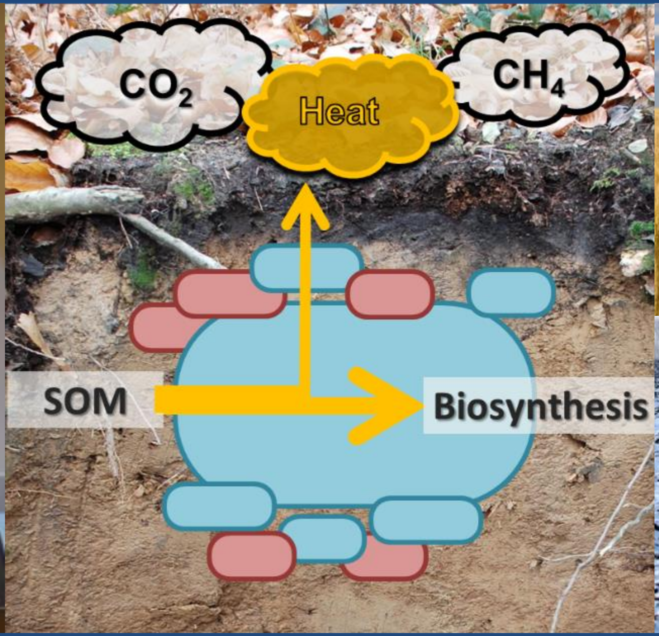
Calorimetric approaches to investigate soil organic matter decomposition



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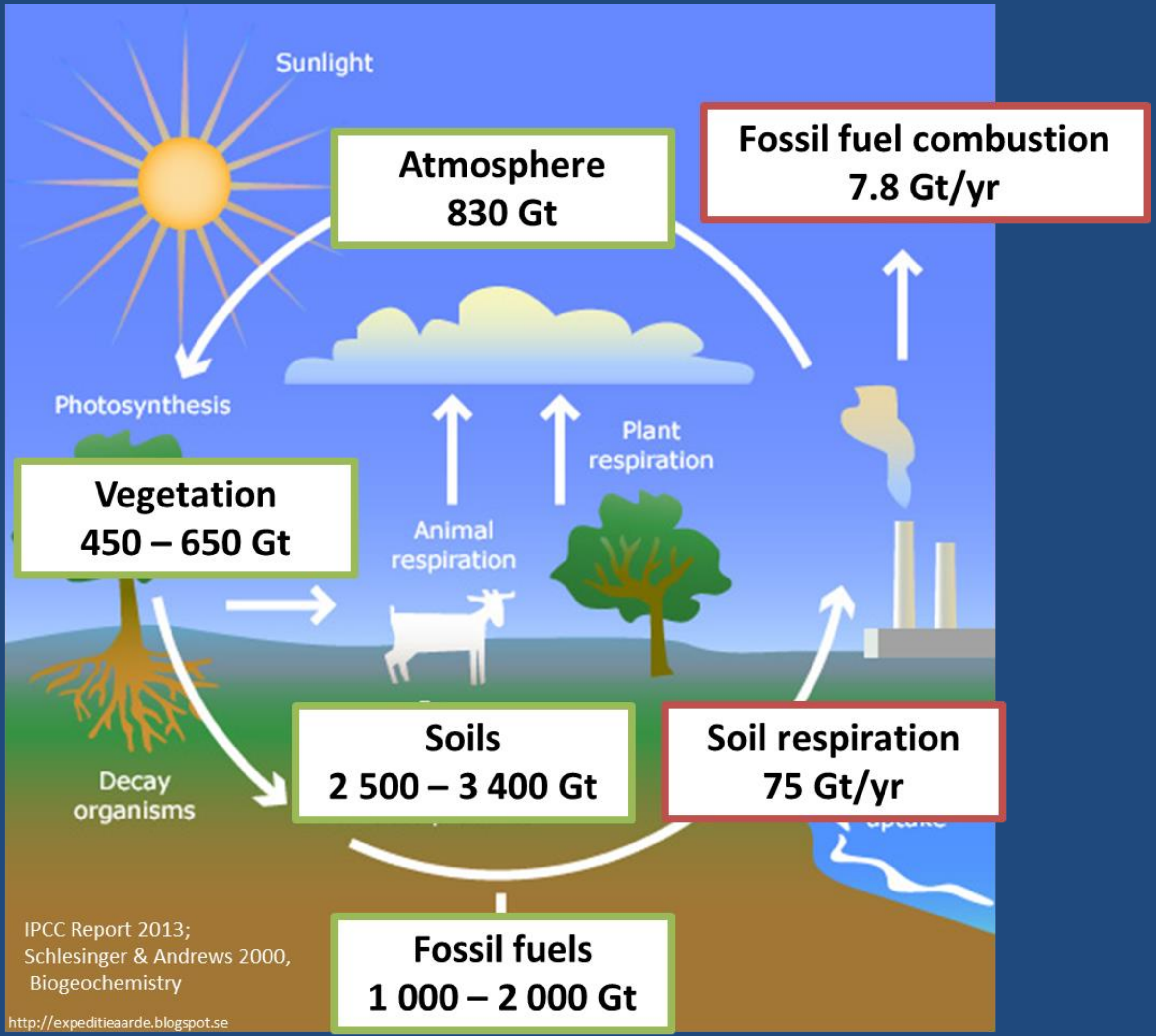
Why do we care about soil organic matter decomposition?

Climate change



Soils as sink or source of carbon?

