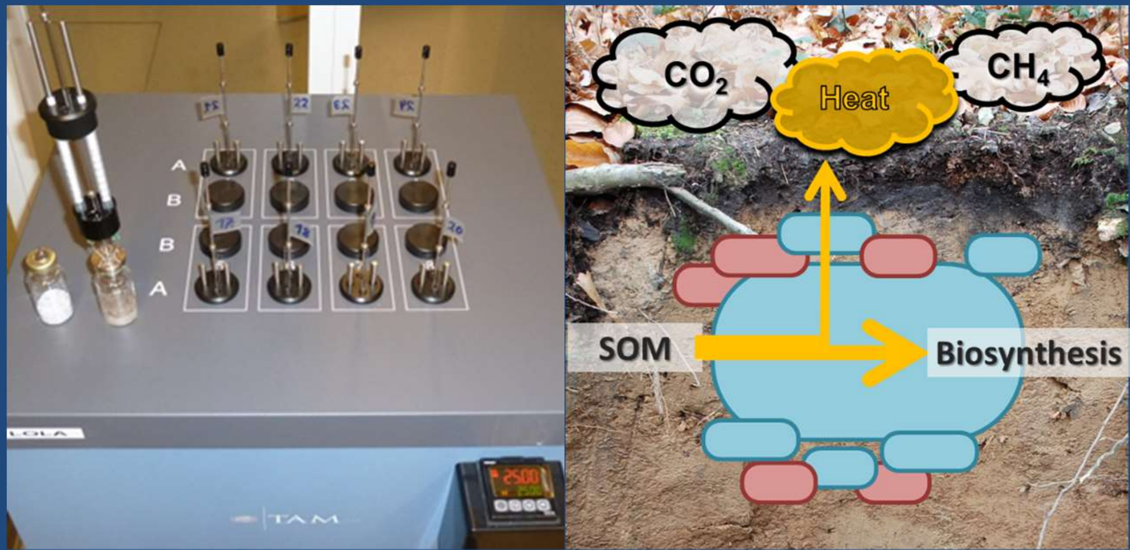
# Energetics perspectives on SOM decomposition



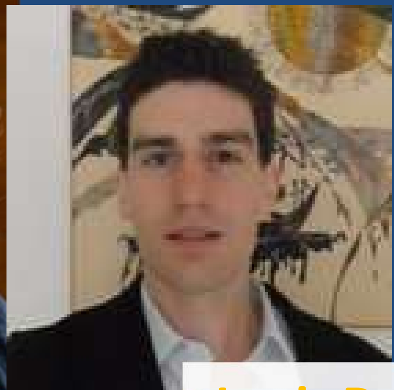

**Tobias Bölscher**
*UMR EcoSys – Université Paris-Saclay, INRAe, AgroParisTech*
*tobias.bolscher@inrae.fr*

# What's on the menu?

- **Definition of energetics**
- **Why energetics approaches?**
  - *The Microbial Engine*
- **Classification and examples focusing on:**
  - *Microorganisms – the Engine*
  - *Soil Organic Matter – the Fuel*
  - *How Microorganisms and SOM interact – Driving the Engine*
  - *The Environmental and its constrains – the Road Network*

# Credits

Anke M. Herrmann



Louis Dufour

SLU

Swedish University of Agricultural Sciences

Naoise Nunan

cnrs

Marco Keiluweit

Unil

UNIL | Université de Lausanne

# Definition

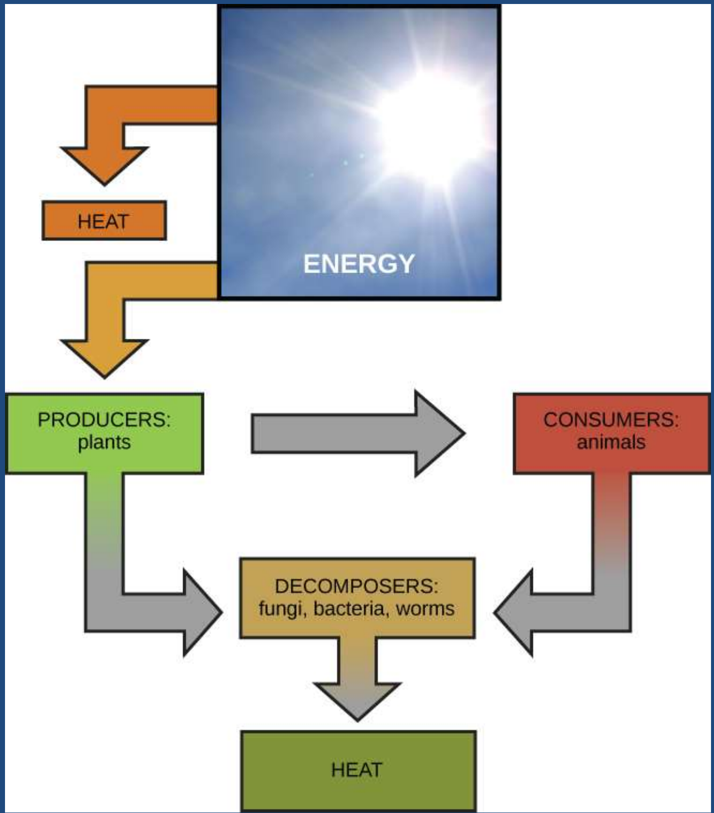
***Energetics:***

"The branch of science which **deals with** the properties of **energy** and the way in which it is redistributed in physical, chemical, or biological processes."

Oxford English Dictionary

# Why using energetics to investigate SOM decomposition?

# Life requires (free) energy




"**All living organisms need energy** to grow and reproduce, maintain their structures, and respond to their environments. Metabolism is the set of life-sustaining chemical processes that enables organisms **transform the chemical energy stored in molecules into energy that can be used for cellular processes**."

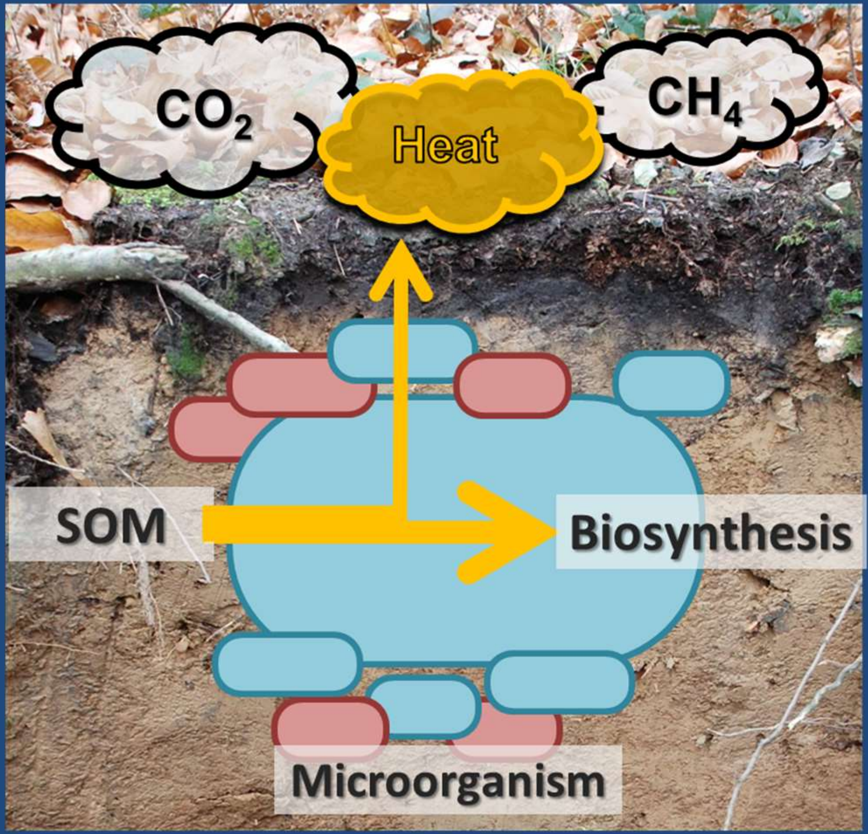
https://courses.lumenlearning.com/boundless-biology/chapter/energy-and-metabolism/

➔ **Energetic demands drive element cycles**

# The microbial engine

*Organic Matter*


***Fuel for the Soil Engine***



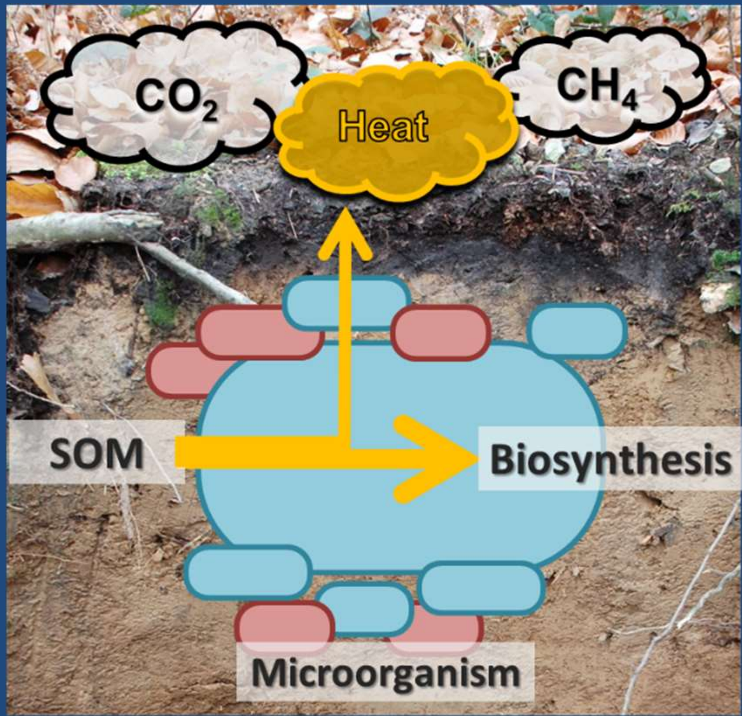

*Microorganisms*

***Biological Engine of the Earth***

# The microbial engine

## Organic Matter


***Fuel for the Soil Engine***




## Microorganisms

***Biological Engine of the Earth***

## Environment

***Road Networks and Conditions to drive the engine***

# A quick reminder

## THERMODYNAMICS

*First law of thermodynamics:*

Energy can be **transformed** (changed from one form to another), but cannot be created or destroyed.

# The engine:

## Approaches focusing on

## *MICROORGANISMS*


# Isothermal calorimetry

## What is isothermal calorimetry?

Calorimeter

- Latin: calor = heat
- Greek: μέτρο (métro) = to measure

➢ Measuring heat flow of biological processes
➔ proportional to the rate of chemical or physical processes

Isothermal = constant temperature

*TAM Air calorimetry*

# History of calorimetry

Antoine Lavoisier (1743-1794)

*Father of modern chemistry*

- Recognized oxygen and hydrogen
- Involved in the reformation of the chemical nomenclature

## *'Ice calorimeter' (1782-83)*

*Lavoisier & Laplace*

Liquid water produced by melting ice

~ heat produced by the reaction taking place atop the ice

# Isothermal calorimetry on soil


TAM Air calorimetry

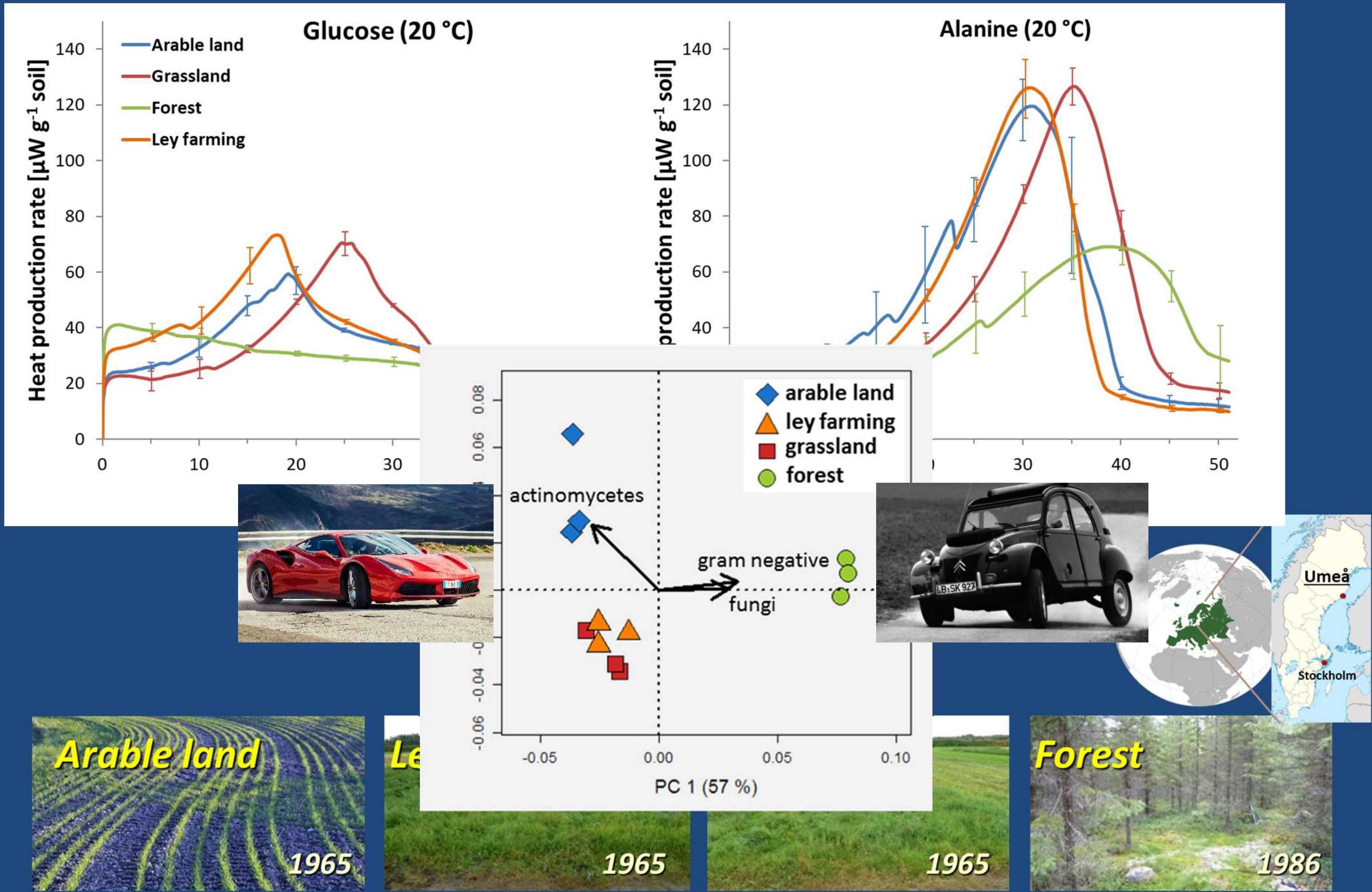
Temperature range: 5 – 90 °C
Thermostat stability: 0.02 °C
Detection limit: 4 µW






