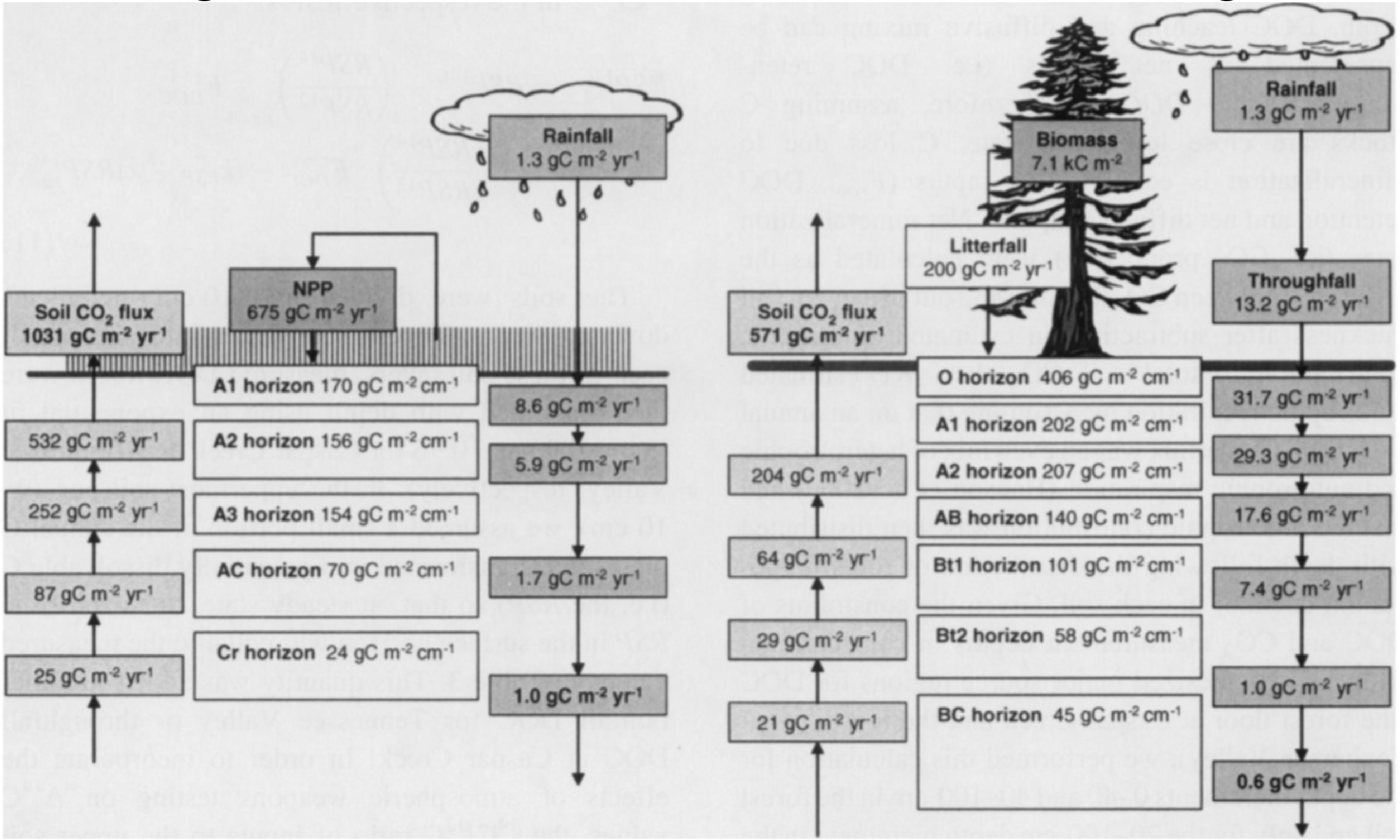
- For a given soil layer, the change in C over time is the difference between input and losses



Overview of modeling equations – C input calculation

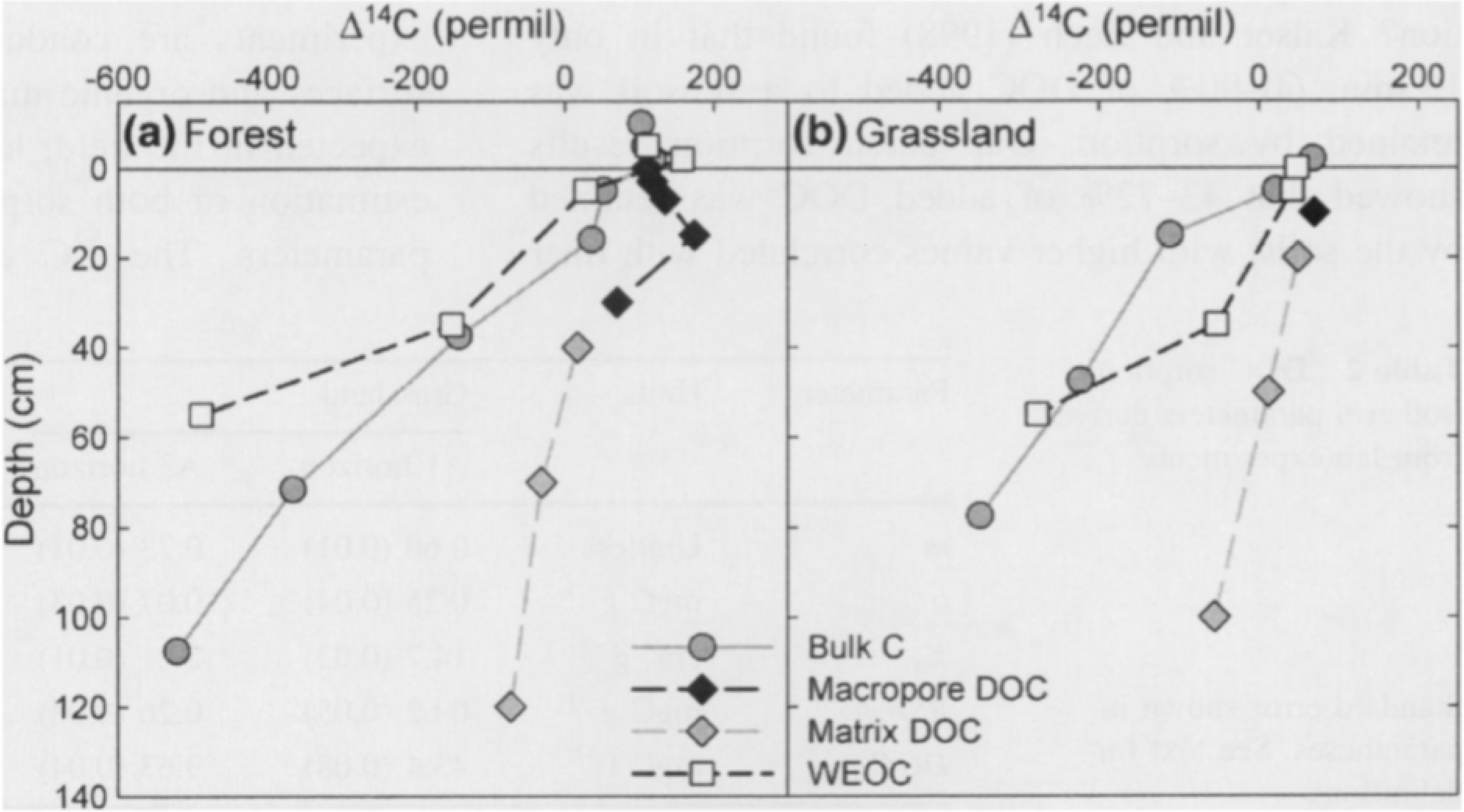
- C inputs = root turnover and exudation (F root), DOC leaching (DOC in), and diffusive mixing of C from above
- C losses = mineralization to CO_2, DOC leaching (DOC out), and diffusive mixing to deeper horizons
- DOC leaching and diffusive mixing can be represented as net inputs (ie. DOC retention = DOC in – DOC out)
- C loss due to mineralization rate (ie. CO_2 production) were calculated as the difference between CO_2 flux into and out of a given soil thickness after subtracting an estimated autotrophic respiration and that the autotrophic contribution was then distributed