Soil fertility

Availability of organic nutrients

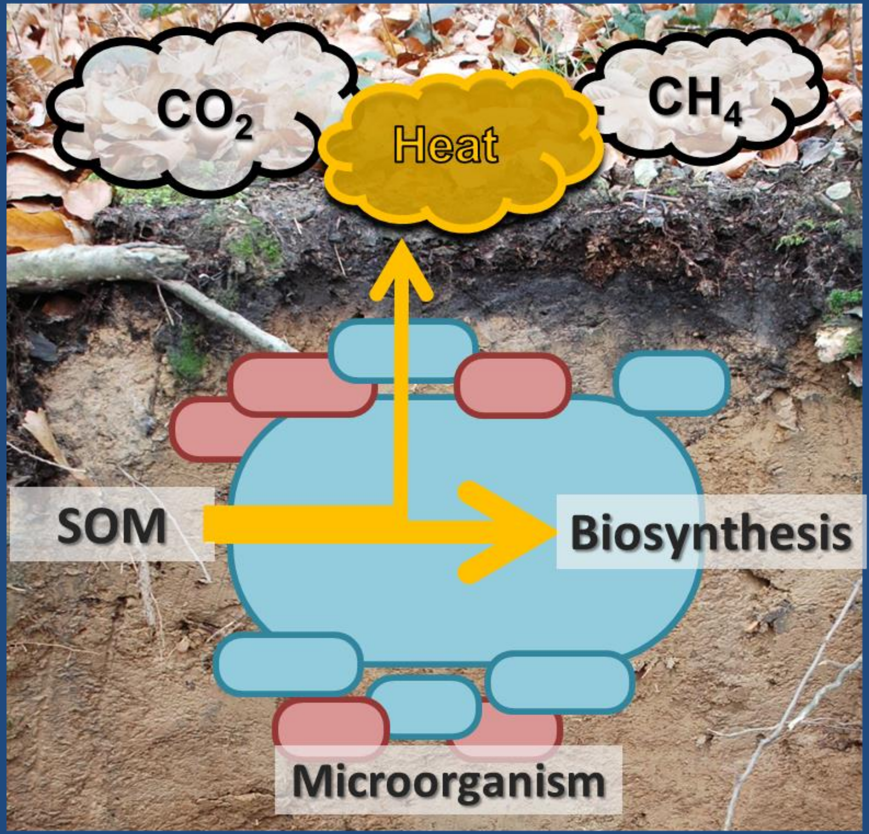
- ***Water retention in soil***
- ***Stability of soils again erosion***
- ***… many more!***

Why using calorimetry to investigate SOM decomposition?

The microbial engine

Organic Matter

Fuel for the Soil Engine



Microorganisms

Biological Engine of the Earth

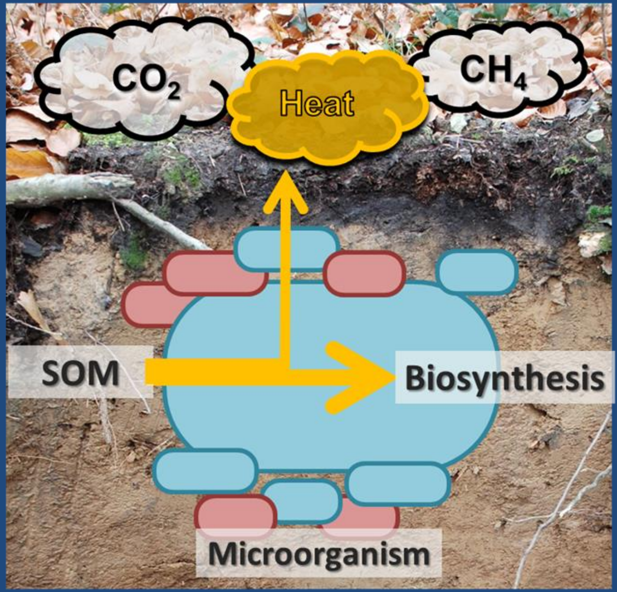
→Energetic demands drive decomposition

→Calorimetric techniques

Calorimetric approaches

Organic Matter

Fuel for the Soil Engine



Microorganisms

Biological Engine of the Earth

- Bomb calorimetry
- Differential scanning calorimetry
  (coupled to thermogravimetry)

- Isothermal microcalorimetry
- Calorespirometry

ISOTHERMAL CALORIMETRY

Microbial activity

during

organic matter decomposition

Isothermal calorimetry

OIKOS 34: 98–102. Copenhagen 1980

Microcalorimetric and gas chromatographic studies of microbial activity in water leached, acid leached and restored soils