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

# Microbial activity



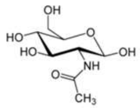
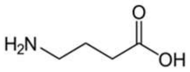
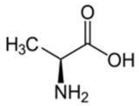
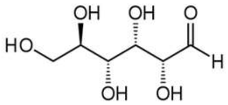
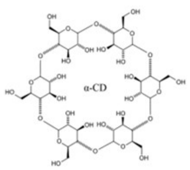
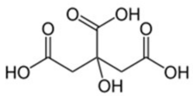
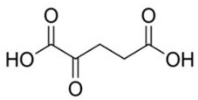

Bölscher et al. (2016) *Biol. Fertil. Soils* 52

# The fuel:

## Approaches focusing on

# *SOIL ORGANIC MATTER*

# I. Energy content of OM

| Substrates | Chemical structures | Standard molar enthalpy of combustion $\Delta H_c^{o*}$ |
|---|---|---|
| *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** |

***Bomb Calorimetry***

**Combustion of organic mater in oxygen atmosphere ➔ measures energy content (as standard enthalpy of combustion)**

[a] Currie (2003) *Glob. Change Biol.* 9
[b] Bölscher et al. (2017) *Soil Biol. Biochem. 109*
[c] Dufour et al. (202) *Soil Biol. Biochem. 173*

# II. Thermal stability of OM

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


**Combustion of OM during constant temperature increase**

DSC: measures <u>heat release</u>
DTG: measures <u>weight loss</u>

→ **Thermal stability** as a proxy of resistance against decomposition

→ **Energy content** (combined integrals of DSC and DTG)

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

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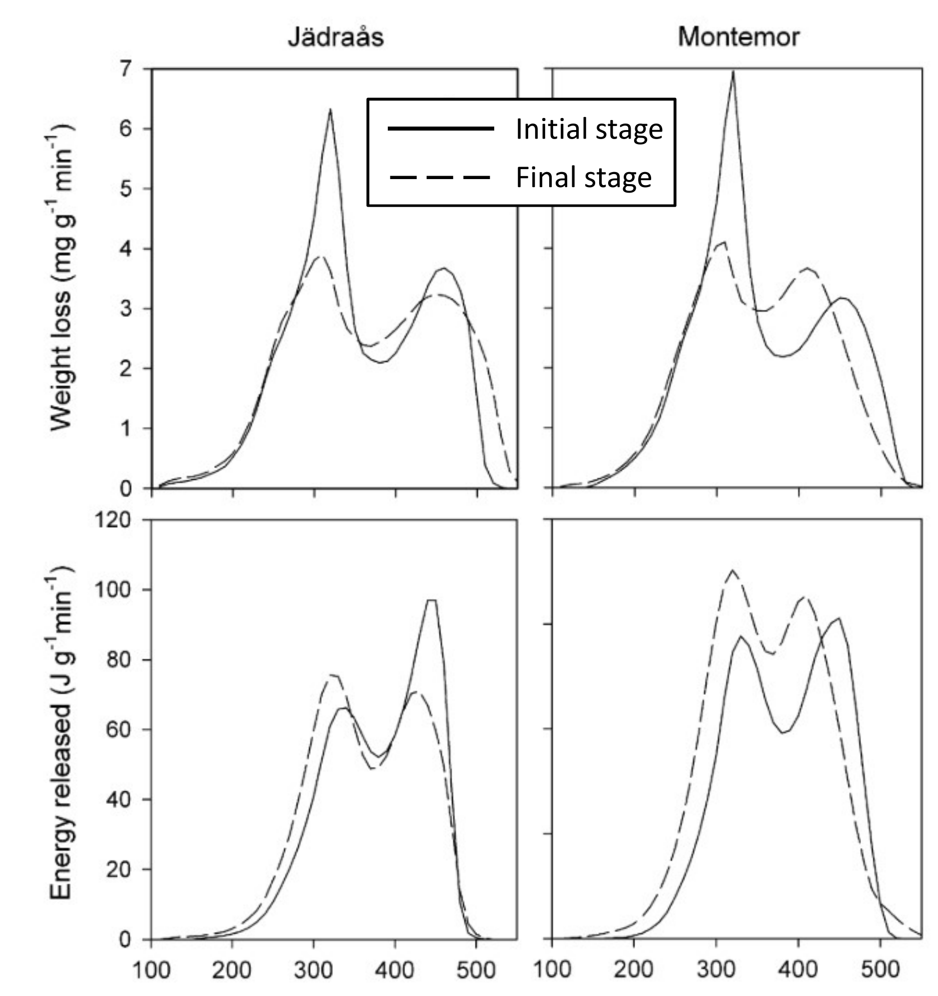


Rovira et al. (2008)

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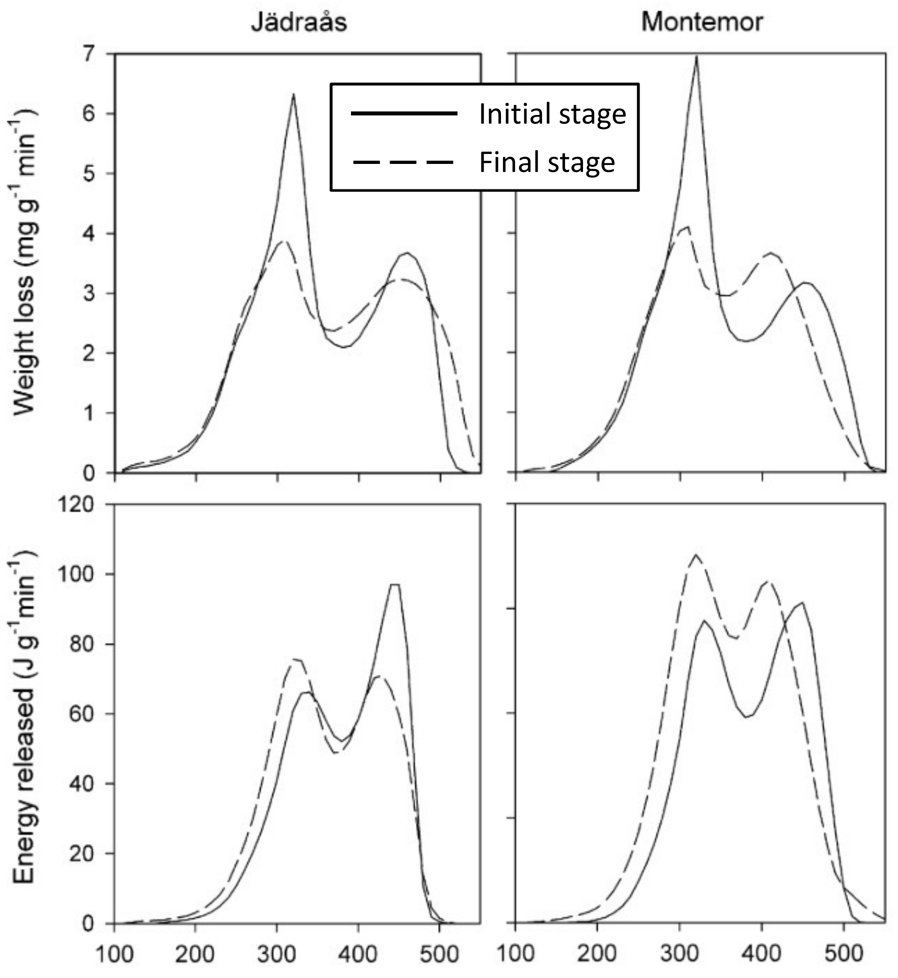


Temperature °C

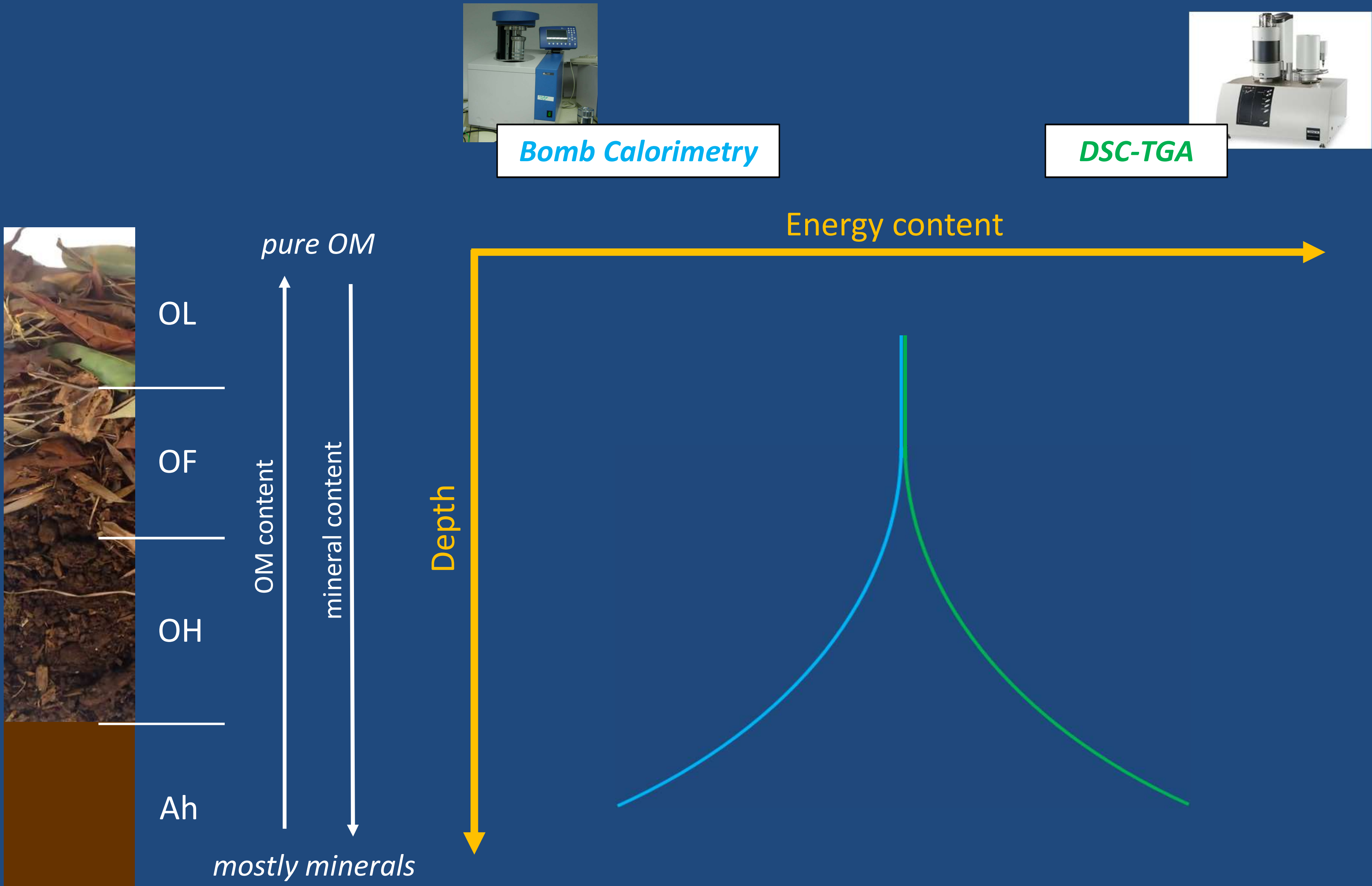
Rovira et al. (2008)