Figures from the article – C budgets



- Annual CO2 fluxes and DOC fluxes
- Grassland C budgets on the left, forested site on the right

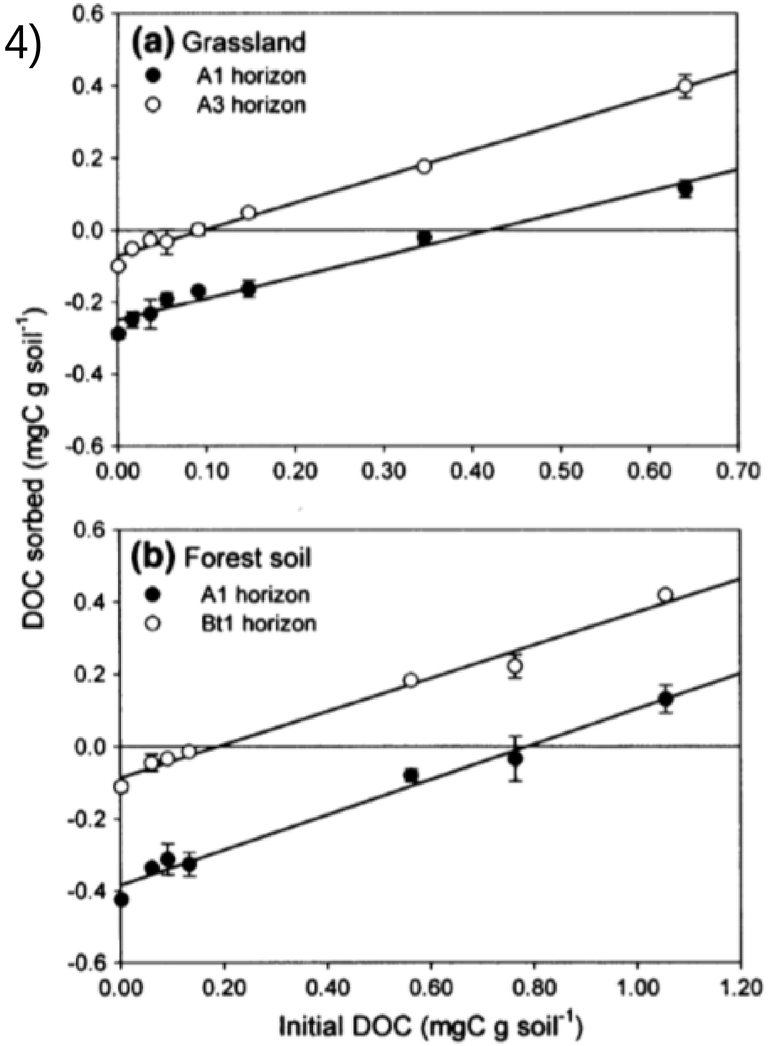
Figures from the article – Figure 3



- Change in ^{14}C values of bulk soil, water extractable organic C, field collected macropore DOC and matrix water DOC in depth

Figures from the article – Figure 4

4)



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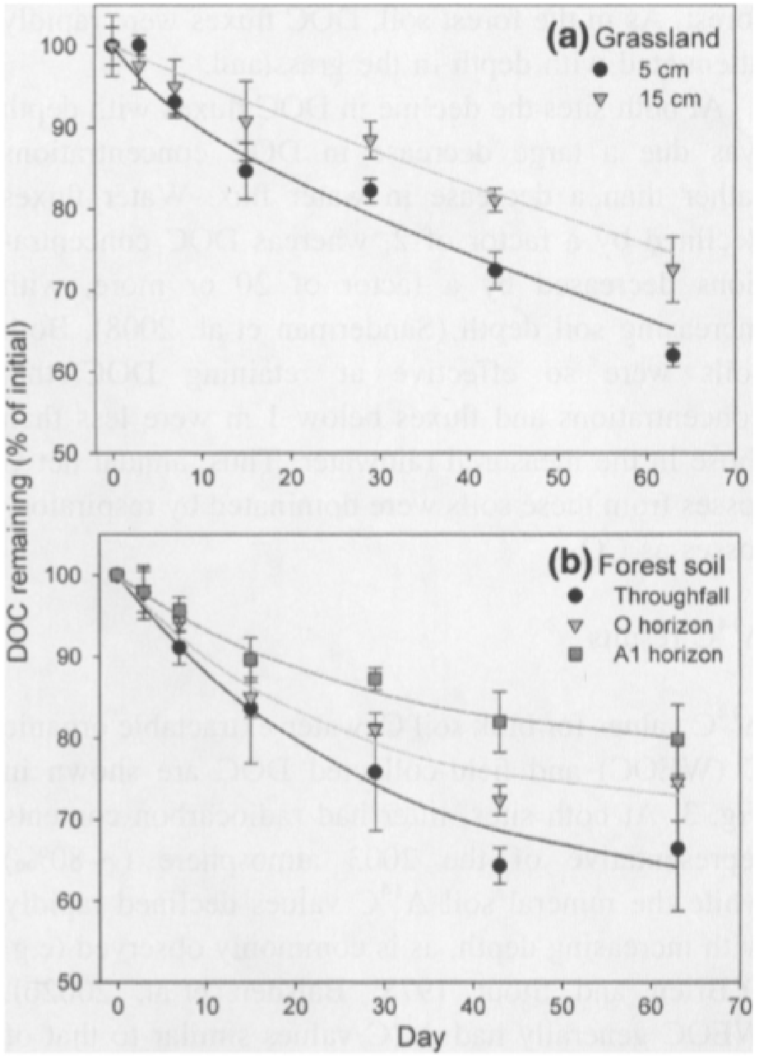
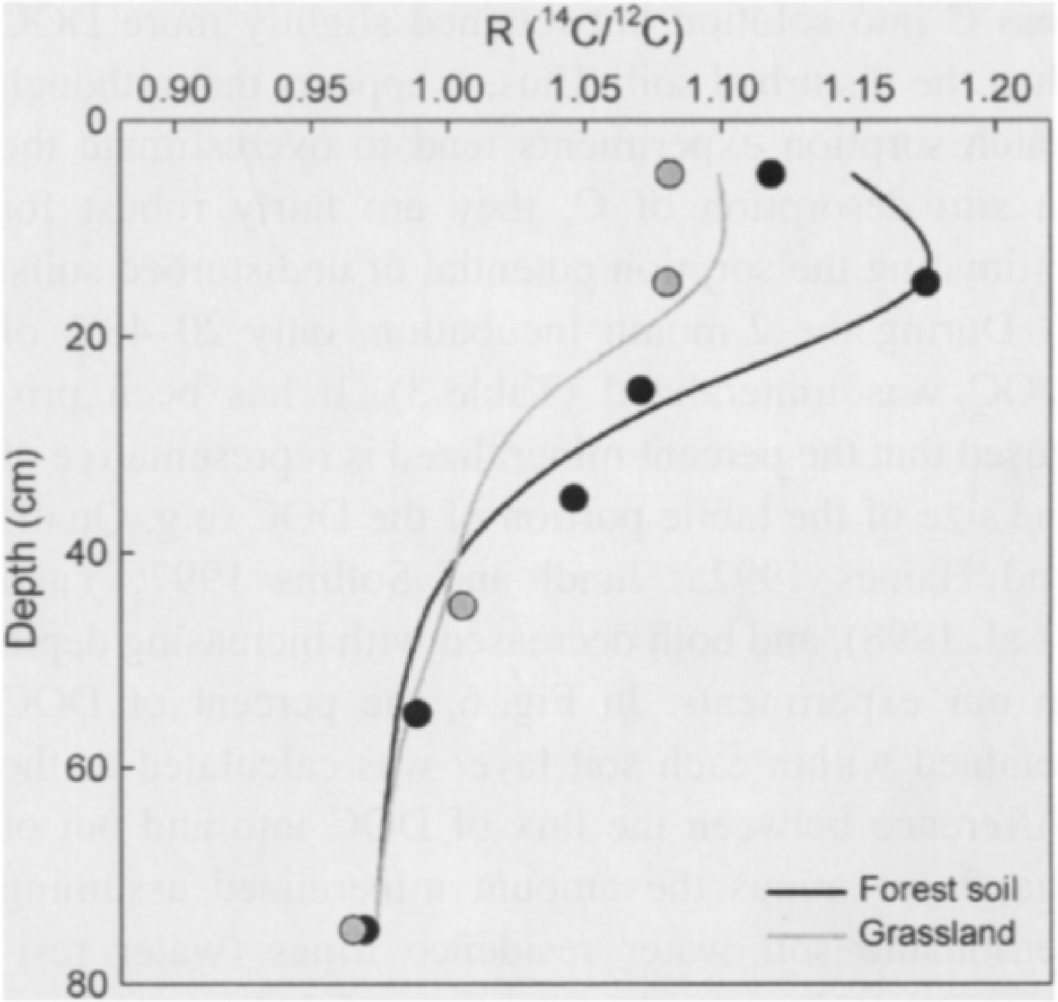


