ROLE OF THERMOKARST In WATERSHED CARBON FLUXES

Figure 1. Conceptual model of linkages and processes governing CO₂ concentrations in soil, bedrock, and surface waters. See the text for details.

Figure 7. Evasion of CO₂ from soils of the West Fork of Walker Branch watershed, Tennessee. The fitted line is a 5-week running average.
STORM HYDROLOGY AND CONTRIBUTING AREAS

DEVELOPMENT OF A SPATIALLY EXPLICIT WATERSHED CARBON MODEL

**Figure 4.9.** Relationship between pathways of flow from a watershed and the resultant streamflow hydrograph: A = channel interception; B = surface runoff, or overland flow; C = subsurface flow, or interflow; D = groundwater, or baseflow; Q = streamflow discharge.

**Figure 4.10.** Schematic of the "variable source" area of stormflow and the relationship between overland flow and the zone of no infiltration. The small arrows on the hydrographs indicate streamflow response changes as the variable source area expands (modified from Hewlett and Troendle 1975 and Hewlett 1982b, © Univ. of Georgia Press, by permission).
CONTRIBUTING AREAS AND SOIL/VEGETATION

COUPLING OF WATERSHED HYDROLOGY TO SPATIAL PATTERNS IN VEGETATION, SOIL AND PERMAFROST
ROLE OF THERMOKARSTS IN WATERSHEDS/LANDSCAPE

- Carbon fluxes from watersheds
  - Gas emissions directly to atmosphere
  - Hydrologic export of:
    - DIC and CO$_2$
      - Challenge separating soil/respiration vs. weathering
    - CH$_4$
    - DOC

- Sediment transport

- Stream channel formation

- Vegetation

- Others?
METHANE AND CARBON DIOXIDE

- Methane (µgC/L)
  - Stream water
  - Springs

- Carbon dioxide (µgC/L)
  - Stream water
  - Springs

Legend:
- C2, C4, C1, C3, CB, CJ, PC
- SP-C2a, SP-C2b, SP-C2c, SP-C2d, SP-C2e, SP-C3a, SP-C3b, SP-C4a, Thermokarst
METHANE AND CARBON DIOXIDE

Stream water

<table>
<thead>
<tr>
<th>Sample</th>
<th>Methane Saturation (g_{aq}/g_{eq})</th>
<th>Carbon Dioxide Saturation (g_{aq}/g_{eq})</th>
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<tbody>
<tr>
<td>C2</td>
<td></td>
<td></td>
</tr>
<tr>
<td>C4</td>
<td></td>
<td></td>
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<tr>
<td>C1</td>
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<td>C3</td>
<td></td>
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<tr>
<td>CB</td>
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<tr>
<td>CJ</td>
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</tr>
<tr>
<td>PC</td>
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</tbody>
</table>

Springs

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<th>Sample</th>
<th>Methane Saturation (g_{aq}/g_{eq})</th>
<th>Carbon Dioxide Saturation (g_{aq}/g_{eq})</th>
</tr>
</thead>
<tbody>
<tr>
<td>SP-C2a</td>
<td></td>
<td></td>
</tr>
<tr>
<td>SP-C2b</td>
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<td>SP-C2c</td>
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<td>SP-C2d</td>
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<td>SP-C2e</td>
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<tr>
<td>SP-C3a</td>
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<tr>
<td>SP-C3b</td>
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<tr>
<td>SP-C4a</td>
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<td></td>
</tr>
<tr>
<td>Thermokarst</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
ROLE OF THERMOKARSTs IN WATERSHEDs/LANDSCAPE

CHALLENGES IN QUANTIFYING HYDROLOGIC CARBON EXPORT

WEATHERING

CARBONATE (e.g., limestone):
\[ \text{CaCO}_3(s) + \text{CO}_2(g) + \text{H}_2\text{O} \leftrightarrow \text{Ca}^{2+}_{(aq)} + 2\text{HCO}_3^{-}_{(aq)} \]
• CARBON FROM WEATHERING AND RESPIRATION

SILICATE (e.g., albite):
\[ 2\text{NaAlSi}_3\text{O}_8 + 2\text{CO}_2 + 11\text{H}_2\text{O} \leftrightarrow \]
\[ \text{Al}_2\text{Si}_2\text{O}_5(\text{OH})_4 + 2\text{HCO}_3^{-} + 2\text{Na}^+ + 4\text{H}_4\text{SiO}_4 \]
• CARBON FROM RESPIRATION