**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

# III. Contradictions – SOM energy content

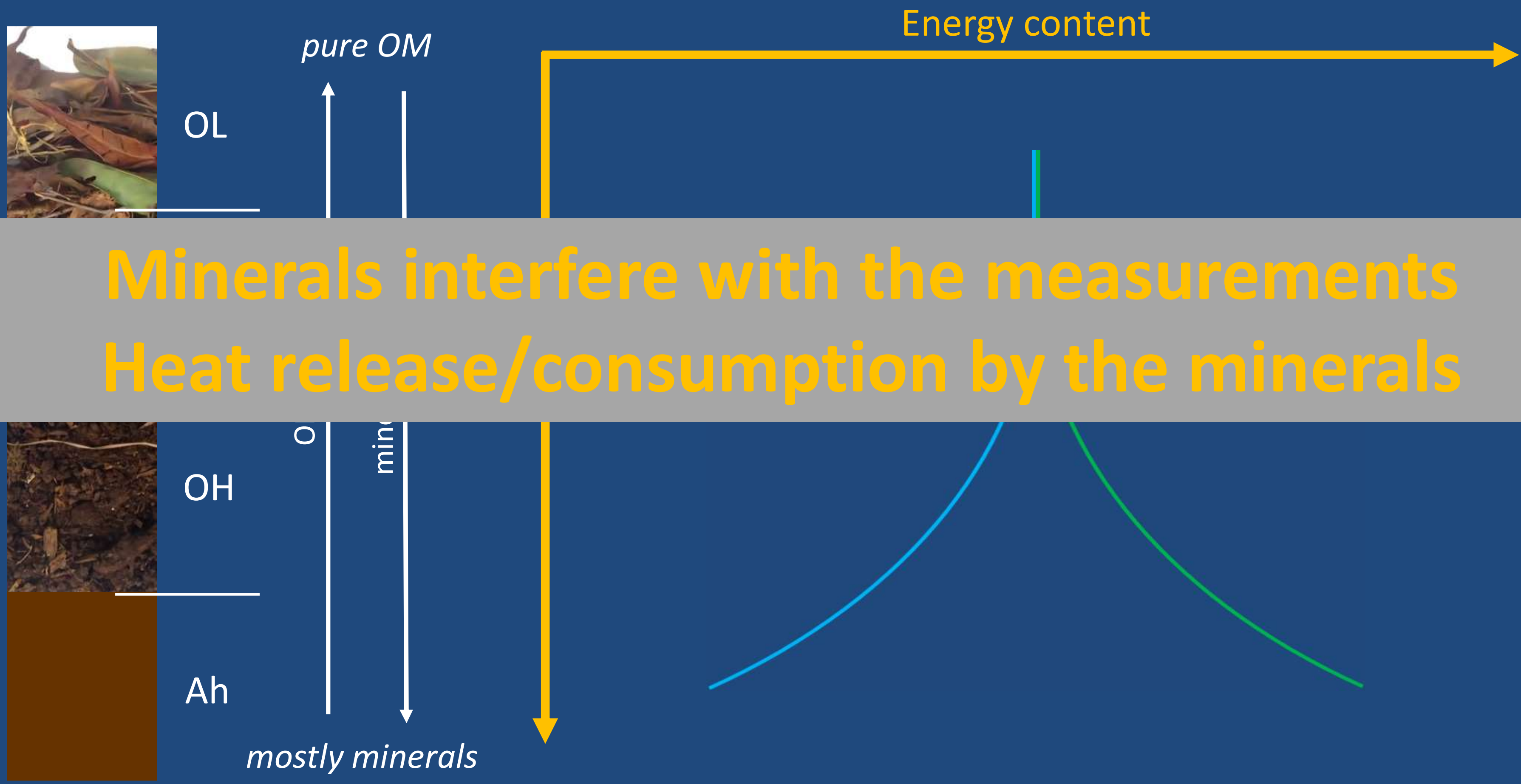



[a] Lorenz (2023) *presentation at EGU23*

# III. Contradictions – SOM energy content

Bomb Calorimetry

DSC-TGA




**Minerals interfere with the measurements**

**Heat release/consumption by the minerals**

[a] Lorenz (2023) *presentation at EGU23*

# <u>Driving of the engine:</u>

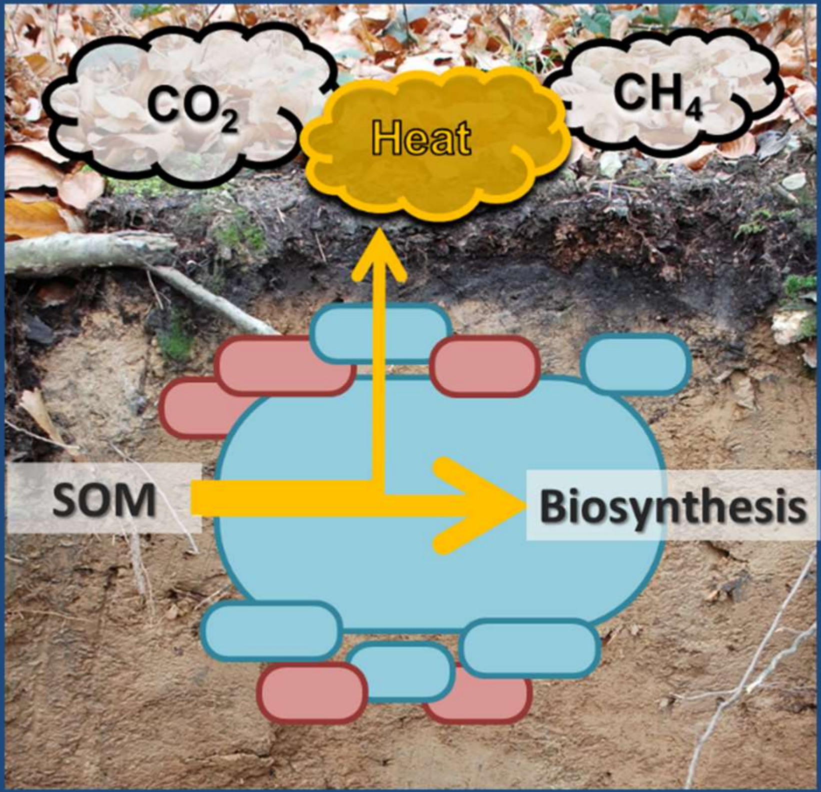
**Approaches focusing on**

***INTERACTIONS*** **of**

***MICROORGANISMS*** **and**

***SOIL ORGANIC MATTER***

# I. Microbial metabolic efficiency




**Common approach addresses C**

**Carbon-Use Efficiency (CUE):**

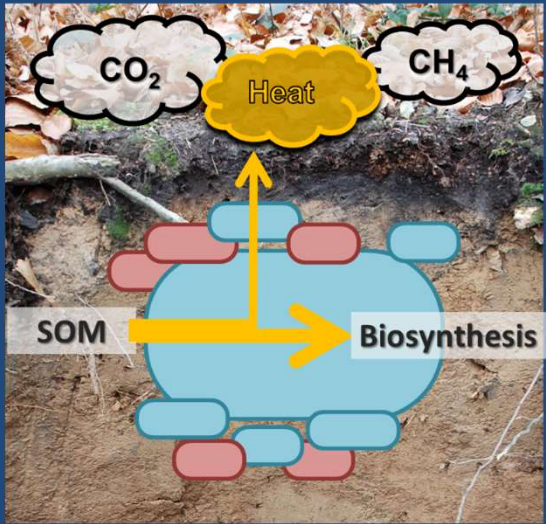
$$CUE = \frac{Biomass - C}{Biomass - C + \sum CO_2 - C}$$

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

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

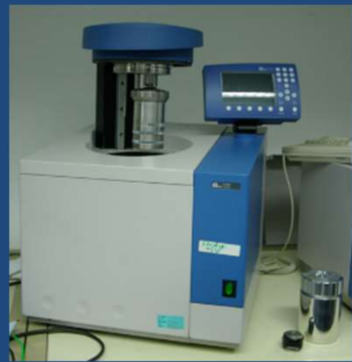
# I. Microbial metabolic efficiency

*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*

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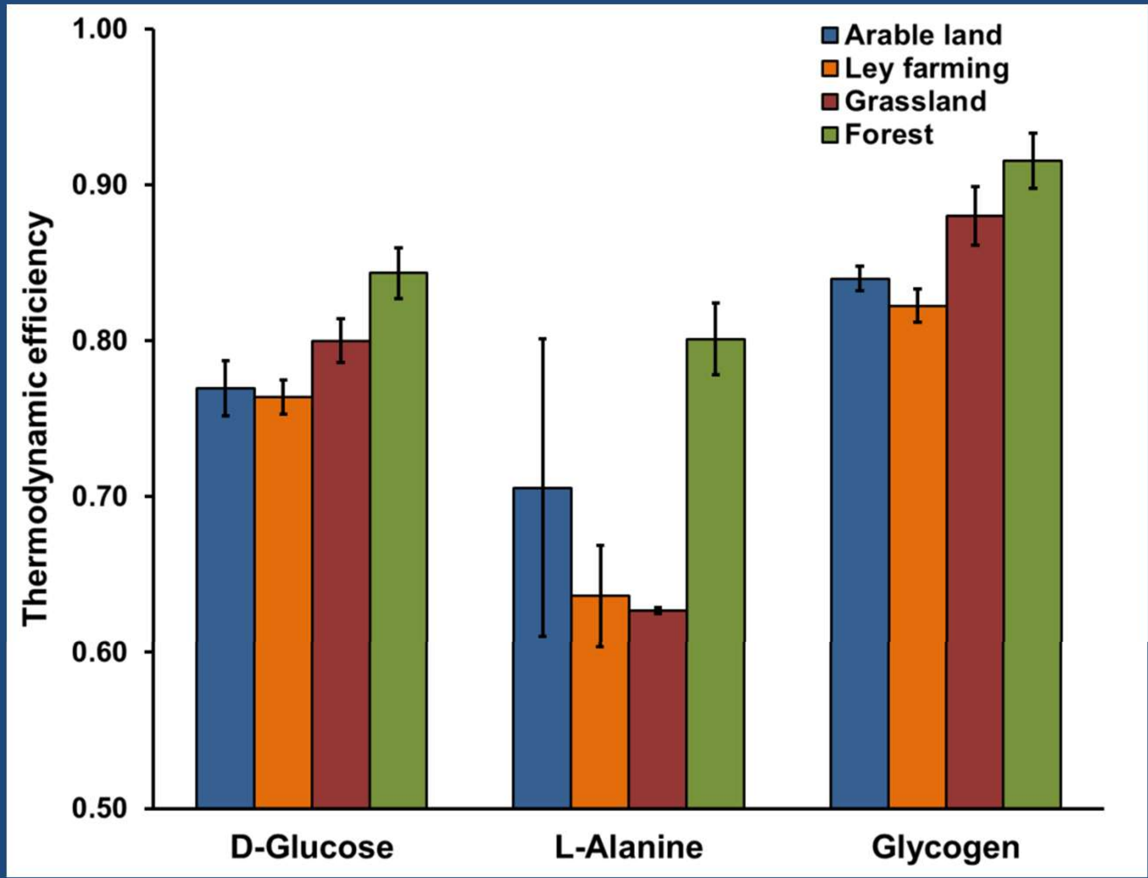


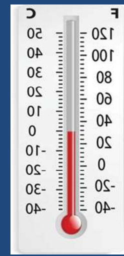

12.5 °C






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

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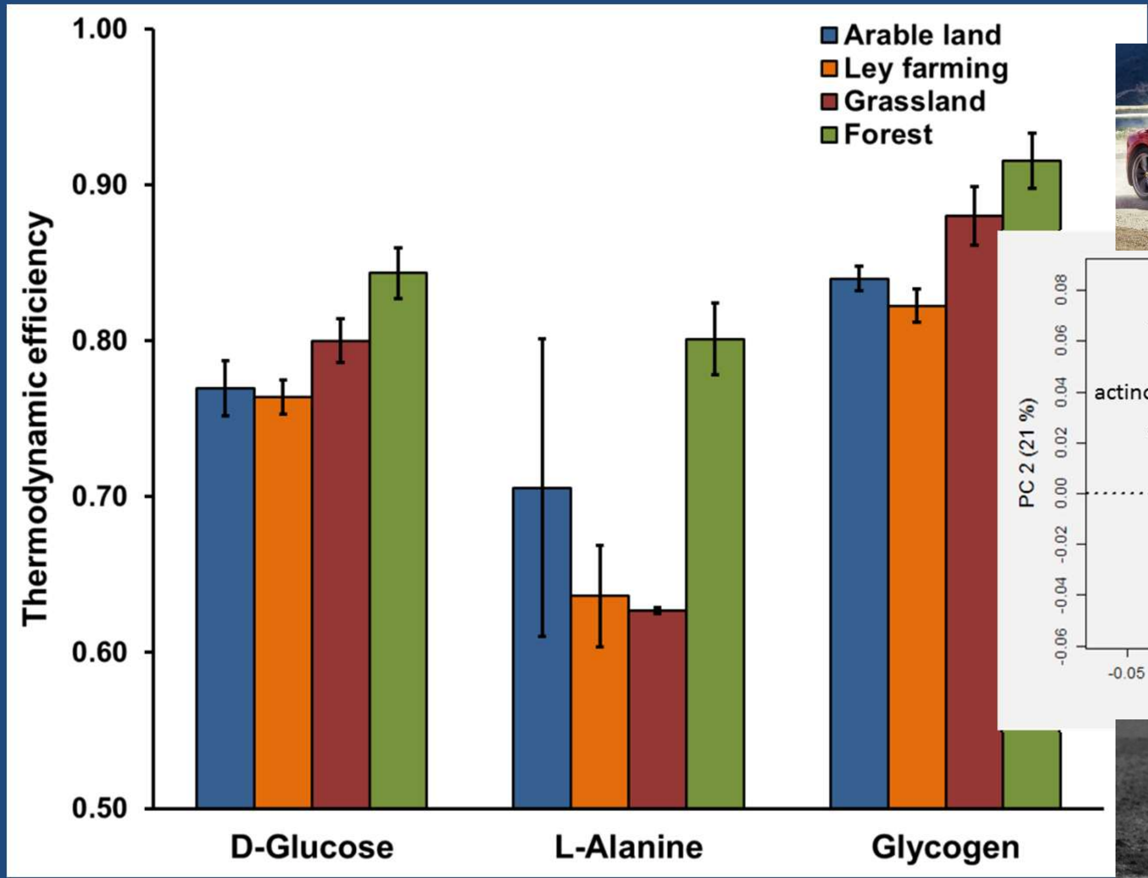
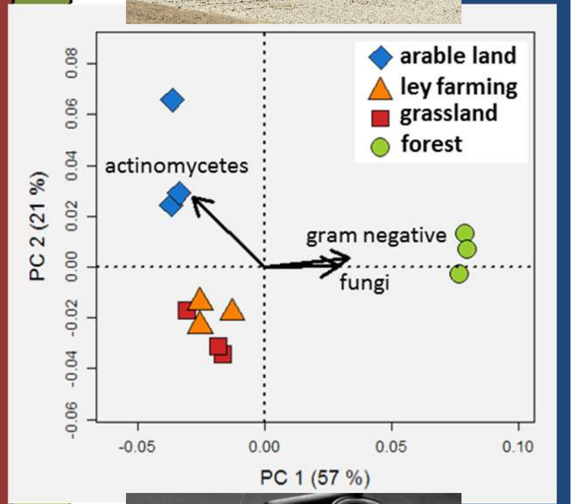