- Figure 4 shows the DOC sorption isotherms for both sites
- Figure 5 shows the DOC incubation results plotted as % of initial DOC concentration remaining for both sites

Figures from the article – Figure 7



- Best fit curves used to calculate mean residence time of the reactive soil pool based on the $^{14}C/^{12}C$ ratio of DOC for forest and grassland soils
- Decreasing V with increasing depth at both sites
- More realistic figure showing both abiotic and biotic processes occurring within soil
- DOC sorptive capacities of mineral surfaces will vary with mineralogy and degree of saturation

Figures from the article – Table 4

Soil C input and loss rates as measures or modeled

Depth	CO_2 production[a]	DOC retention[b]	Unaccounted inputs[c] (root + net diffusive)		DOC retention[d]
cm	gC m^{-2} $year^{-1}$	gC m^{-2} $year^{-1}$	gC m^{-2} $year^{-1}$	% of total inputs	% of total inputs
Forest					
0–40	268	24.3	243.7	90.9	9.1
40–100	31	6.8	24.2	78.1	21.9
Grassland					
20–100	283	4.8	278.2	98.3	1.7

See text for details

[a] CO_2 production is for heterotrophic respiration only (estimated as 50% of total soil respiration with the autotrophic contribution exponentially decreasing similar to the observed drop in root abundance)

[b] DOC retention = DOC flux in – DOC flux out of given depth increment

[c] Unaccounted inputs = CO_2 production – DOC retention

[d] DOC retention as a percentage of total inputs

Results and Conclusions

- ***DOC and the soil C cycle*.**
- Focusing on soil as a single unit, annual DOC losses are minor relative to respiratory losses
- However, that is a simplistic view, this paper focused on the importance of DOC in translocating and sequestering C at depth in the mineral soil
- In a redwood forest with deeply weathered Ultisols, nearly 31.7gC m^{-1} yr^{-1} are leached as DOC from the forest floor, 17.6gC m^{-1} yr^{-1} percolates through the A horizon, and only 0.6 gC m^{-1} yr^{-1} leaves the B horizon
- Given the lack of biophysical mixing and low root inputs at depth, DOC movement and subsequent adsorption is likely the most import C input to the deep mineral soil
- Due to the adsorption mechanisms by which DOC is stabilized in the subsoil, the downward translocation of C in soil solution represents a unique pathway in the soil C cycle where material that would be mineralized in a few years at the soil surface is stabilized against mineralization for centuries

Case Study – Michalzik et al. 2001

Fluxes and concentrations of dissolved organic carbon and nitrogen – a synthesis for temperate forests

Karsten Kalbitz, PhD
University of Amsterdam

B. Michalzik – Author for correspondence, center of ecology and hydrology

J.-H Park, S. Solinger and E. Matzner

Department of Soil Ecology, Bayreuth of Terrestrial Ecosystem Research (BITOK).

Biogeochemistry **52:** 173–205, 2001.
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Fluxes and concentrations of dissolved organic carbon and nitrogen – a synthesis for temperate forests

B. MICHALZIK*, K. KALBITZ, J.-H. PARK, S. SOLINGER & E. MATZNER
*Department of Soil Ecology, Bayreuth Institute of Terrestrial Ecosystem Research (BITÖK), University of Bayreuth, D-95444 Bayreuth, Germany (*author for correspondence, Centre for Ecology and Hydrology, CEH Windermere, The Ferry House, Ambleside Cumbria LA22 0LP, U.K. e-mail: bmi@ceh.ac.uk)*

Key words: dissolved organic carbon, dissolved organic nitrogen, forest ecosystems, regional scale

Abstract. Dissolved organic carbon (DOC) and nitrogen (DON) represent an important part of the C and N cycles in forest ecosystems. Little is known about the controls on fluxes and concentrations of these compounds in soils under field conditions. Here we compiled published data on concentrations and fluxes of DOC and DON from 42 case studies in forest ecosystems of the temperate zone in order to evaluate controls on a larger temporal and spatial scale. The focus was on annual fluxes and concentrations in throughfall, forest floor leachates and soil solutions. In all compartments considered, concentrations and fluxes differed widely between the sites. Highest concentrations of DOC and DON were generally observed in forest floor leachates and in A horizons. Highest fluxes occurred in forest floor leachates. The fluxes of DOC and DON in forest floor leachates increased with increasing annual precipitation and were also positively related to DOC and DON fluxes with throughfall. Variation in

Case Study – Michalzik et al. 2001

- Complied and synthesize published data on concentrations and annual fluxes of DOC and DON along a vertical profile in forest ecosystems and to evaluate the relevance of DOC and DON for the overall C and N turnover.
- Little is known about the controls on fluxes and concentration dissolved organic carbon as well as nitrogen in soils under field conditions.
- Impossible to quantify the individual contributions of each of these sources to DOM release.

Case Study – Methods

Table 1. Solution concentrations and fluxes of DOC and DON in throughfall, forest floor percolates and soil solutions of the mineral soil