Karin Ljungholm, Börje Norén and Göran Odham

Soil Biol. Biochem. Vol. 13, pp. 373 to 376, 1981
Printed in Great Britain

0038-0717/81/050373-04$02.00/0
Pergamon Press Ltd

HEAT OUTPUT OF THE SOIL BIOMASS

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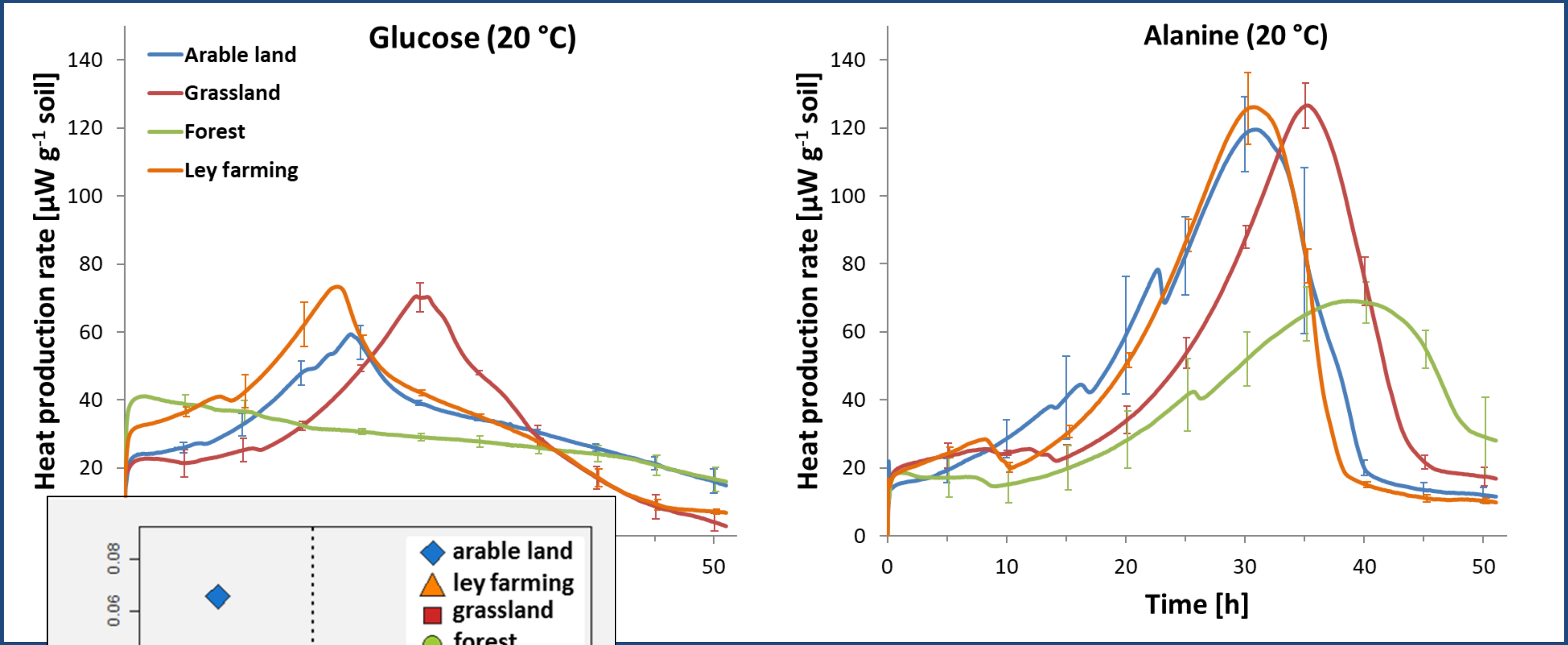
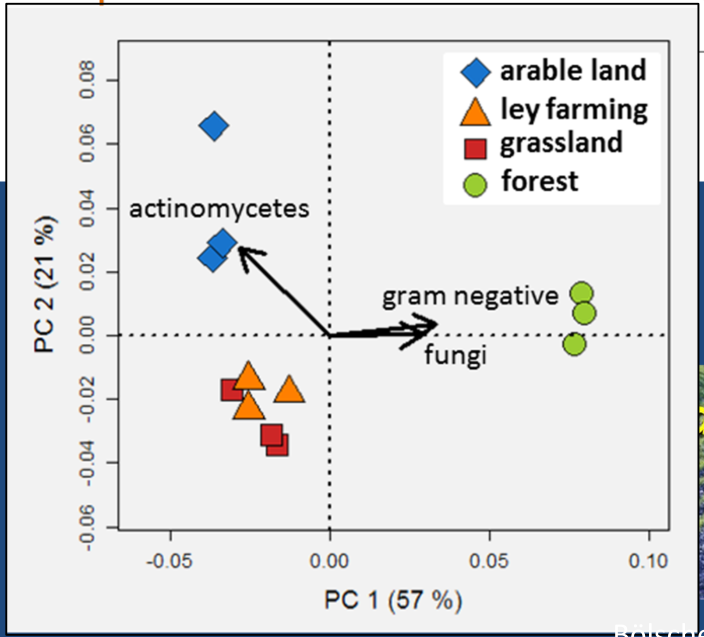
Department of Microbiology, Macaulay Institute for Soil Research,
Craigiebuckler, Aberdeen AB9 2QJ, Scotland

Isothermal calorimetry

Bölscher et al. (2016) *Biol. Fertil. Soils* 52

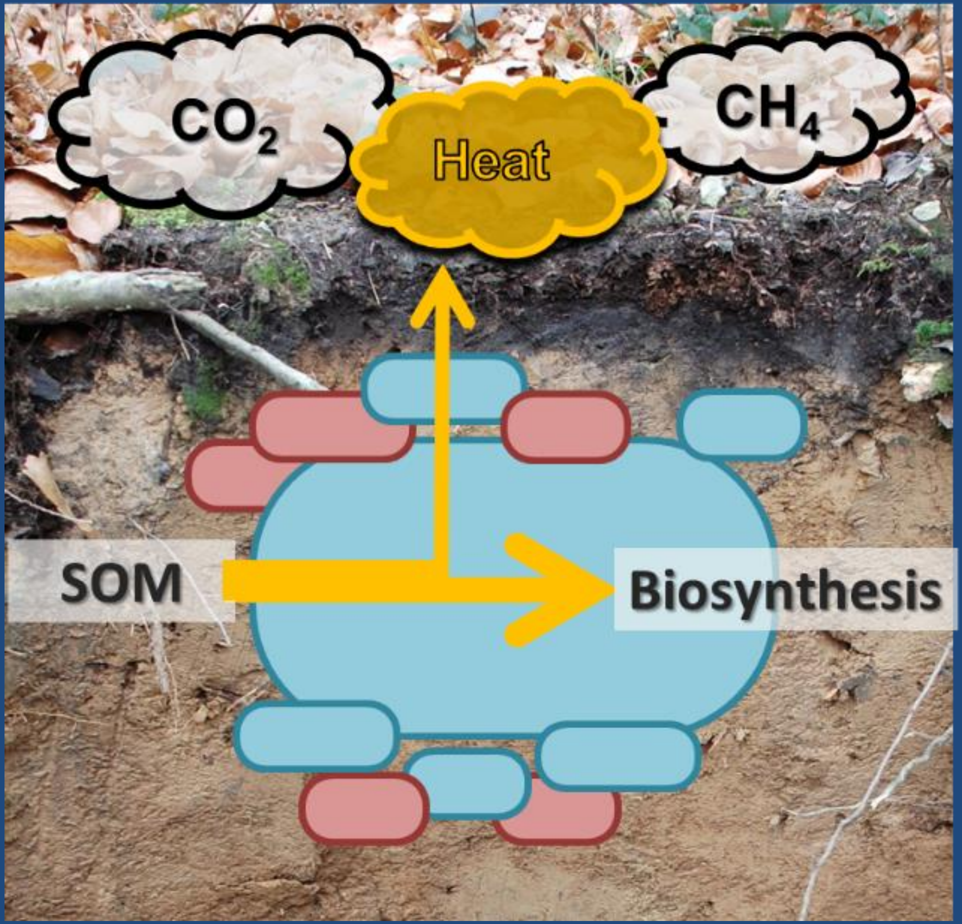
Microbial activity





Bölscher et al. (2016) *Biol. Fertil. Soils* 52

Microbial metabolic efficiency



Common approach addresses C

Carbon-Use Efficiency (CUE):