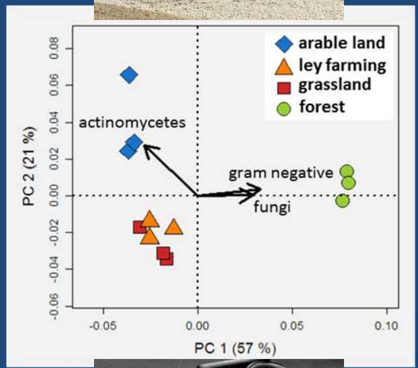

**Glycogen > D-Glucose > L-Alanine**

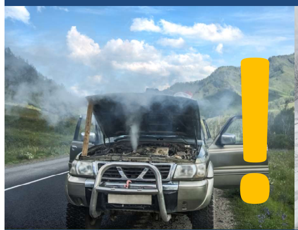
**Forest > Arable land, Ley farming and Grassland**

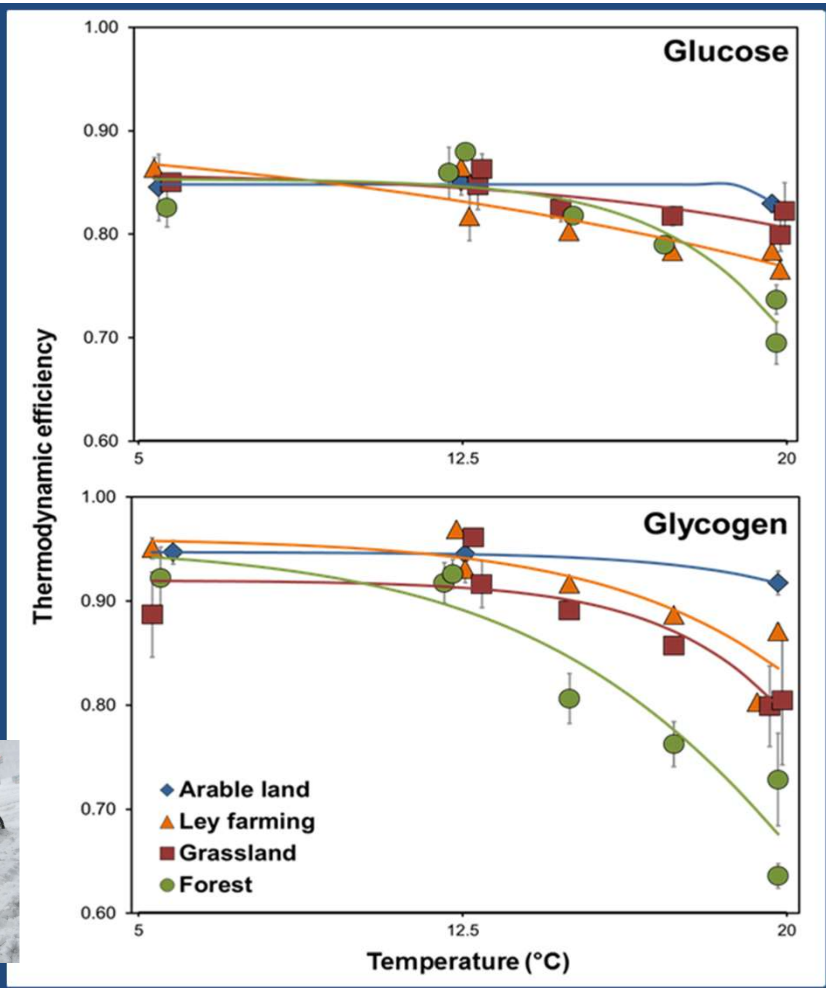
Bölscher et al. (2016) *Biol. Fertil. Soils* 52

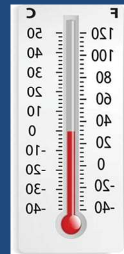
# I. Microbial metabolic efficiency





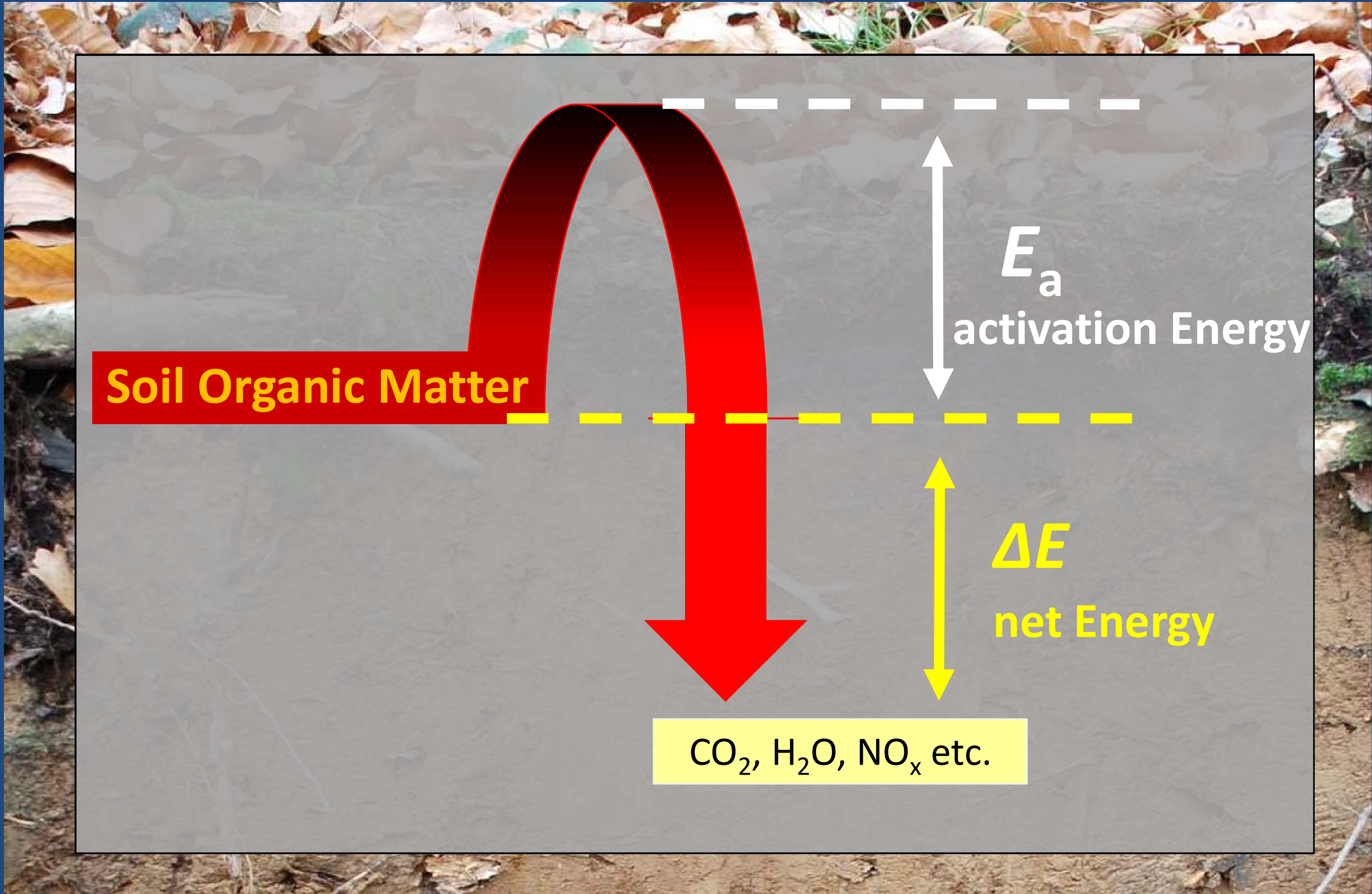




5-20 °C


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

# II. 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

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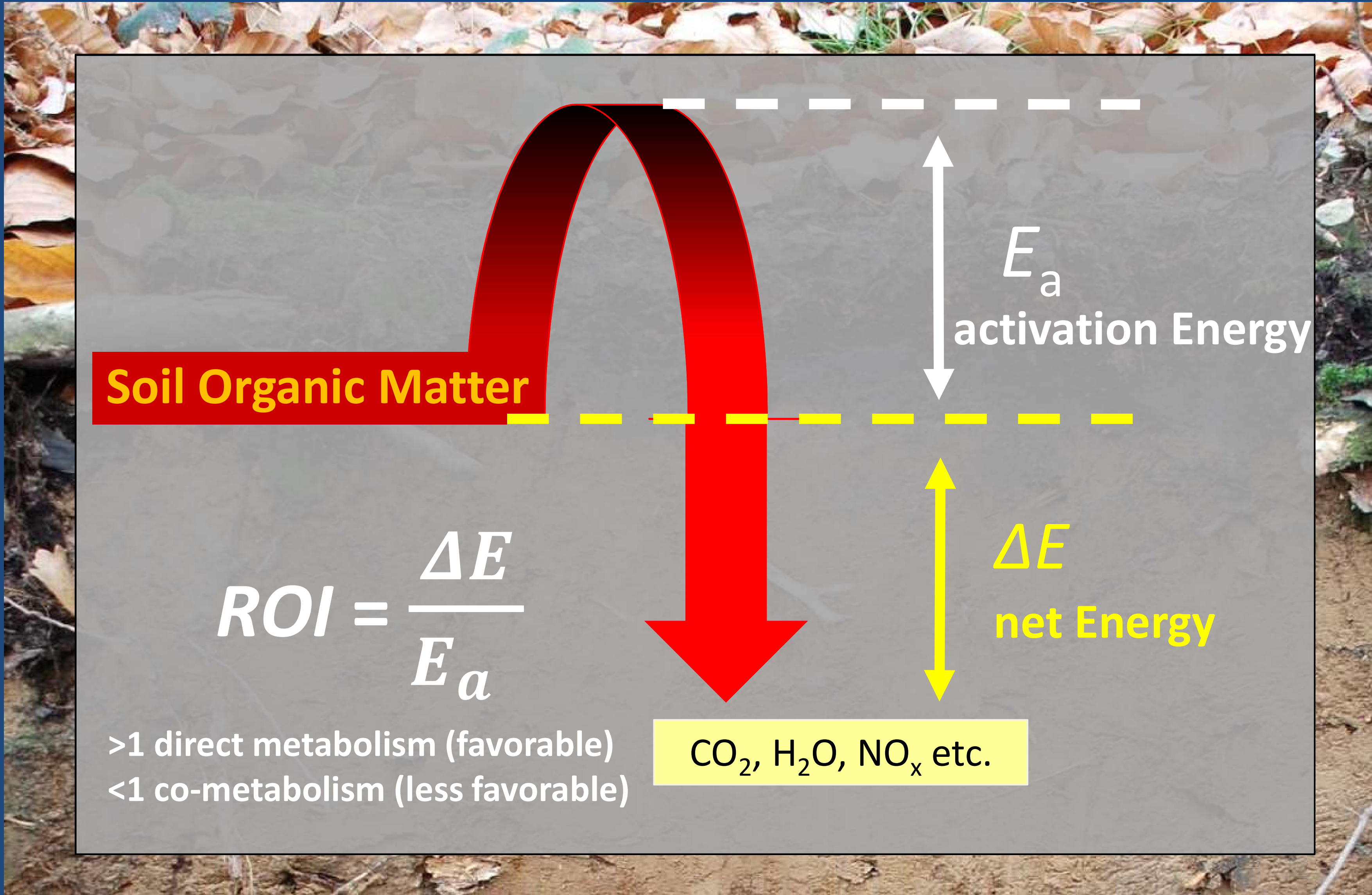



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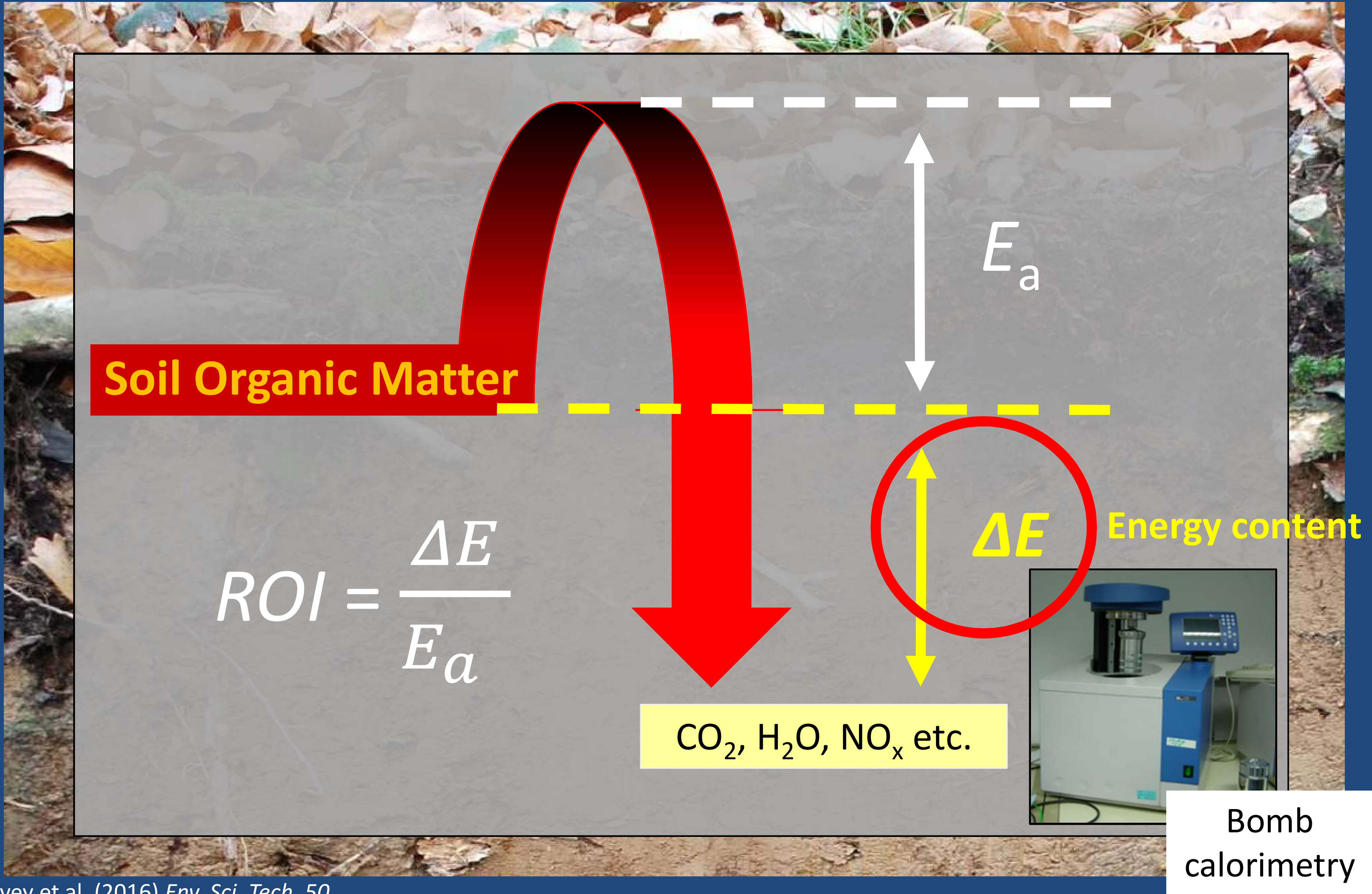