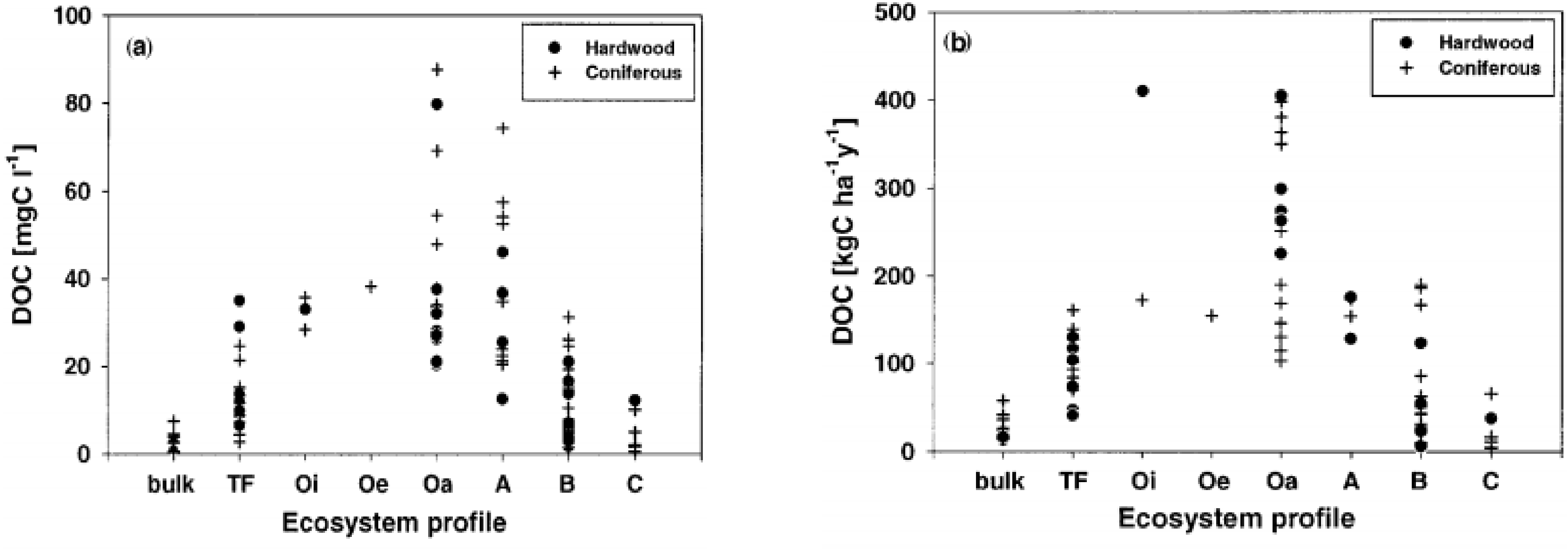
Location	Climate[1]	Dominant vegetation[2]	Soil[3]	Compartment	DOC Concentration[4] [mg l^{-1}]	DOC Fluxes[5] [kg ha^{-1} a^{-1}]	DON Concentration[4] [mg l^{-1}]	DON Fluxes[5] [kg ha^{-1} a^{-1}]	Reference[6]
Adirondack Park, New York State, U.S.	Temperate, 1000 mm a^{-1}; 5 °C; 174, 122 and 561 m a.s.l.	Northern hardwood forest, Fa, Ac, B, Ts, Pic, Pin,	Series of Spodosols Haplorthods, Fragiorthods, Haplaquods	**Oa layer** of					Cronan and Aiken, 1985
				Site 1	32 ± 7[a]	—	—	—	
				Site 2	21 ± 6	—	—	—	
				Site 3	27 ± 5	—	—	—	
				B horizon of					
				Site 1	7 ± 2[a]	—	—	—	
				Site 2	5 ± 1	—	—	—	
				Site 3	7 ± 1	—	—	—	
Medicine Bow Mountains, SE Wyoming, U.S.	Subalpine, 600 mm a^{-1}	Coniferous forest Pin	Cryocrepts to Cryoboralfs	**Throughfall**	—	—	0.58	1.2	Fahey et al., 1985
				O-layer	—	—	1.48[b]	6.2	
				B horizon (40 cm)	—	—	0.48	1.2	
				C horizon (180 cm)	—	—	0.08	0.1	
Study site of Solling project, Niedersachsen, Germany	Temperate, 1032 mm a^{-1}; 6.4 °C; 500 m a.s.l.	Hardwood forest Fa Coniferous forest Pic	Cambisols	**Throughfall**					Matzner, 1998
				Hardwood	—	—	0.95	7.0[b]	
				Coniferous	—	—	1.28	9.6	
				O layer					
				Hardwood	—	—	2.03	12.5	
				Coniferous	—	—	1.64	11.8	
				C horizon (90 cm)					

Site Locations

- Many of the studies (38) encompassed temperate forest ecosystems. The studies cover 26 coniferous, 14 deciduous, one mixed forest site and one peat site with stand ages ranging from 30 to 250 years.

- The dominant soil types according to Soil Survey Staff (1992) are spodosols and cambisols followed by ultisols, inceptisols, alfisols and histosols.

Case Study – Michalzik et al. 2001 Results



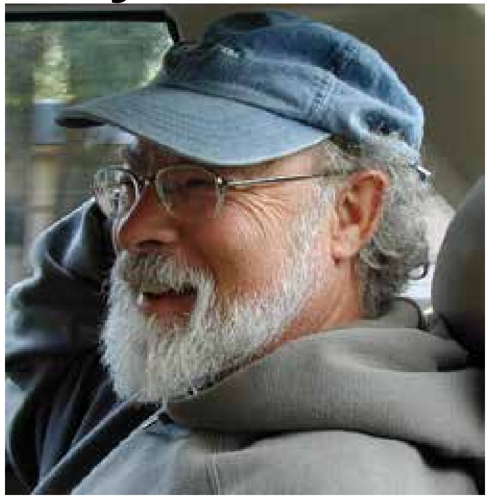
Case Study – Michalzik et al. 2001 Conclusion

- Varying sites differs in concentration of DOC and DON
- Highest concentrations of DOC and DON observed in forest floor leachates and in A horizons.
- Throughfall fluxes explains 46% and 65% of the variation in DOC and DON fluxes from the forest floor.
- No difference in DOC and DON concentrations and fluxes in forest floor leachates between coniferous and hardwood sites.
- Concentrations of DOC in forest floor leachates were positively correlated to the pH of the forest floor.
- Annual fluxes and concentrations of DON and DOC at regional scale differed from those reported for smaller time and space scales.

Case Study – Kramer et al. 2012
Long-term C storage through retention of dissolved aromatic acids by reactive particles in soil

Marc Kramer, PhD
UC Santa Cruz

Jonathan Sanderman, PhD
CSIRO, Australia



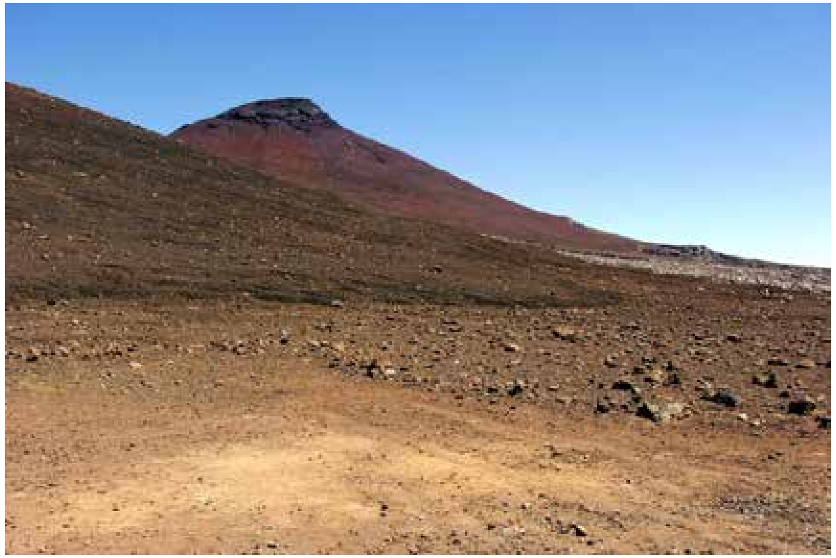
Oliver Chadwick, PhD
UC Santa Barbara

Jon Chorover, PhD
University of Arizona

Peter Vitousek, PhD
Stanford University

Case Study – Kramer et al 2012

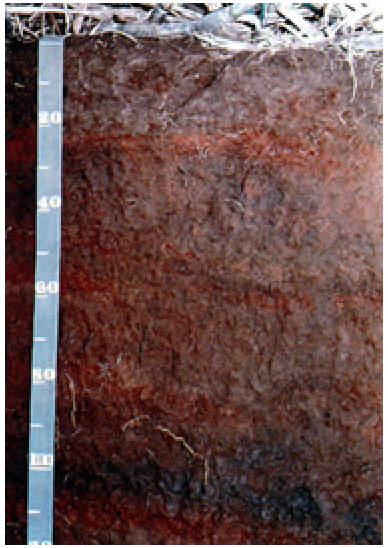
- Examined the biochemistry of dissolved and solid organic carbon in potential source and sink horizons across a chronosequence of volcanic soils in Hawai'i
- Soils were derived from similar basaltic parent material, support the same vegetation assemblage, and yet exhibit strong shifts in soil mineralogy and soil carbon content as a function of volcanic substrate age