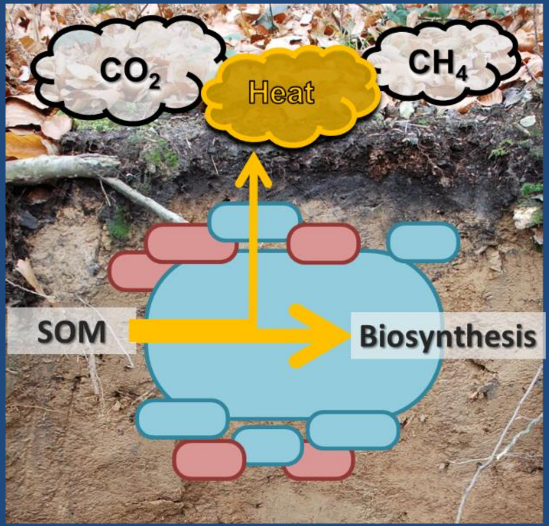
$$CUE = \frac{Biomass - C}{Biomass - C + \sum CO_2 - C}$$

Biomass: substrate incorporation into microbial biomass
$\sum CO_2$-C: cumulative respiration from substrate

e.g. Manzoni et al. (2012) *New Phyt. 196*

Microbial metabolic efficiency

Microbial metabolic-use efficiency



Calorimetry

Residual substrate assays

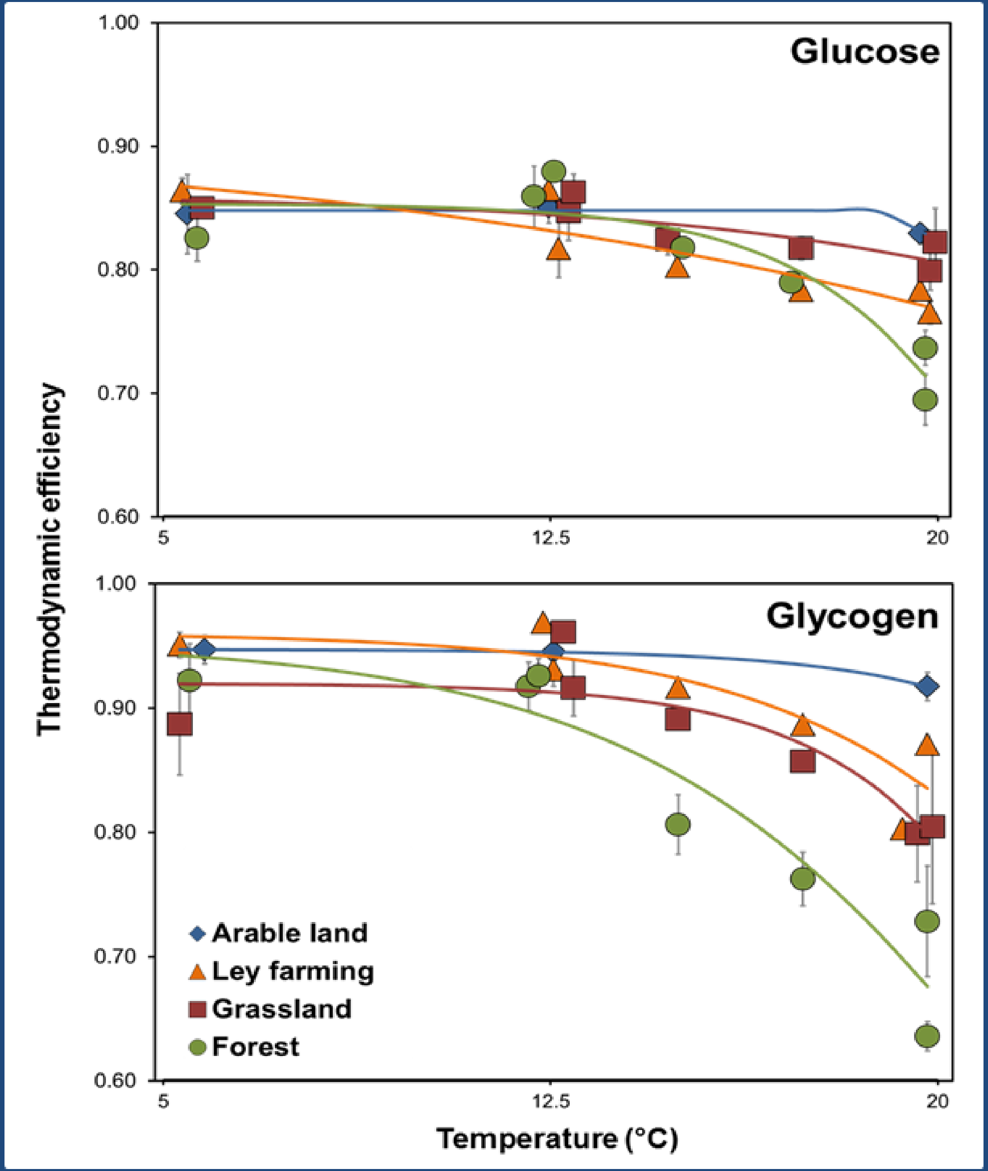
Thermodynamic Efficiency

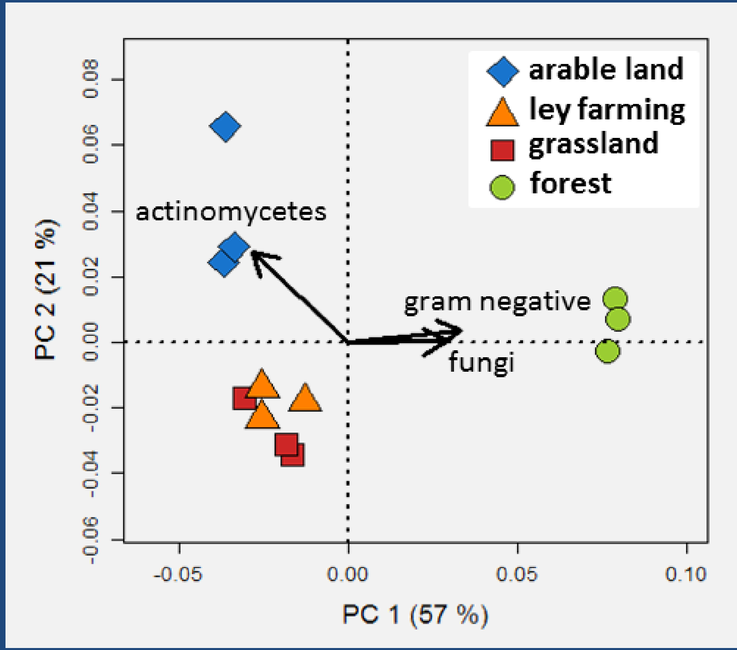
$$= 1 - \frac{Heat_{released}}{Energy_{added} - Energy_{residual}}$$

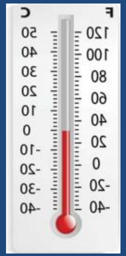
Determined after 15% added substrate was used
➔ Same workload for microorganisms

Bölscher et al. (2020) Soil Biol. Biochem. 140
Bölscher et al. (2017) Soil Biol. Biochem. 109
Bölscher et al. (2016) Fert. Biol. Soils 52

I. Microbial metabolic efficiency







5-20 °C

Bölscher et al. (2020) *Soil Biol. Biochem.* 140

Isothermal calorimetry

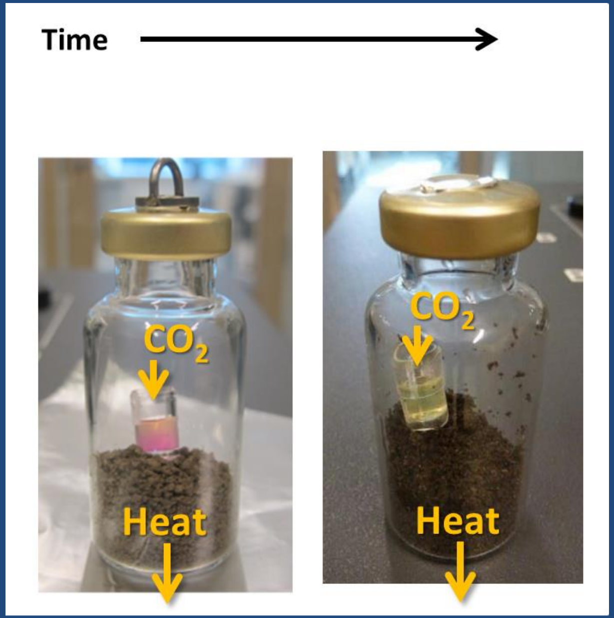
Advantages

- Non-destructive; continuous real-time data
- High sensitivity and accuracy
- Aerobic and anaerobic metabolism: e.g. sulfate reduction, denitrification, fermentation
  ➔ provides additional information to CO_2 evolution
- Multi-channel instruments (8-42 channels)
- Simplicity and passivity

Challenges

- Not process specific
- Relative small sample volume
- Still relative low sample throughput