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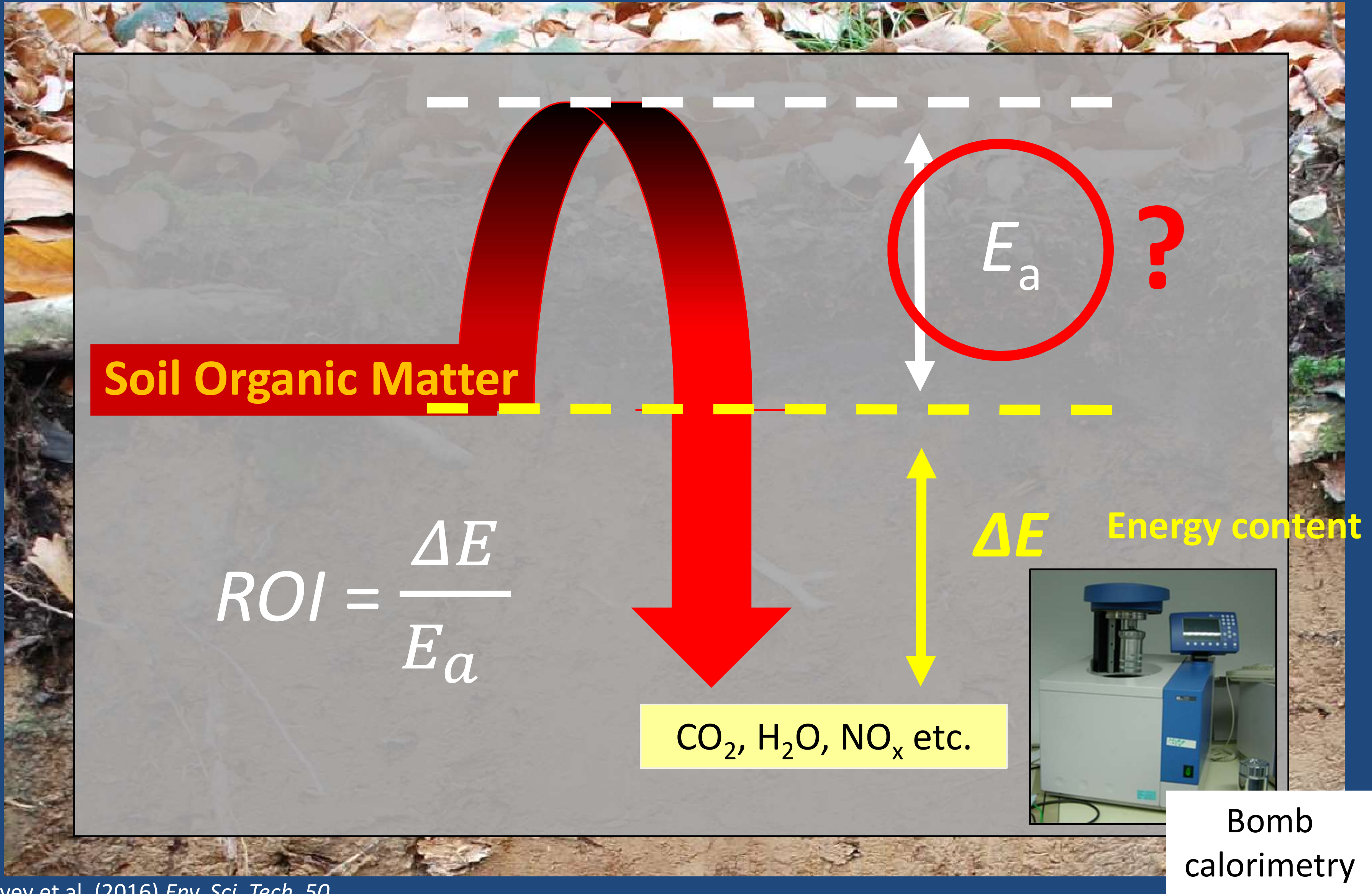


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# II. Energetic return-on-investment

## ***Decomposition → redox reactions***

*Example: a **lipid***

*Gibbs energy*

***Overall:*** $C_{18}H_{32}O_6 + 26O_2 \rightarrow 18CO_2 + 18H_2O$ — $-10420$ kJ $Mol^{-1}$

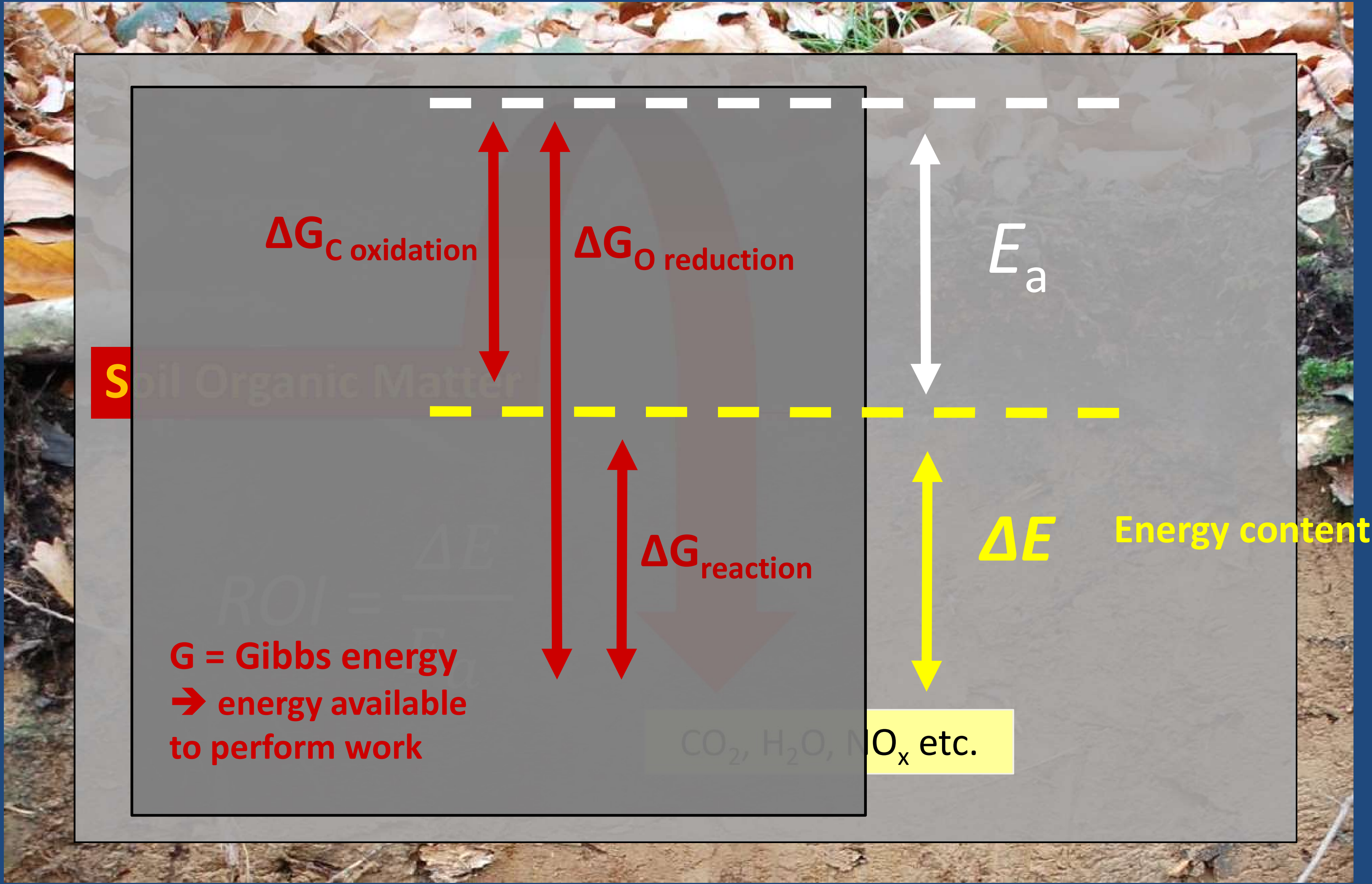
***Oxidation:*** $C_{18}H_{32}O_6 + 34H_2O \rightarrow 18CO_2 + 104e^- + 104H^+$ — **+1924** kJ $Mol^{-1}$

***Reduction:*** $26O_2 + 104e^- + 104H^+ \rightarrow 52H_2O$ — $-12344$ kJ $Mol^{-1}$

**→ The oxidation half-reaction (i.e. the breakdown of the lipid) requires an energy input. Energy is gained from producing water molecules rather than breaking carbon substrate.**

Courtesy M. Kleber

# II. Energetic return-on-investment





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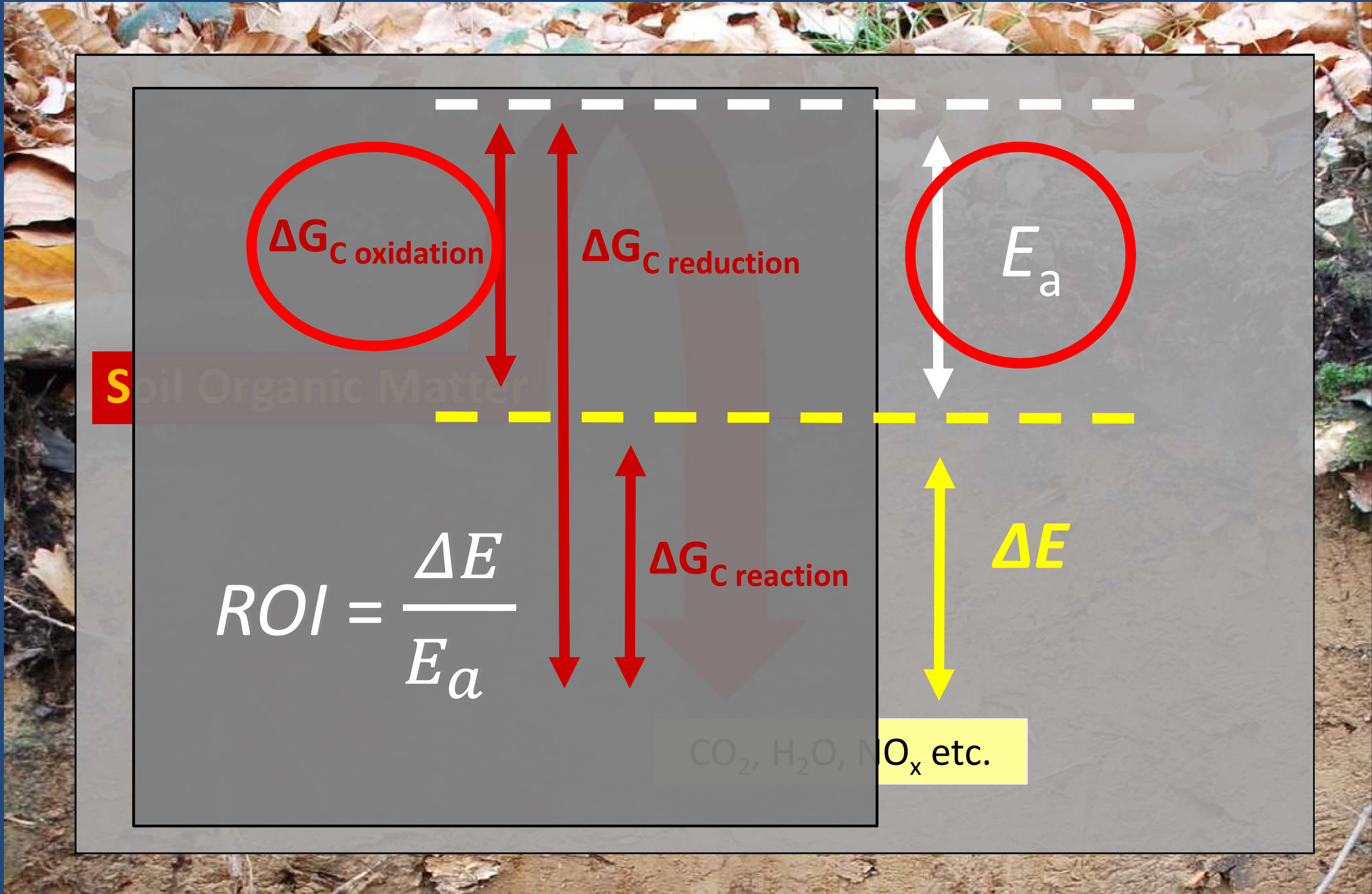