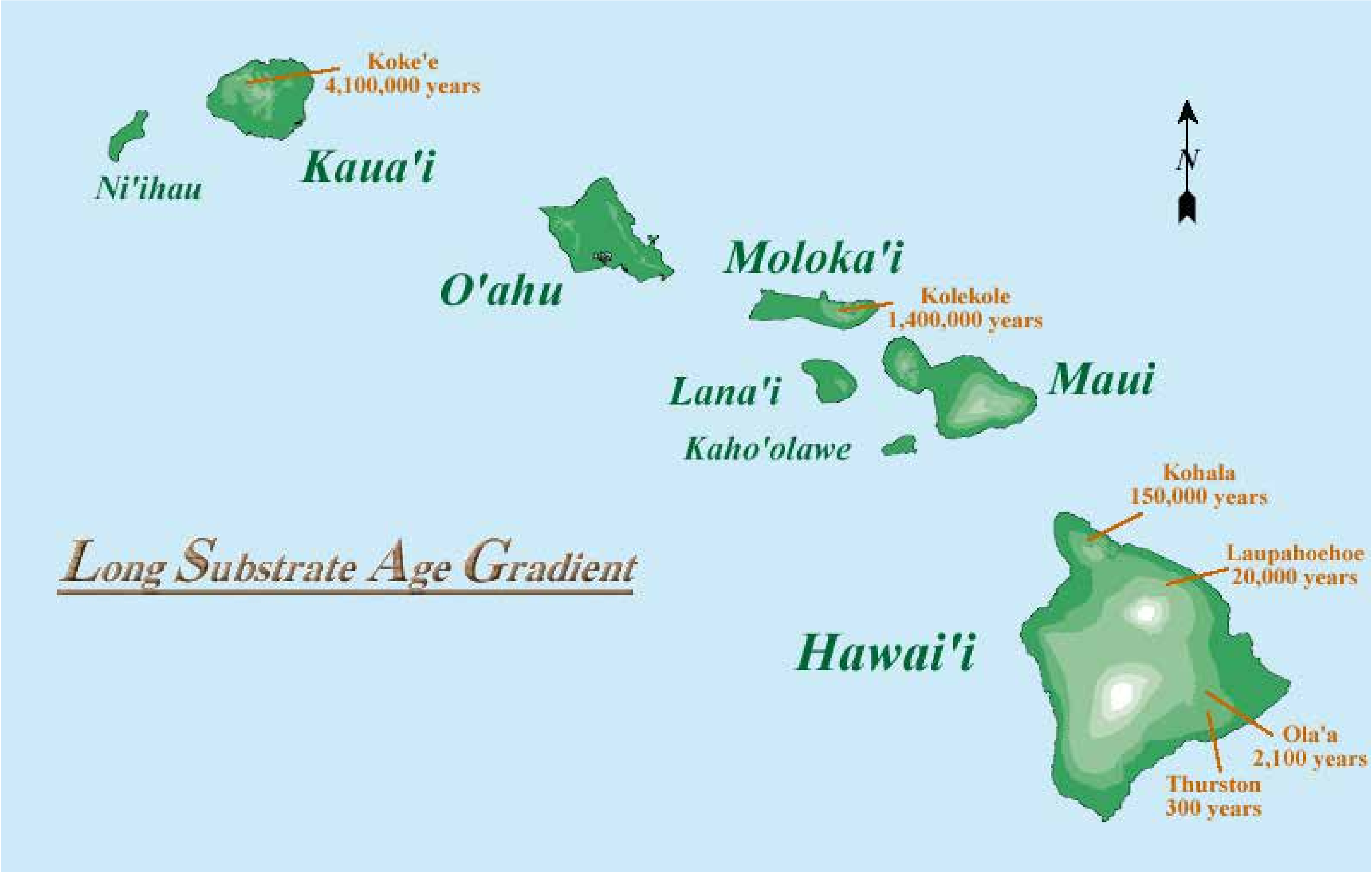
Case Study – Methods

- Soils were sampled by horizon to weather rock of ~1m depth along a chronosequence of volcanic soil in Hawaii
- Ages of substrate ranged from 0.3, 20, 150, 250, 1400, and 4100 ky with similar climate (MAT = 16°C and MAP 2500mm)
- Vegetation dominated by Ohi’a trees with numerous ferns and herbaceous plants in the understory