- Equilibration time (ca. 1 h at 20 °C, ca. 24 h at 5 °C)
  ➔ can be circumvented by using the titration system

Calorespirometry



<u>Provides information about:</u>

- Microbial growth yield (i.e. carbon use efficiency)
- Degree of reduction of C in substrate
- Incomplete oxidation of substrate
- Microbial physiology
  ➔ aerobic vs. anaerobic respiration

Calorespirometric ratios:

$$\frac{R_q}{R_{CO_2}} = \frac{Q}{CO_2}$$

➔ 0-600 kJ mol^{-1} CO_2

$$\frac{R_q}{R_{O_2}} = \frac{Q}{O_2}$$

➔ ~455 kJ mol^{-1} O_2 (less commonly used)

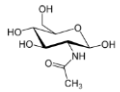
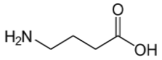
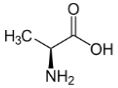
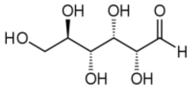
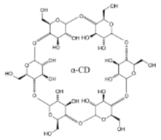
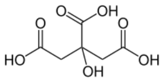
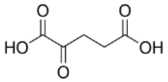
Hansen et al. (2004) *Themochim. Acta* 422; Wadsö & Hansen (2015) *Methods* 76; Herrmann & Bölscher (2015) *Soil Biol. Biochem.* 83

BOMB CALORIMETRY

Energy content of

organic matter

Bomb calorimetry

Substrates	Chemical structures	Standard molar enthalpy of combustion ΔH_c^{o*}
N-acetyl glucosamine		-3 958.9 kJ mol^{-1}
γ-aminobutyric acid		-2 280 kJ mol^{-1}
L-alanine		-1 621 kJ mol^{-1}
D-glucose		-2 813.6 kJ mol^{-1}
α-cyclodextrin		-15 333.6 kJ mol^{-1}
citric acid		-1 960.6 kJ mol^{-1}
α-ketoglutaric acid		-1 801.11 kJ mol^{-1}