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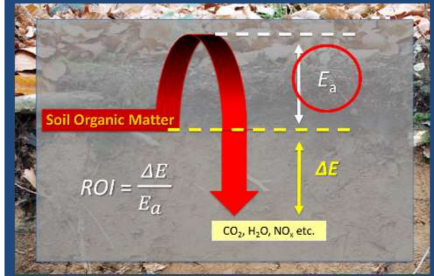
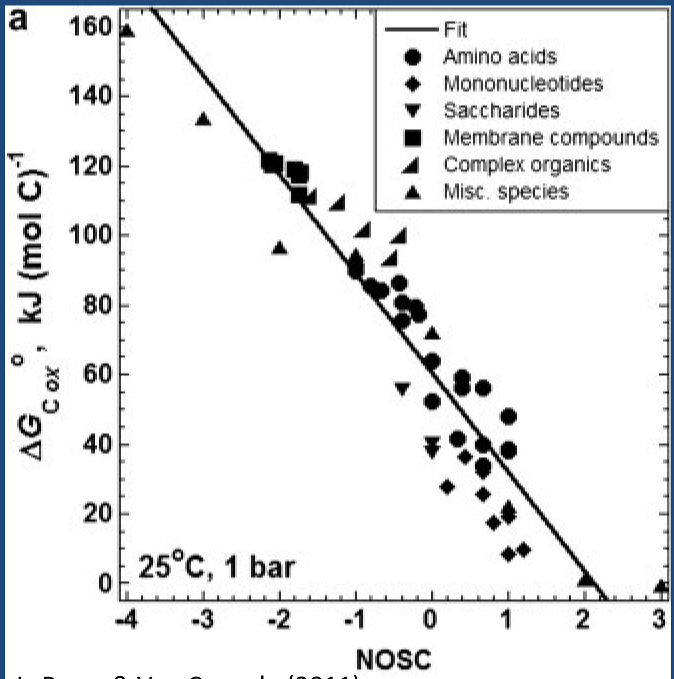


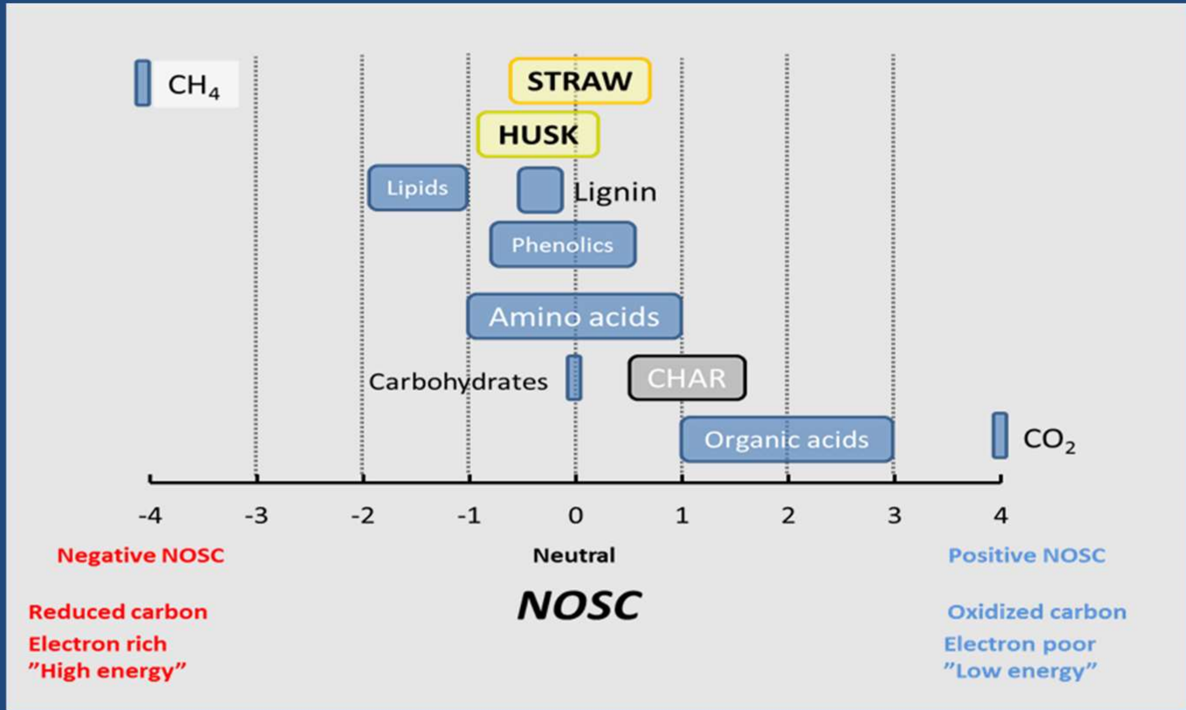

$E_a$ via $\Delta G^0_{C_{ox}}$ &

nominal oxidation state of carbon $NOSC$

$$\Delta G^0_{C_{ox}} = 60.3 - 28.5 * \text{NOSC}$$




LaRowe & Van Cappeln (2011)





LaRowe & Van Cappeln (2011) *Geochim. Cosmochim. Acta* 75
Willems et al. (2013) *Polym. Degrad. Stab.* 98

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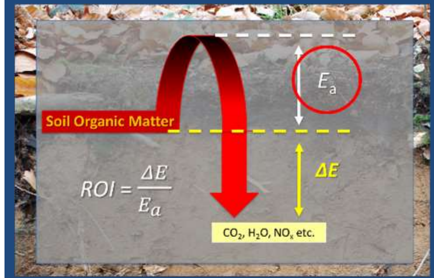
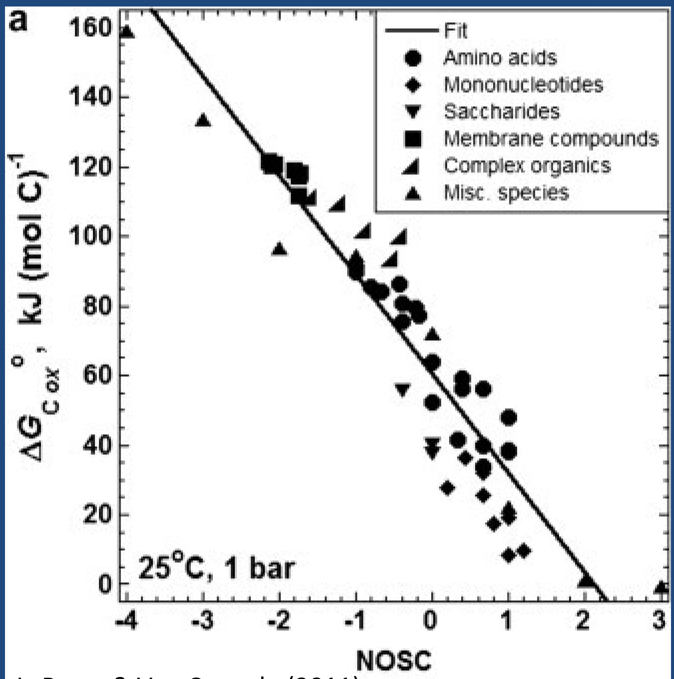
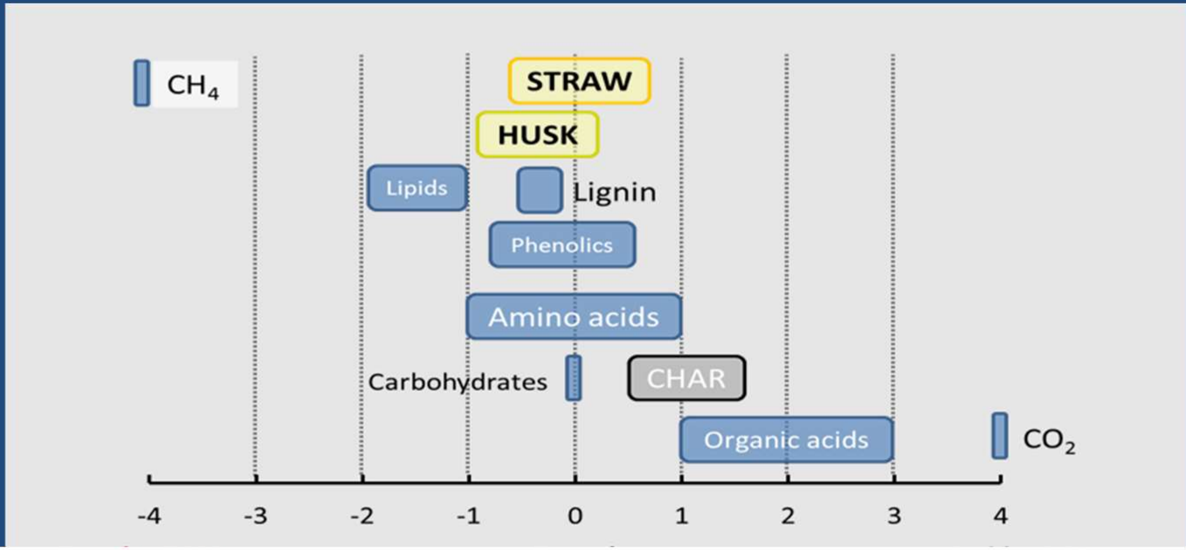



$E_a$ via $\Delta G^0_{C_{ox}}$ &
nominal oxidation state of carbon ***NOSC***




LaRowe & Van Cappeln (2011)

$$\Delta G^0_{C_{ox}} = 60.3 - 28.5 * \text{NOSC}$$




$$\text{NOSC} = -\frac{(-Z + 4*C + H - 3N - 2O + 5P - 2S)}{C} + 4$$

LaRowe & Van Cappeln (2011) *Geochim. Cosmochim. Acta* 75
Willems et al. (2013) *Polym. Degrad. Stab.* 98

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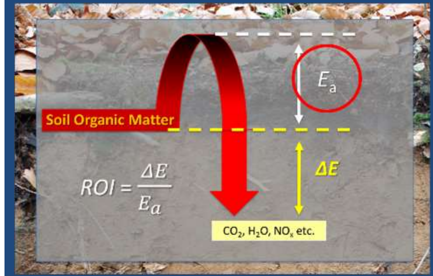