RELATIVE CONTRIBUTION OF SOIL RESPIRATION VS. WEATHERING?
ROLE OF THERMOKARSTS IN WATERSHEDS

CHEMICAL STIOCHOMETRIC APPROACHES TO SOLVING WEATHERING CONTRIBUTION

Sum Cations vs Conductivity

- Evaporites
- Carbonates
- Siliceous
- Highly weathered

Conductivity (µS/cm)

Sum Total Cation Charge (µEq/L)
ROLE OF THERMOKARST IN WATERSHEDS
CHEMICAL STIOCHOMETRIC APPROACHES TO SOLVING WEATHERING CONTRIBUTION

Carbonate Alkalinity = \( HCO_3^- + 2CO_3^{2-} \)

Sedimentary weathering:
\( NaCl \rightarrow Na^+ + Cl^- \)

\( CaSO_4 \rightarrow Ca^{2+} + SO_4^{2-} \)

\( CaCO_3 + H_2CO_3 \rightarrow Ca^{2+} + 2HCO_3^- \)

\( CaMg(CO_3)_2 + 2H_2CO_3 \rightarrow Ca^{2+} + Mg^{2+} + 4HCO_3^- \)

\( CaCO_3 + H_2SO_4 \rightarrow Ca^{2+} + SO_4^{2-} + H_2CO_3 \)

\( CaMg(CO_3)_2 + H_2SO_4 \rightarrow Ca^{2+} + Mg^{2+} + 2SO_4^{2-} + 2H_2CO_3 \)
ROLE OF THERMOKARSTs IN WATERSHEDS

ISOTOPIC APPROACHES TO SOLVING WEATHERING CONTRIBUTION

13C-DIC vs Sum of Total Cations

- Sum Total Cation Charge (µEq/L)
- 13C-DIC

Samples:
- C1
- C2
- C3
- C4
- P6
- C2-300
- C2-400
- C2-450
- C2-460
- C2-560
- C3-150
- C3-160
- C3-650
- DG
- Thermokarst
- Lysimeter
DIC = CO$_{2(AQ)}$ + HCO$_3^-$ + CO$_3^{2-}$
ROLE OF THERMOKARSTS IN WATERSHEDS

ISOTOPIC APPROACHES TO SOLVING WEATHERING CONTRIBUTION

Fig. 5-5 The $^{13}$C composition of dissolved inorganic carbon (DIC) in equilibrium with soil CO$_2$ at 25°C. Values are calculated using the relative contribution of individual DIC species (Fig. 5-2) to weight their respective enrichment factor. Equilibrium is assumed with soil CO$_2$ which has $\delta^{13}$C = $-$23‰ VPDB.
ROLE OF THERMOKARSTS IN WATERSHEDS

• CARBON FLUXES FROM WATERSHEDS
  • GAS EMISSIONS DIRECTLY TO ATMOSPHERE
  • HYDROLOGIC EXPORT OF:
    • DIC AND CO$_2$
      • CHALLENGE SEPARATING SOIL/RESPIRATION VS. WEATHERING
    • CH$_4$
    • DOC

• SEDIMENT TRANSPORT

• STREAM CHANNEL FORMATION

• VEGETATION

• OTHERS?
ROLE OF THERMOKARST IN WATERSHEDS

Sum Cations vs Conductivity

Conductivity (µS/cm)
0 50 100 150 200 250 300 350

Sum Total Cation Charge (µEq/L)
0 1000 2000 3000 4000

Evaporites
Carbonates
Siliceous
Highly weathered

C1
C2
C3
C4
P6
C2-300
C2-400
C2-450
C2-460
C2-560
C3-150
C3-160
C3-650
DG
Thermokarst
Lysimeter
ROLE OF THERMOKARSTS IN WATERSHEDS

The diagram illustrates the role of thermokarst processes in watersheds through a ternary plot of Cl+SO₄, Si, and Carbonate Alkalinity. Different markers represent various samples identified by codes such as C1, C2, C3, C4, P6, C2-300, C2-400, C2-450, C2-460, C2-560, C3-150, C3-160, C3-650, DG, Thermokarst, and Lysimeter. The plot indicates regions of significant and insignificant carbonate weathering, with clusters of data points highlighting the impact of thermokarst processes on water chemistry.