Litter [a]	**-39 to -43 kJ g^{-1} C**
SOM [b]	**-34 to -37 kJ g^{-1} C**
DOM [c]	**-45 to -56 kJ g^{-1} C**

Enthalpy of combustion
➔ energy content

Challenges:

- Soil are mixtures of mineral phases and organic matter
- Confounding by thermal effects of:
  - ➢ hygroscopic water
  - ➢ Calcium carbonate formation
  - ➢ …
- **Discrepancies with results from DSC-TGA!!**

[a] Currie (2003) *Glob. Change Biol.* 9
[b] Bölscher et al. (2017) *Soil Biol. Biochem. 109*
[c] Dufour et al. (2022) *Soil Biol. Biochem. 173*

DIFFERENTIAL SCANNING CALORIMETRY

Thermal stability and energetic properties of organic matter

Differential scanning calorimetry

Differential Scanning Calorimetry (DSC) - Differential Thermogravimetry (DTG)

Combustion of OM during constant temperature increase under oxygen atmosphere

- ➔ **Thermal stability** as a proxy of resistance against decomposition
- ➔ **Enthalpy of combustion** (combined integrals of DSC and DTG)
- ➔ **Activation energy of thermal oxidation** (Arrhenius equation)

➔ Potential to estimate *Degree of reduction, Gibbs energy* when applying estimated oxycaloric quotient

Rovira et al. (2008) *Soil Biol. Biochem.* 40
Plante et al. (2009) *Geoderma* 153
Barros et al. (2020) *Oikos* 129

Differential scanning calorimetry

Differential Scanning Calorimetry (DSC) - Differential Thermogravimetry (DTG)

Challenges:

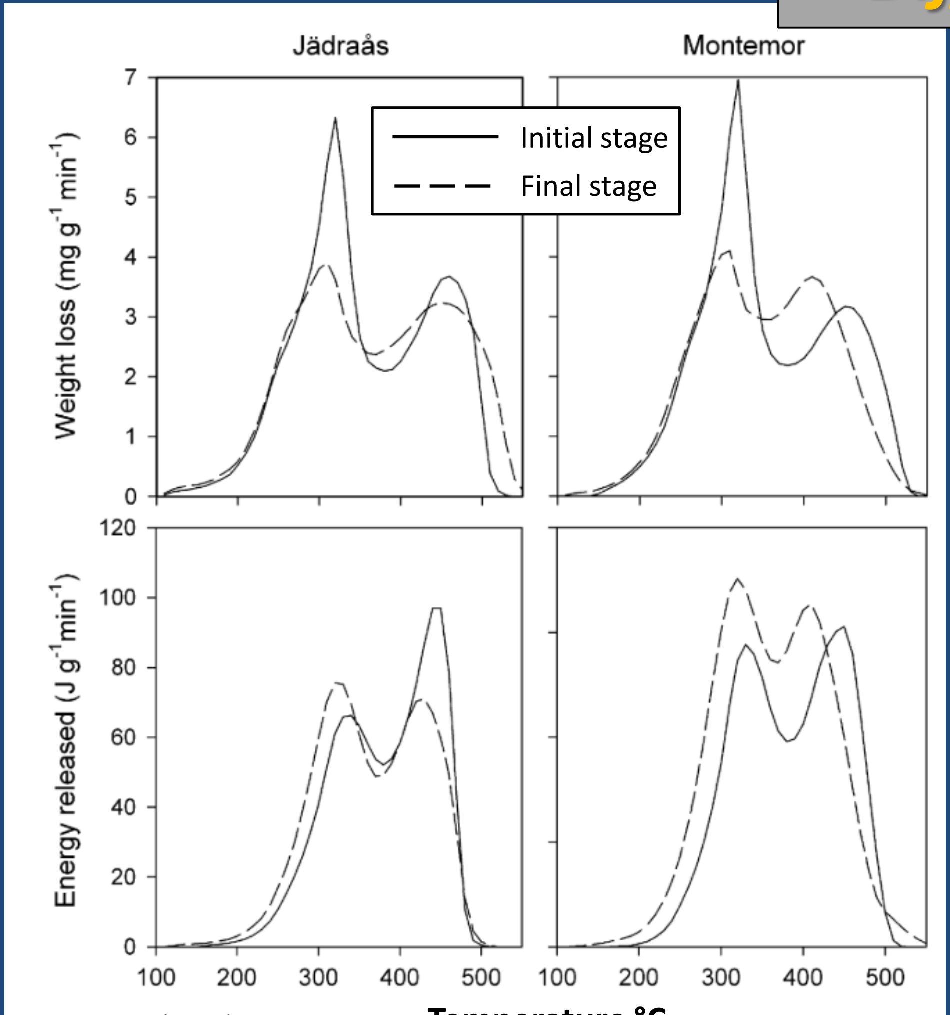
- Soil are mixtures of mineral phases and organic matter
- Confounding by thermal effects of:
  - hygroscopic water
  - Calcium carbonate formation
  - …
- **Discrepancies with results from DSC-TGA!!**

➔ **Easier application on pure organic matter (e.g. organic soil amendments)**
  - Compost
  - Digestates
  - …

Rovira et al. (2008) *Soil Biol. Biochem.* 40
Plante et al. (2009) *Geoderma* 153
Barros et al. (2020) *Oikos* 129

Thermal stability of organic matter

Differential Scanning Calorimetry (DSC) - Differential Thermogravimetry (DTG)