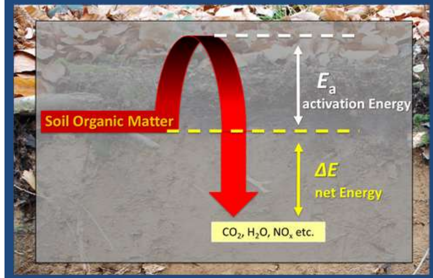

$E_a$ via $\Delta G^0_{C_{ox}}$ &
nominal oxidation state of carbon $NOSC$

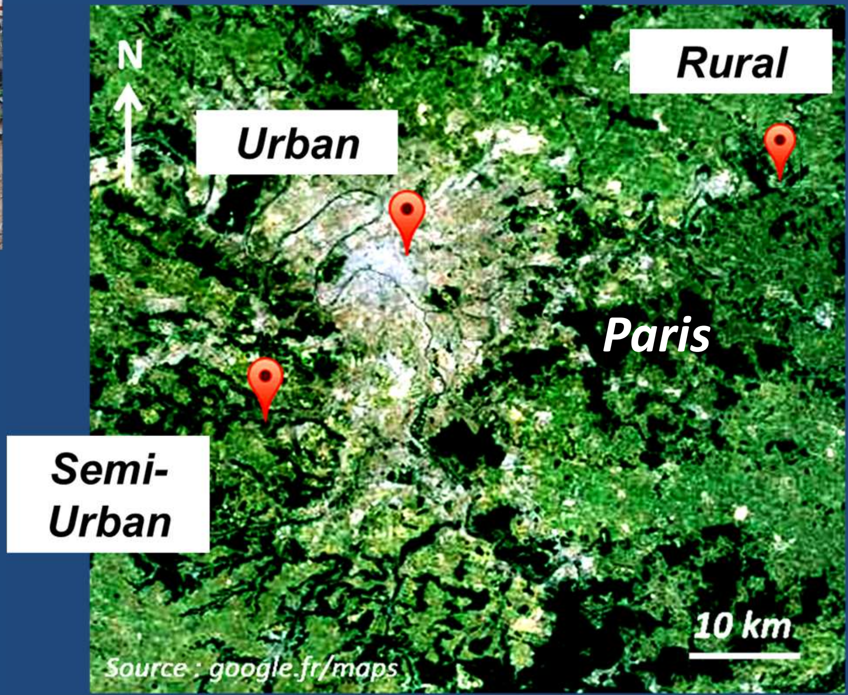

***Fourier-Transform Ion Cyclotron Resonance Mass Spectrometry***
***(FT-ICR-MS)***

$$\text{NOSC} = -\frac{(-Z+4*C+H-3N-2O+5P-2S)}{C} + 4$$

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

# II. Energetic return-on-investment




3 X

Park

Forest

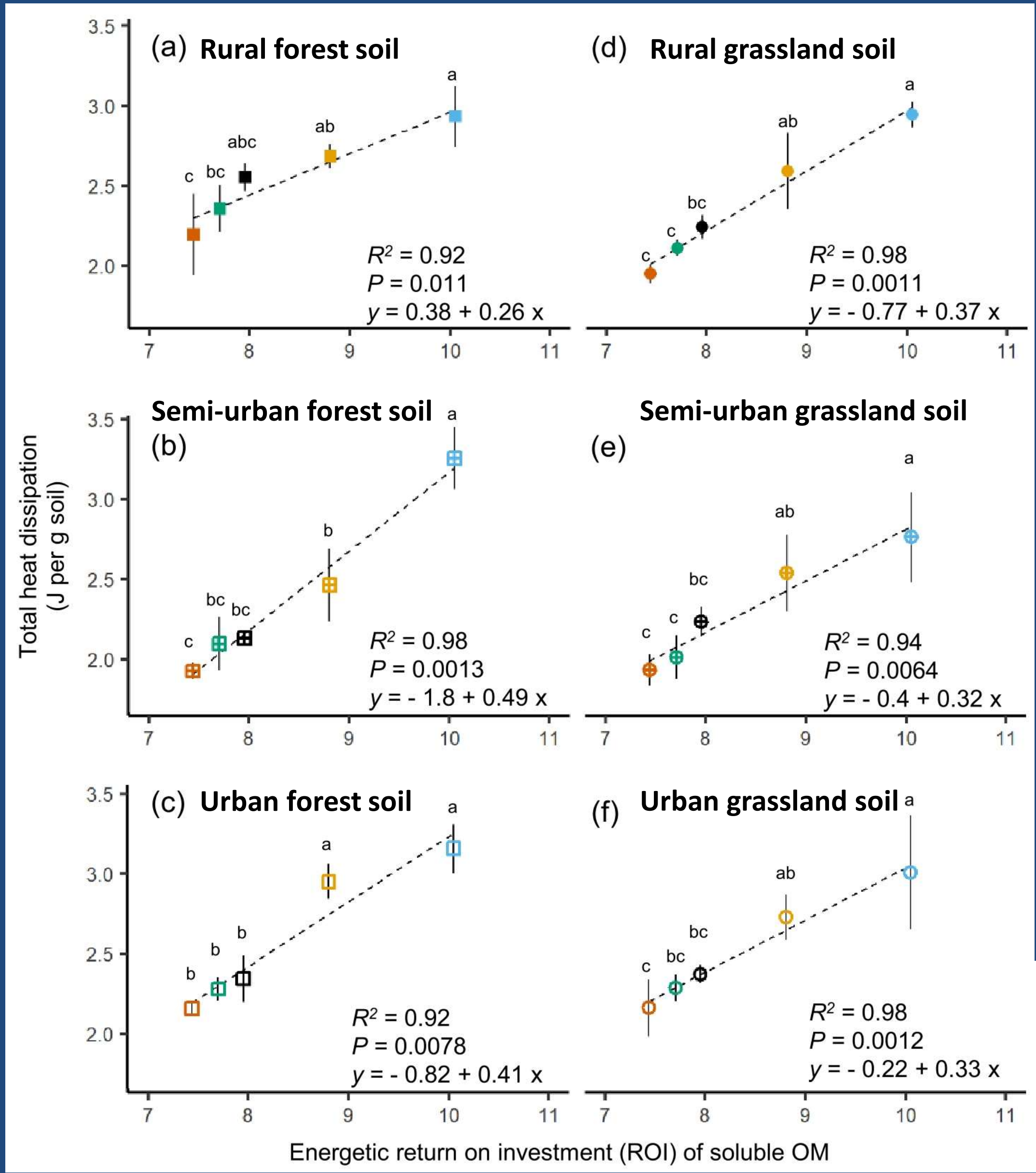
DOC extraction
Cross incubation

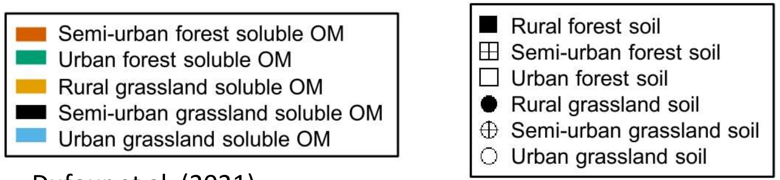
<u>Microbial activity</u>
over 24 h at 25 °C

*TAM Air calorimetry*

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

# II. Energetic return-on-investment

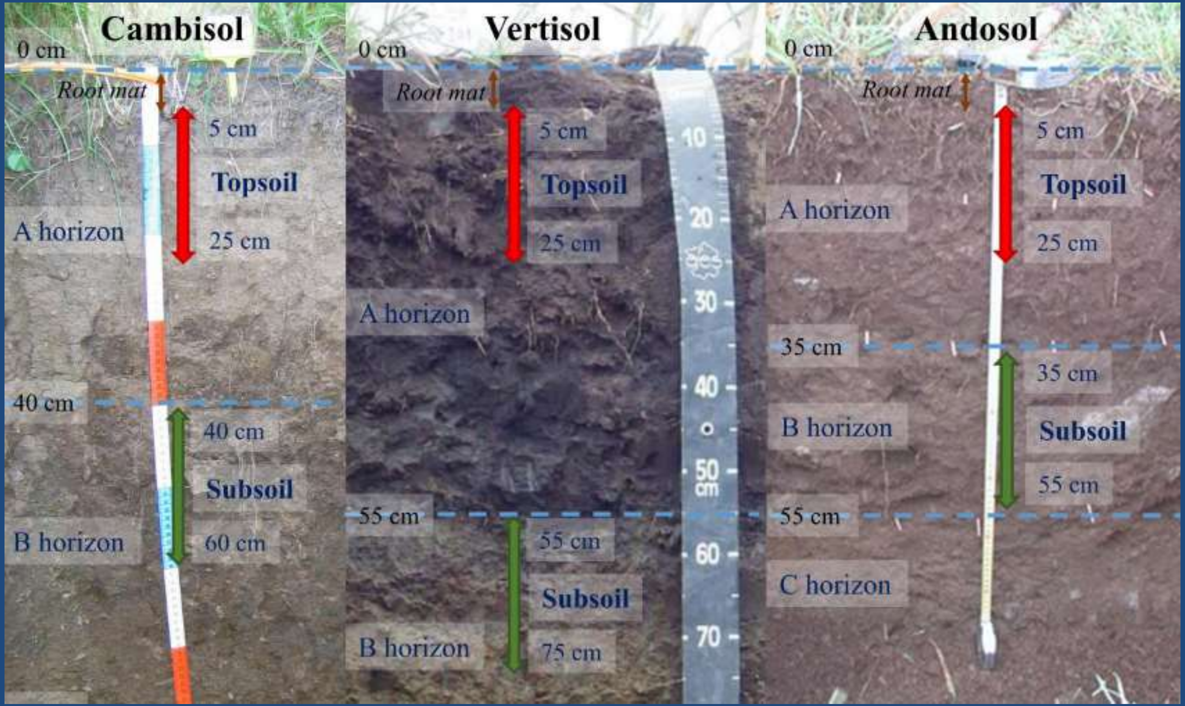



Dufour et al. (2021)

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

# II. Energetic return-on-investment




**Incubation experiment**
(279 days)

*Treatments*

A. Soil planted with grass
B. Soil without plants

*Soil respiration*

Continues labelling with $^{13}C/^{14}C$ depleted air

➔ Destination between native SOM derived C and C rhinoceroses

*Energetic ROI*

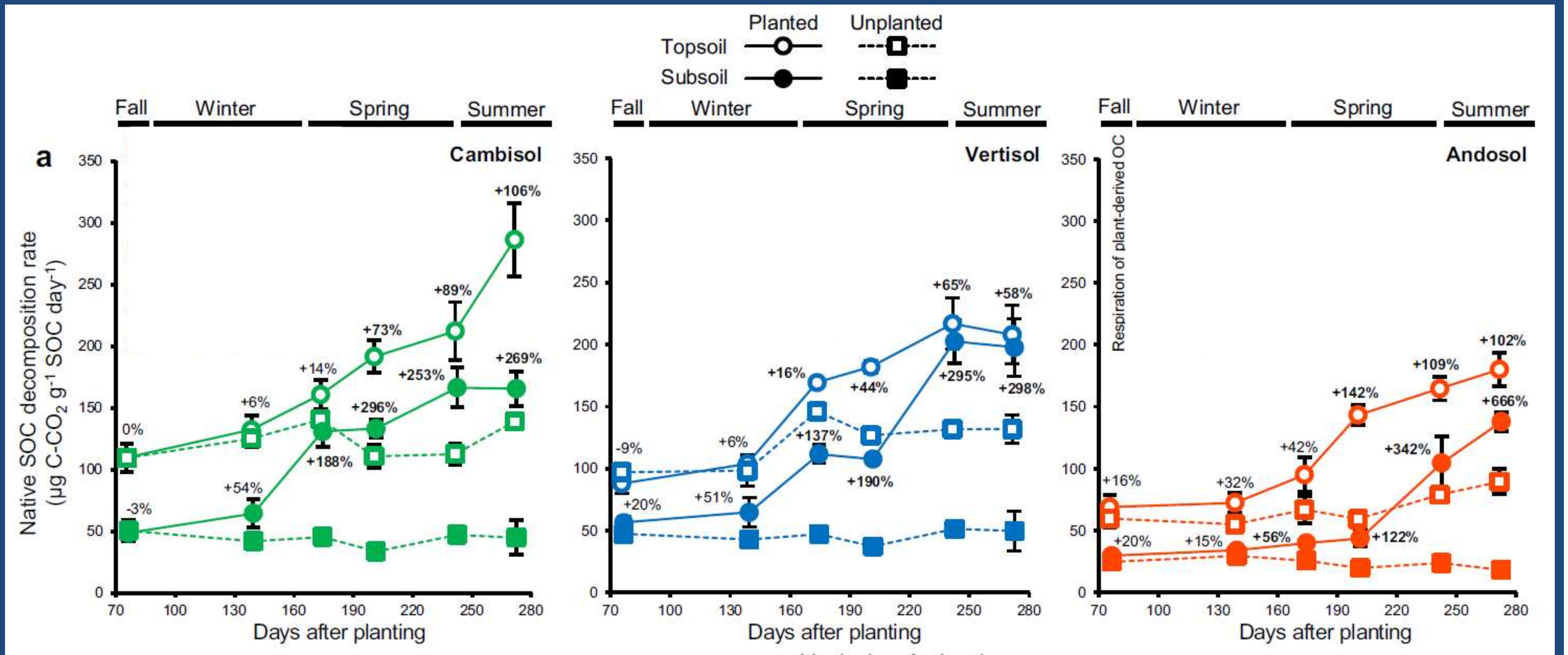
- Bomb calorimetry → ΔE
- Rock-Eval® → $E_a$

Henneron et al. (2022) *Nat. Comm. 13*

# II. Energetic return-on-investment

## Bioenergetics control soil C dynamics across depth

Cambisol Vertisol Andosol




Henneron et al. (2022) *Nat. Comm. 13*

# II. Energetic return-on-investment

## Bioenergetics control soil C dynamics across depth

| | | Cambisol | Vertisol | Andosol |
|---|---|---|---|---|
| Topsoil | Energy content – ΔE (kJ $mol^{-1}$ SOM) | 158.6 | 190.9 | 175.7 |
| | Activation Energy – $E_a$ (kJ $mol^{-1}$ SOM) | 157.8 | 161.3 | 159.5 |
| | ***Energetic ROI*** | ***1.01*** | ***1.18*** | ***1.10*** |
| Subsoil | Energy content – ΔE (kJ $mol^{-1}$ SOM) | 111.9 | 127.7 | 140.6 |
| | Activation Energy – $E_a$ (kJ $mol^{-1}$ SOM) | 158.4 | 165.9 | 161.5 |
| | ***Energetic ROI*** | ***0.71*** | ***0.77*** | ***0.87*** |

Henneron et al. (2022) *Nat. Comm. 13*

# The road network:

## Approaches focusing on

## the ENVIRONMENT

## and ITS CONSTRAINS

# Thermodynamic constrains of metabolism

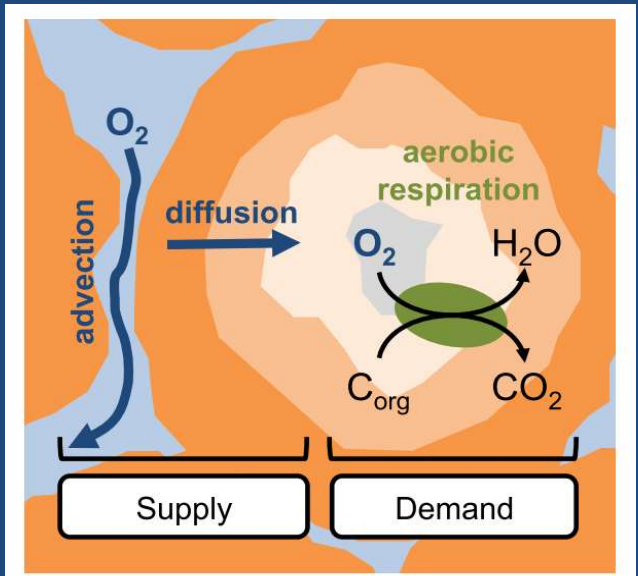
Biogeochemistry (2016) 127:157–171
DOI 10.1007/s10533-015-0180-6

SYNTHESIS AND EMERGING IDEAS

**Are oxygen limitations under recognized regulators of organic carbon turnover in upland soils?**

Marco Keiluweit · Peter S. Nico ·
Markus Kleber · Scott Fendorf

**Aggregation**




Keiluweit et al. (2016)

**Rhizosphere**


**<u>Aerobic metabolism</u> most common metabolism in upland soil.**

**➔ $O_2$ as electron acceptor**

**But, <u>oxygen limitations</u>**

- **in aggregations**
  (microbial consumption, limited diffusion)
- **around roots**
  (root respiration, release of reductants, stimulated microbial activity)

**➔SOM mineralization decreases under $O_2$ limitation**

Keiluweit et al. (2016) *Biogeochem.* 127

# Thermodynamic constrains of metabolism

$$R_{C-min} = R_{max} * \mathbf{B} * F_k * F_T$$

*$R_{c-min}$: rate of the C mineralization reaction*
*$R_{max}$: maximum reaction rate per unit biomass*
*B: active microbial biomass*
*$F_k$: kinetic factor representing the microbes' ability to quire and process reactants (i.e. enzyme kinetics, mineral protection, physical isolation)*
**$F_T$: Thermodynamic driving force**

} $0 \leq F \leq 1$

$$F_T = 1 - \exp\left(\frac{\Delta G_{C\,reaction} + m\,\Delta G_{ATP}}{nRT}\right)$$

*$\Delta G_{C\,reaction}$: Gibbs free energy of the C mineralization reaction (i.e. catabolic reaction)*
*$\Delta G_{ATP}$: Gibbs free energy required for ATP synthesis (i.e. provides energy for anabolism)*
*n: stoichiometry of reaction*
*m: stoichiometry of ATP production*
*R: gas constant*
*T: temperature*

LaRowe & Van Cappeln (2011) *Geochim. Cosmochim. Acta* 75
Keiluweit et al. (2016) *Biogeochem.* 127