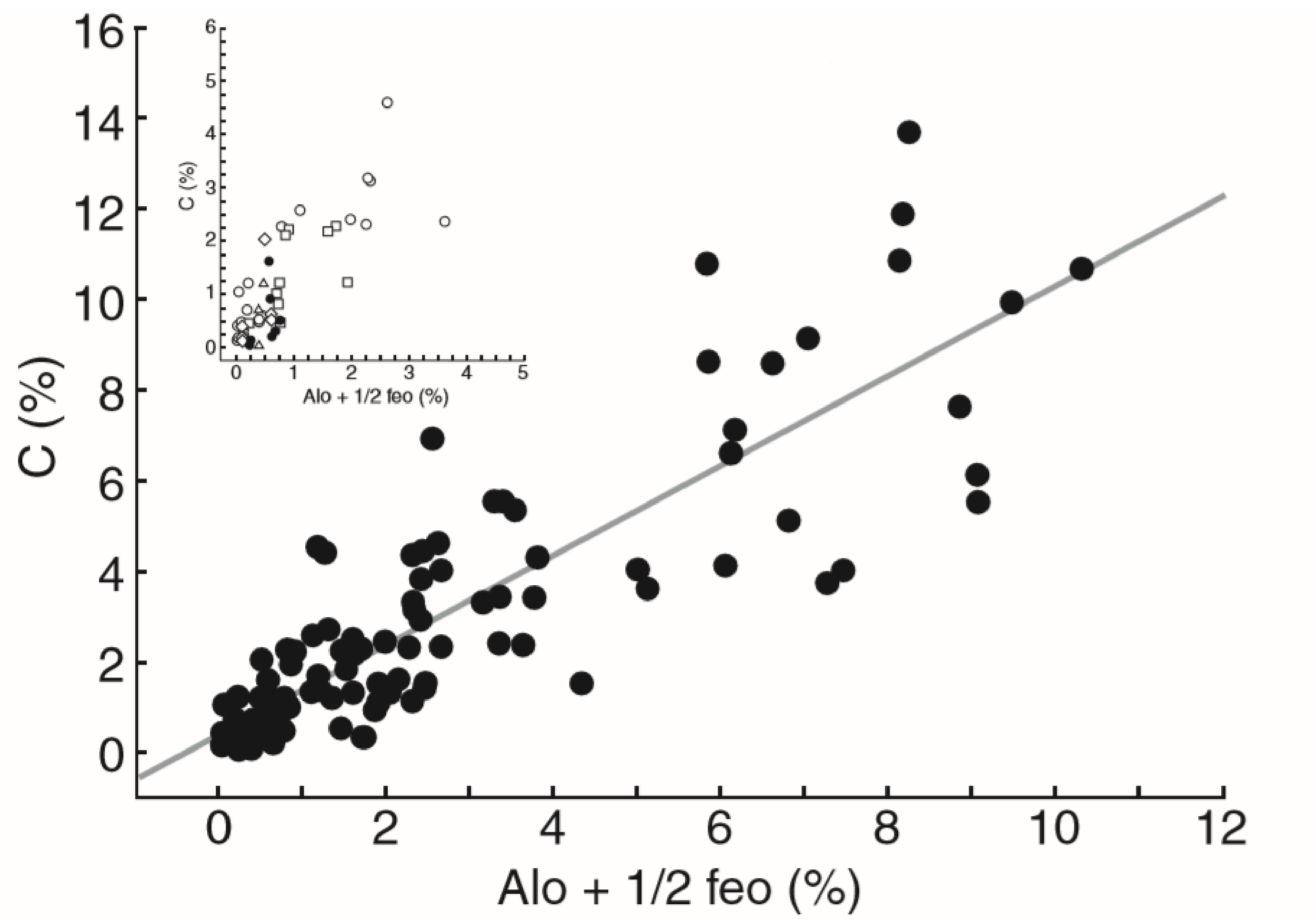



Site Locations – Long substrate age gradient



- Thurston
  - Lithic Hapludand
- Laupahoehoe, Kohala, and Ola’a
  - Aquic Hydrudand
- Kolekole
  - Aquic Hapludand
- Koke’e
  - Plinthic Kandiudox

Importance of short ranged order minerals (SRO)



- Distribution of SRO minerals and soil C content from soils worldwide
- As SRO mineral abundance increases, soil C content increases
- SRO calculated as Alo + ½ Feo (%)

Case Study – Methods

- SRO minerals were quantified using a series of progressively harsher extractions

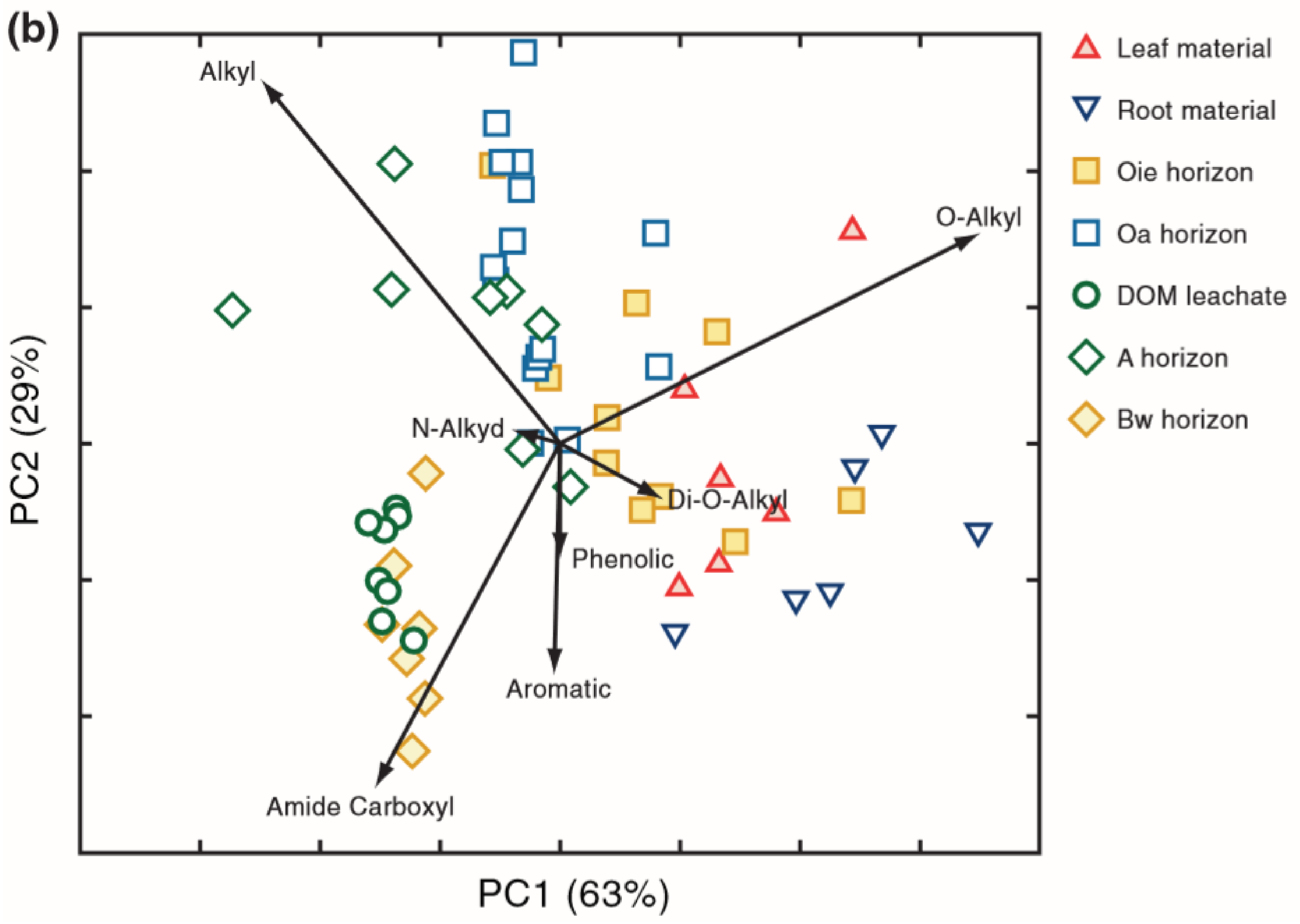
Case Study – Methods

- C, N and N^{15} analysis was measured with a coupled continuous-flow elemental analyzer-isotope ratio mass spectrometer with a Carlo-Erba model 1108 EA interfaced to a Thermo-Finnigan delta plus CP IRMS
- Solid state 13C- nuclear magnetic resonance (NMR) Data was recorded with a Bruker AVANCE500 spectrometer