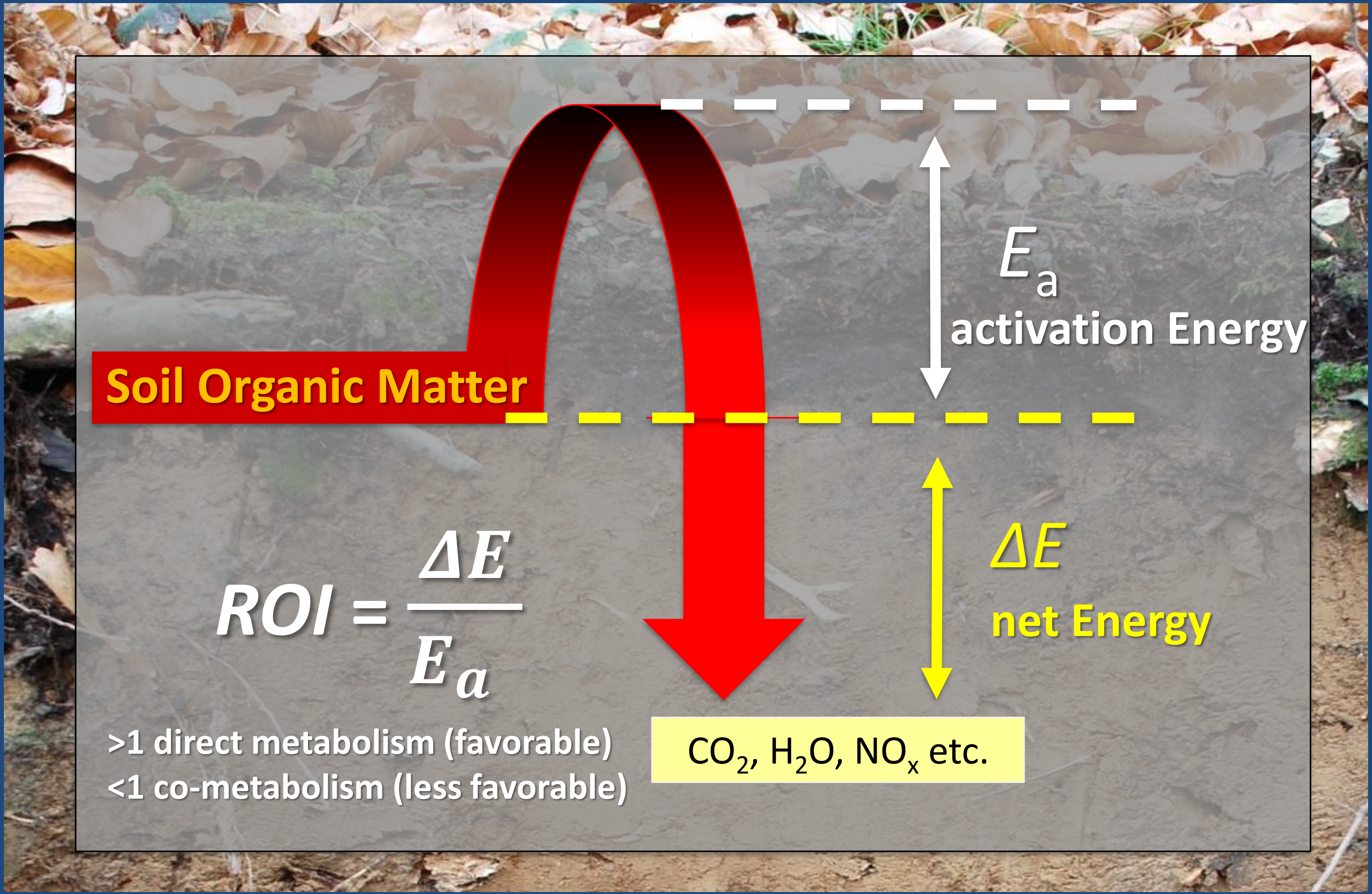
Rovira et al. (2008)

Thermal indices:

- **DSC-T_{50}**: Temperature at which 50% of the energy release has occurred
- **TG-T_{50}**: Temperature at which 50% of the weight loss has occurred

Rovira et al. (2008) *Soil Biol. Biochem.* 40
Plante et al. (2009) *Geoderma* 153
Barros et al. (2020) *Oikos* 129

Potential energetic return-on-investment



Harvey et al. (2016) *Env. Sci. Tech. 50*
Rovira et al. (2008) *Soil Biol. Biochem.* 40
Willems et al. (2013) *Polym. Degrad. Stab.* 98

Potential energetic return-on-investment

Linking the Energetic Return-On-Investment to microbial decomposition of organic soil amendments


Plant residues


Manure


Compost


Digestates


Biochar

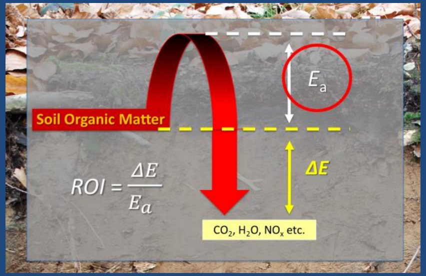
Do the energetic properties of organic amendments differ?

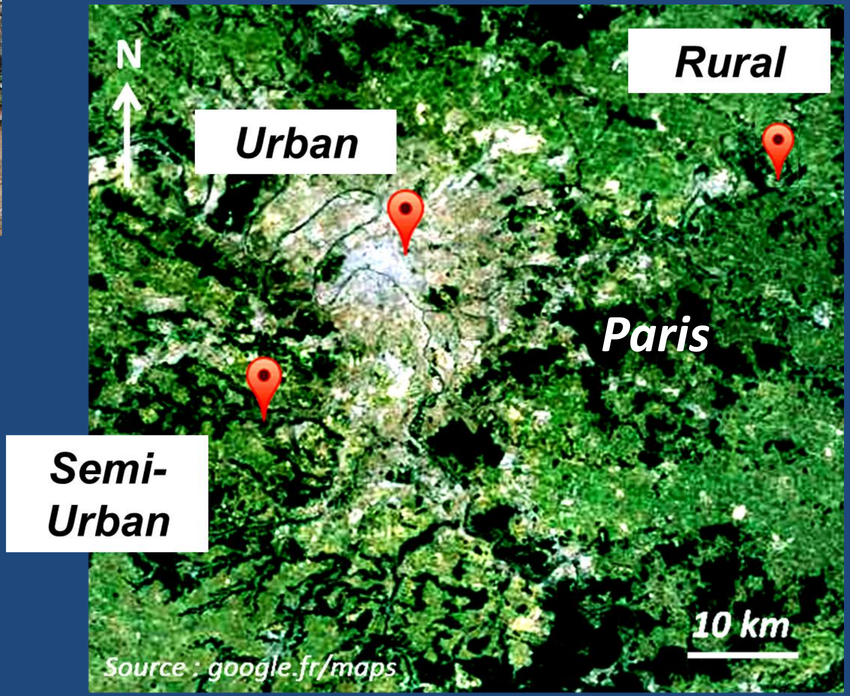
Do the energetic properties drive the decomposition of amendments in soil?