Case Study – Results

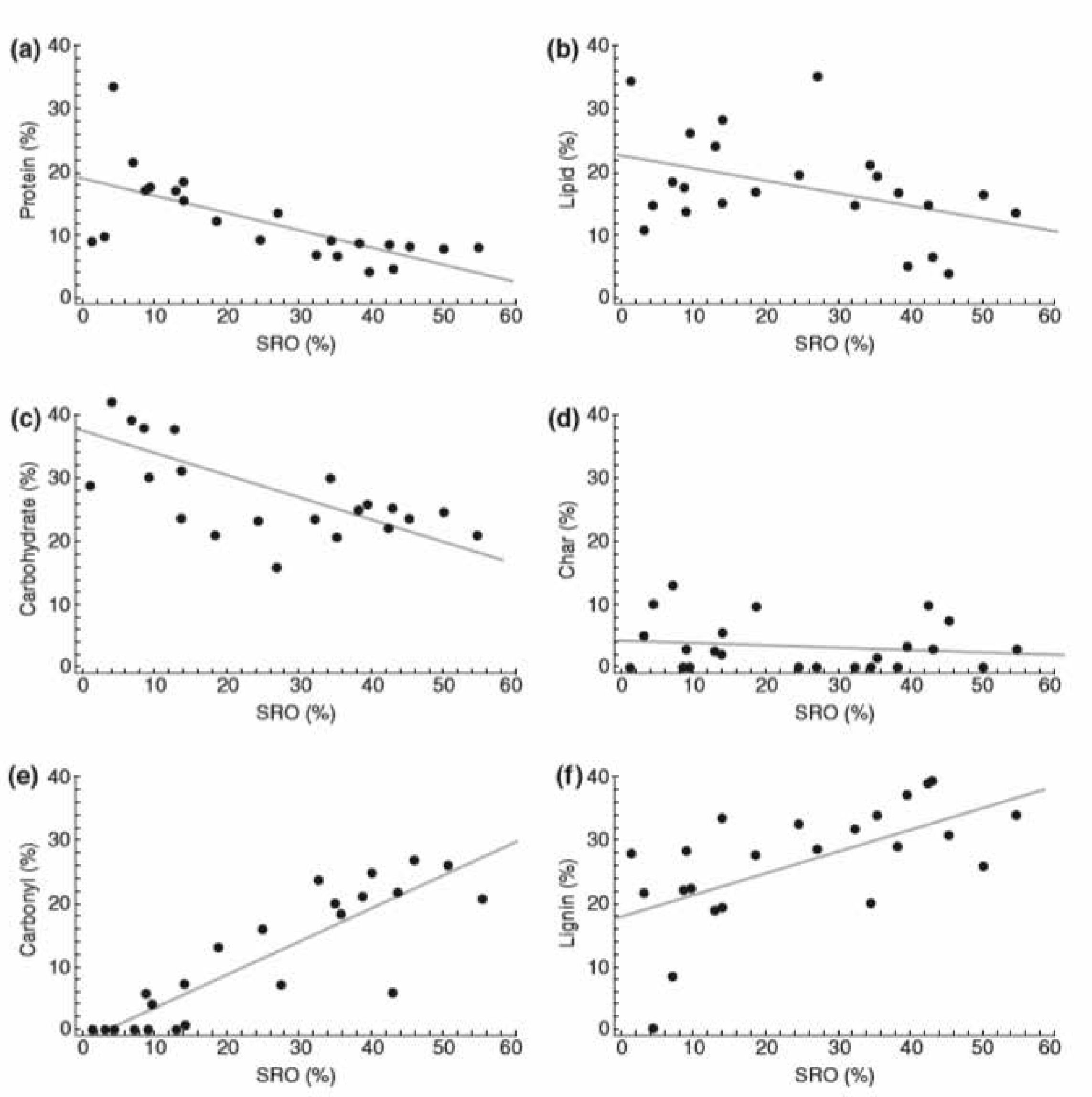
- Soil column leaching experiments

Case Study



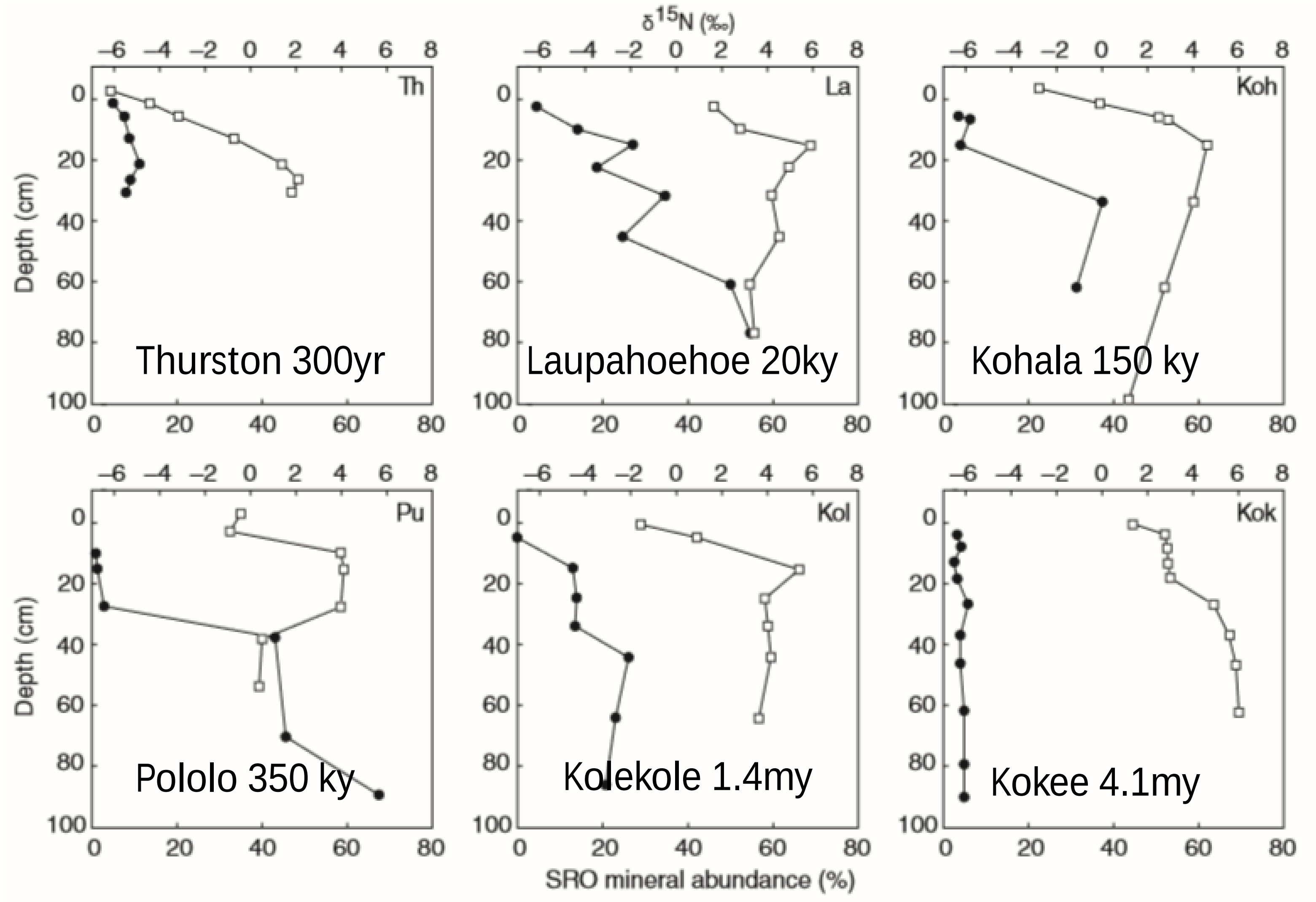
- Principle component analysis showing statistical similarity between DOM and Bw soil C
- Aromatic and carboxyl C NMR regions explain much of the statistical similarity between DOM and Bw

Case Study – Results



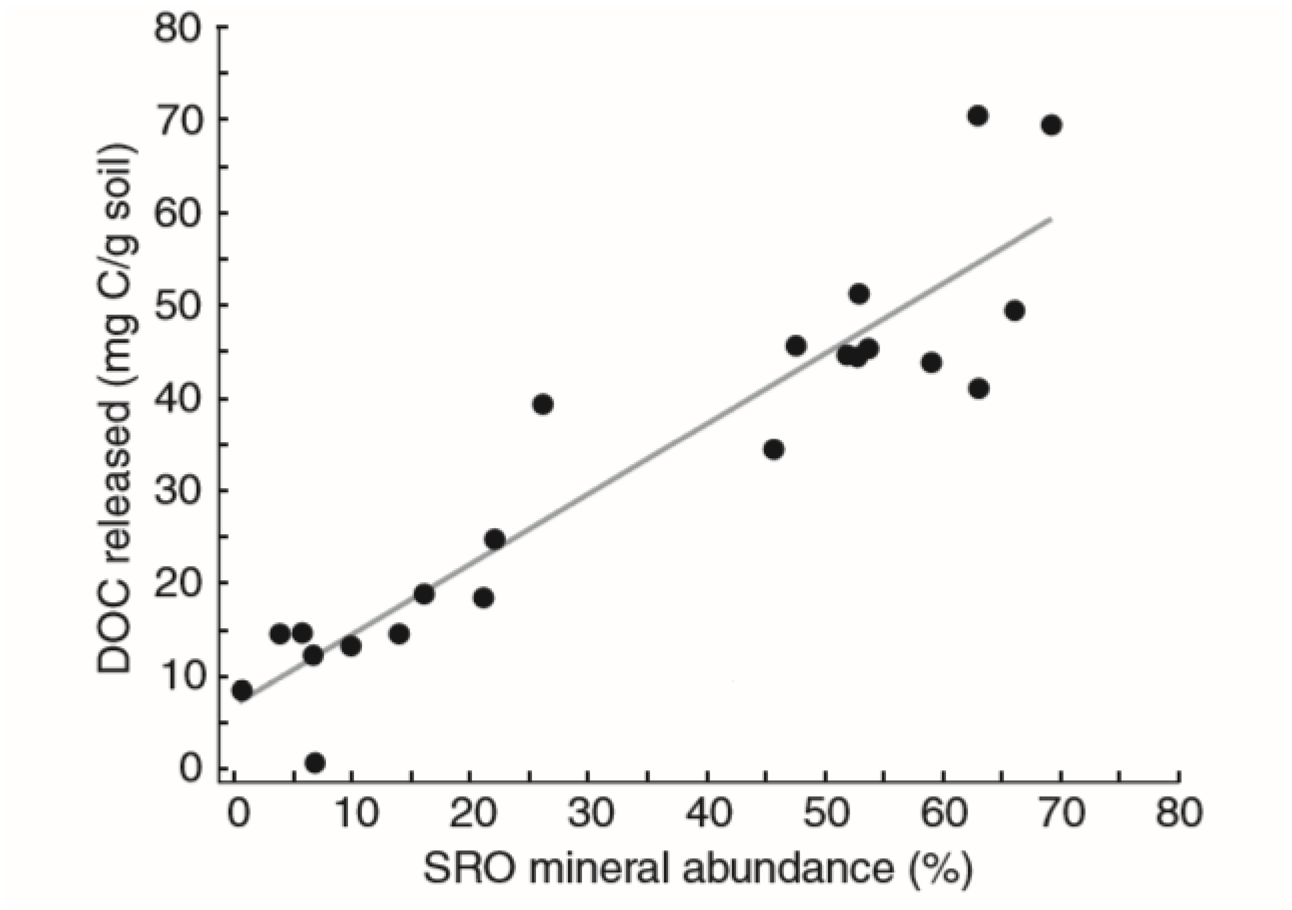
- Changes in biochemical components as a function of SRO mineral abundance in mineral soil horizons across the chronosequence

Case Study – Results



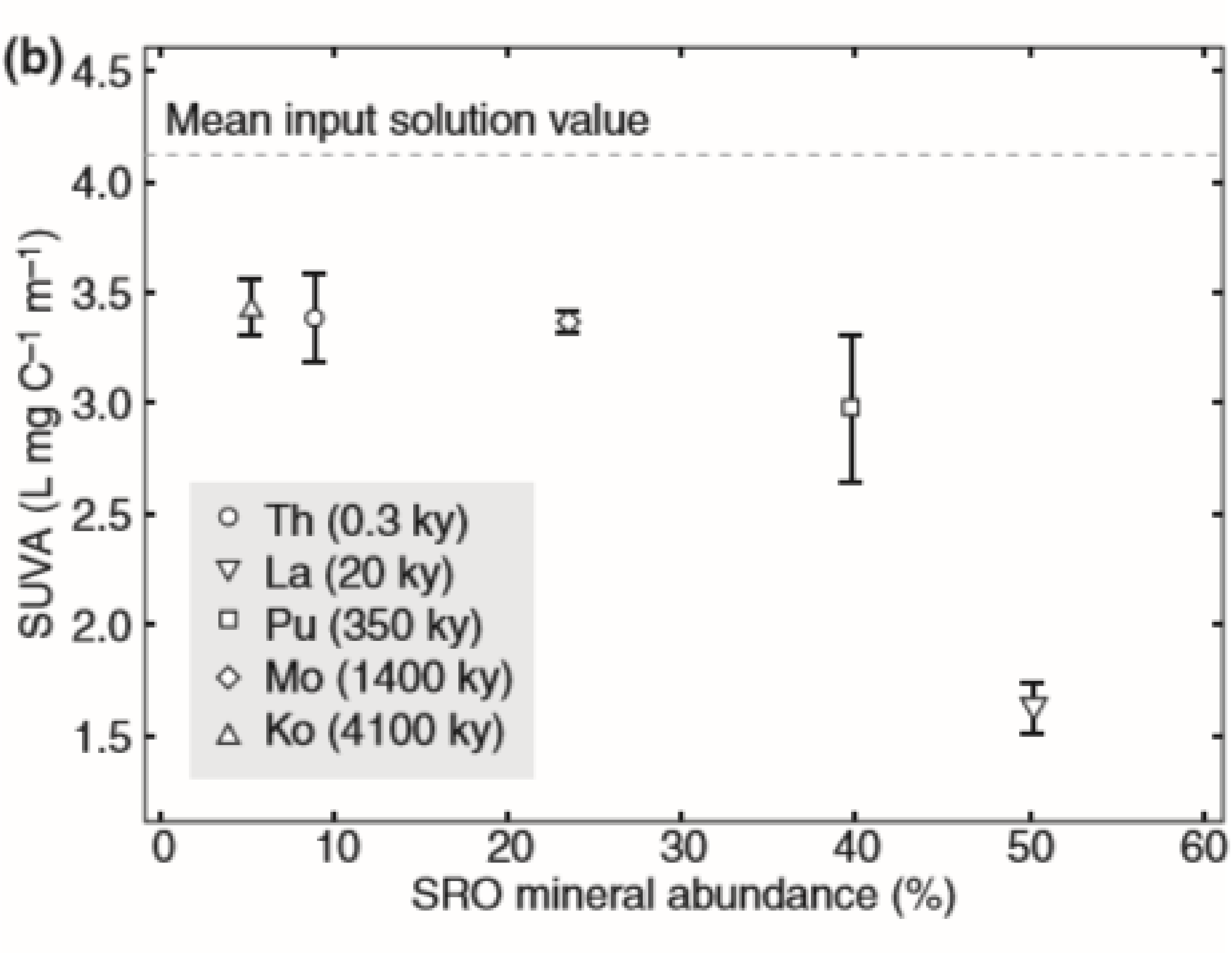
- Soil depth profiles of delta ^{15}N (hollow) and SRO minerals (black circles) across the chronosequence
- Gradual N enrichment with depth

Case Study – Results



- Amount of C released from soil as DOC after SRO mineral dissolution
- Samples from the Bw mineral horizon across the chronosequence

Case Study – Results



- SUVA values showing that aromatic compounds were preferentially retained in all soil sorption columns
  - Strongest in soil columns with higher SRO minerals
  - Ultraviolet light absorption was measured on a spectrophotometer at 254nm normalized to DOC concentration.

Case Study – Conclusion/Implications

- DOM is comprised largely of aromatic acids accumulated preferentially with SRO mineral concentration
- Soil column leaching and NMR data show that DOM derived from plant litter was the source for this material
- Correlation between aromatic acids and SRO minerals and soil column sorption suggest chemical retention via binging (sorption) to soil minerals through reactive OH sites as the dominant mechanism
- When solutions rich in dissolved organic matter were passed through Bw-horizon mineral cores, aromatic compounds were preferentially sorbed with the greatest retention occurring in horizons containing the greatest amount of short-range ordered minerals.
- These minerals are reactive metastable nanocrystals that are most common in volcanic soils, but exist in smaller amounts in nearly all major soil classes.
- Our results indicate that long-term carbon storage in short-range ordered minerals occurs via chemical retention with dissolved aromatic acids derived from plant litter and carried along preferential flow-paths to deeper B horizons.