Can the energetic return-on-investment be used to predict the long-term stability of organic amendments in soil?

THANK YOU FOR YOUR ATTENTION!

Potential energetic return-on-investment





3 X

Park

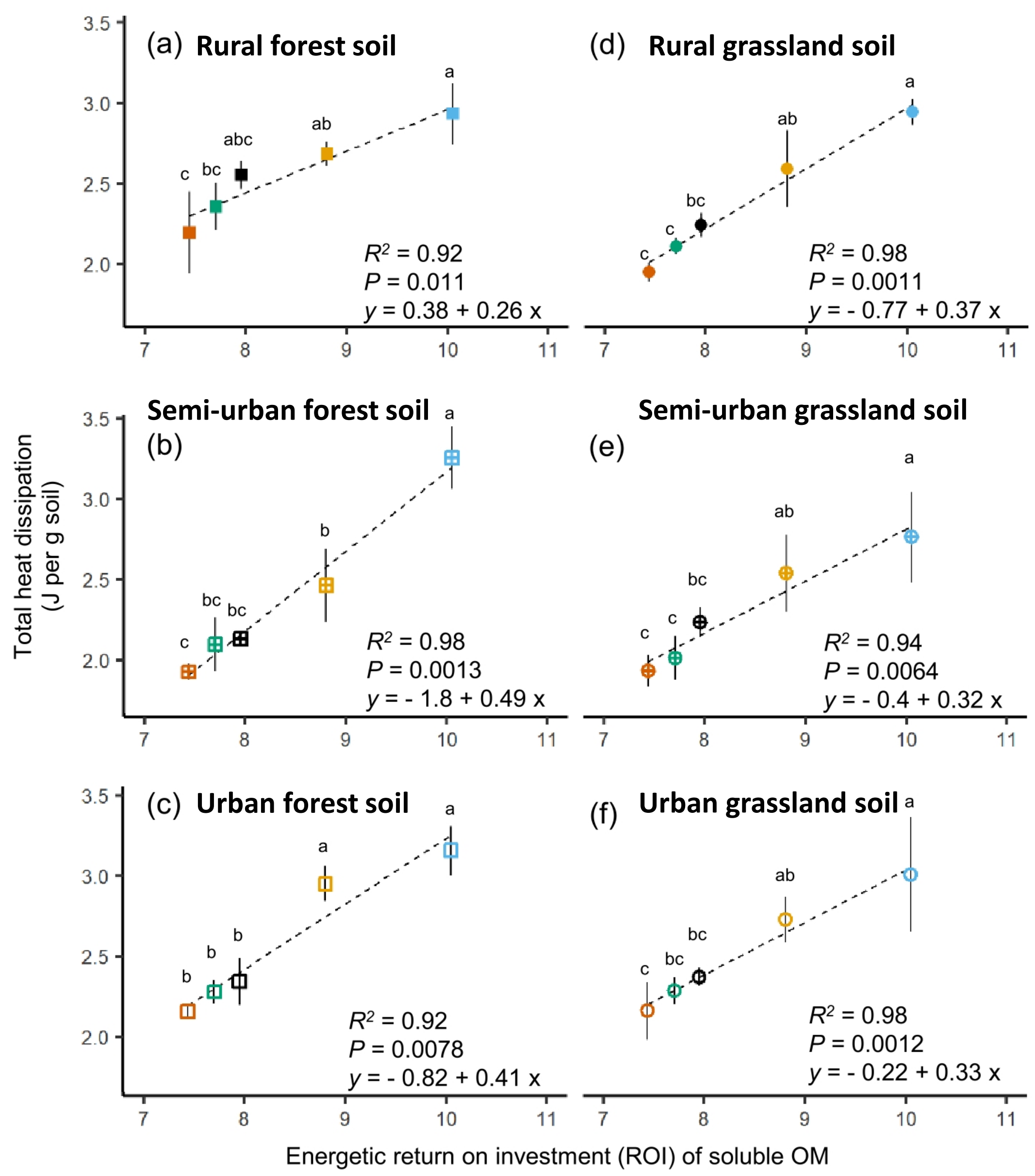
Forest

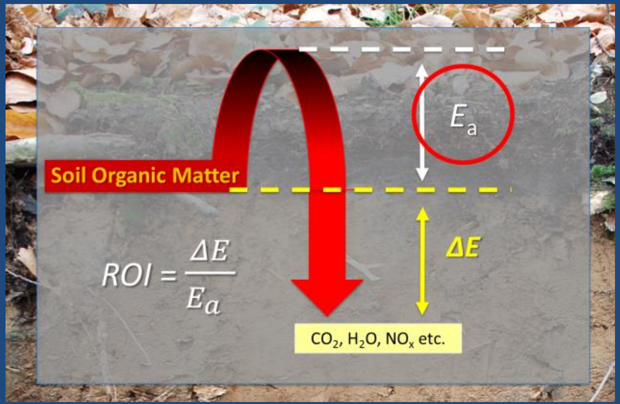
DOC extraction
Cross incubation

<u>Microbial activity</u>
over 24 h at 25 °C

Dufour et al. (2022) *Soil Biol. Biochem. 173*

Potential energetic return-on-investment





Dufour et al. (2022) *Soil Biol. Biochem. 173*