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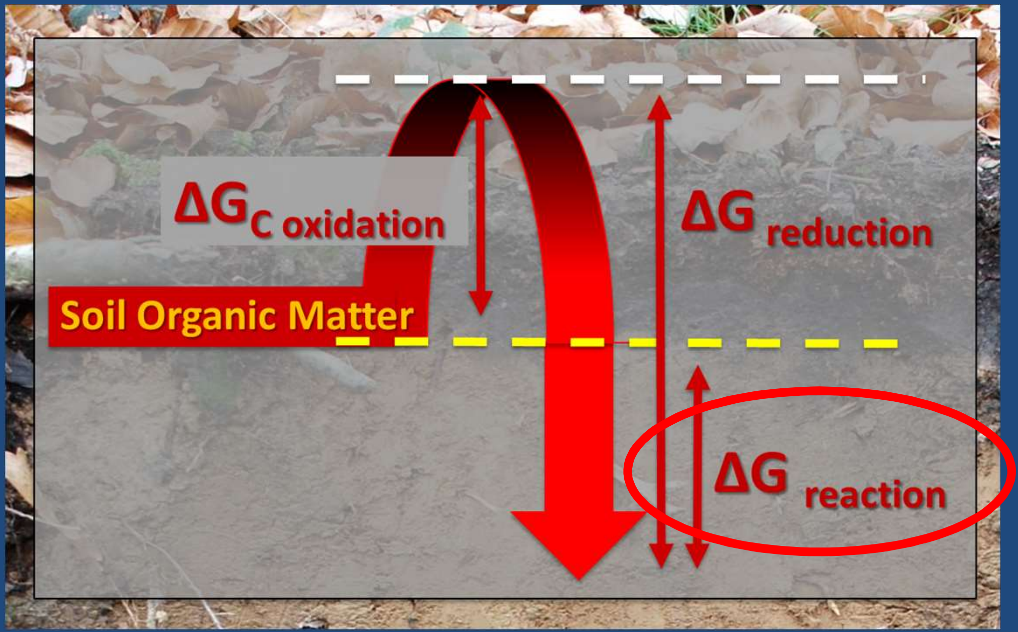


LaRowe & Van Cappeln (2011) *Geochim. Cosmochim. Acta* 75
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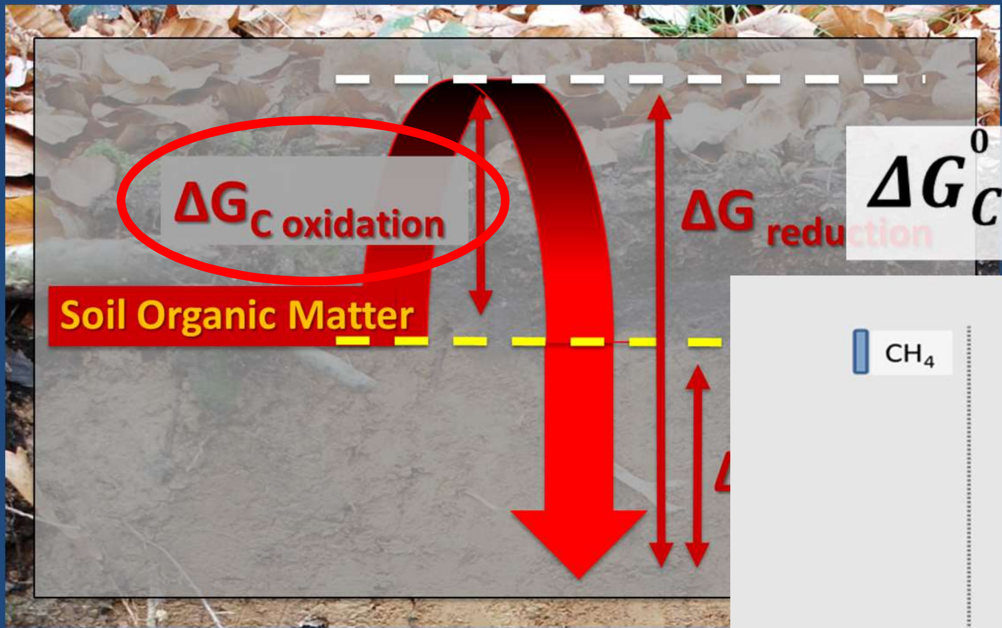
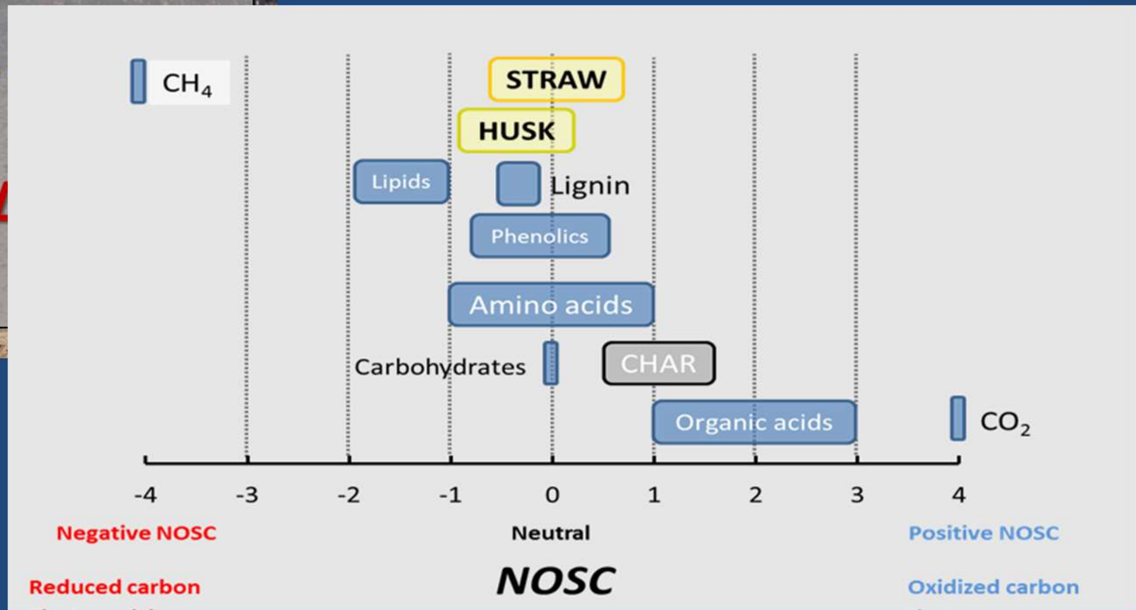



$$\Delta G^{0}_{C_{ox}} = 60.3 – 28.5 * \text{NOSC}$$




LaRowe & Van Cappeln (2011) *Geochim. Cosmochim. Acta* 75
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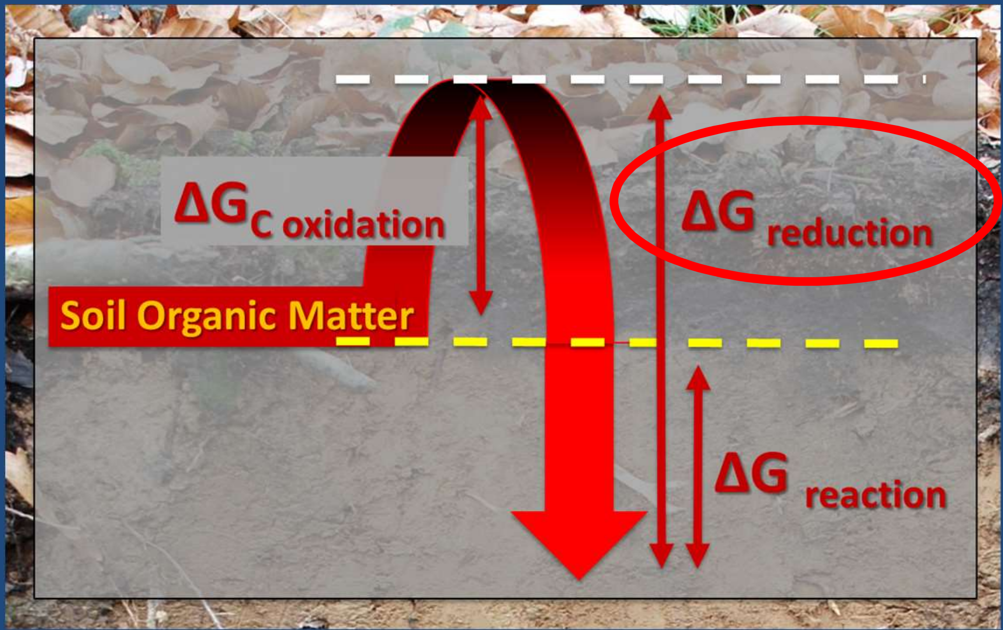



LaRowe & Van Cappeln (2011) *Geochim. Cosmochim. Acta* 75
Keiluweit et al. (2016) *Biogeochem.* 127

# Reminder

## *Decomposition → redox reactions*

*Example: a **lipid*** | *Gibbs energy*

***Overall:*** $C_{18}H_{32}O_6 + 26O_2 \rightarrow 18CO_2 + 18H_2O$ — *-10420 kJ Mol⁻¹*

***Oxidation:*** $C_{18}H_{32}O_6 + 34H_2O \rightarrow 18CO_2 + 104e^- + 104H^+$ — ***+1924*** *kJ Mol⁻¹*

***Reduction:*** $26O_2 + 104e^- + 104H^+ \rightarrow 52H_2O$ — -12344 kJ Mol⁻¹

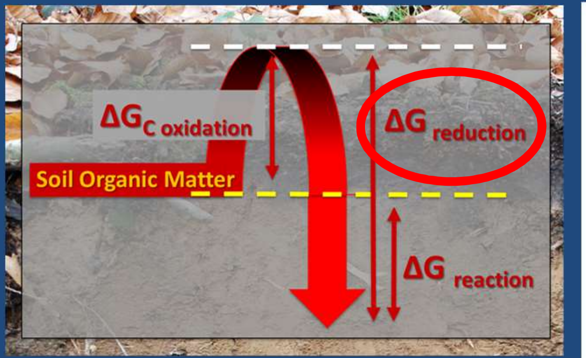
**Oxygen as electron acceptor!**

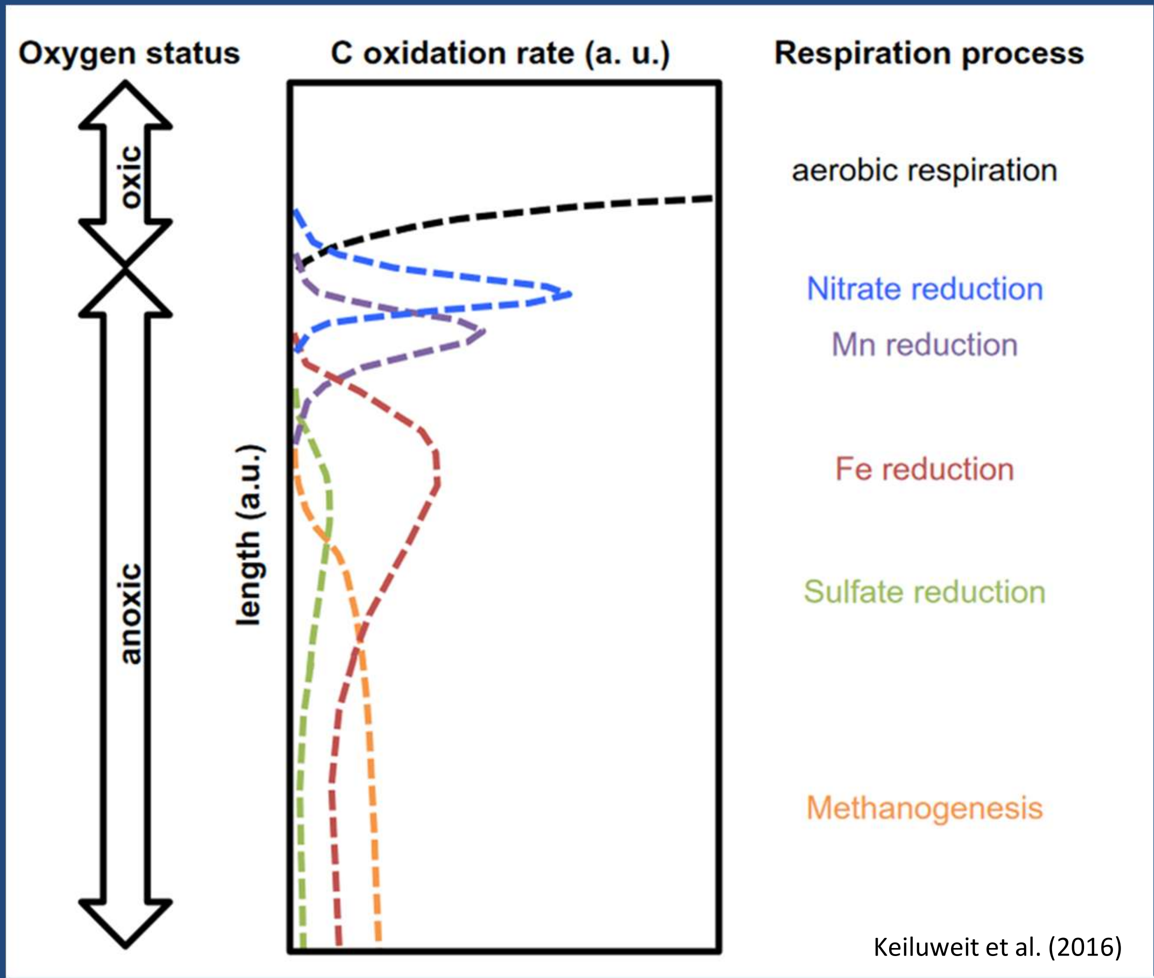
**What about other electron acceptors? → anaerobic conditions**

Courtesy M. Kleber

# Thermodynamic constrains of metabolism

$$F_T = 1 - \exp\left(\frac{\Delta G_{C\ reaction} + m\ \Delta G_{ATP}}{nRT}\right)$$




Keiluweit et al. (2016) *Biogeochem.* 127

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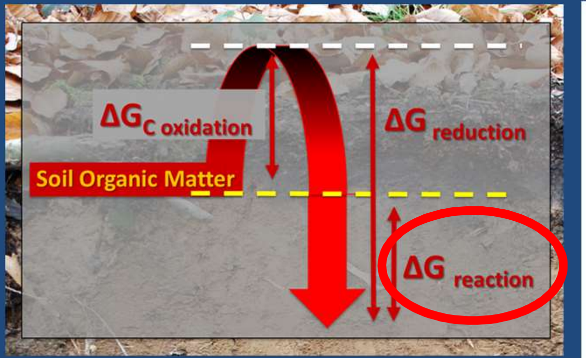
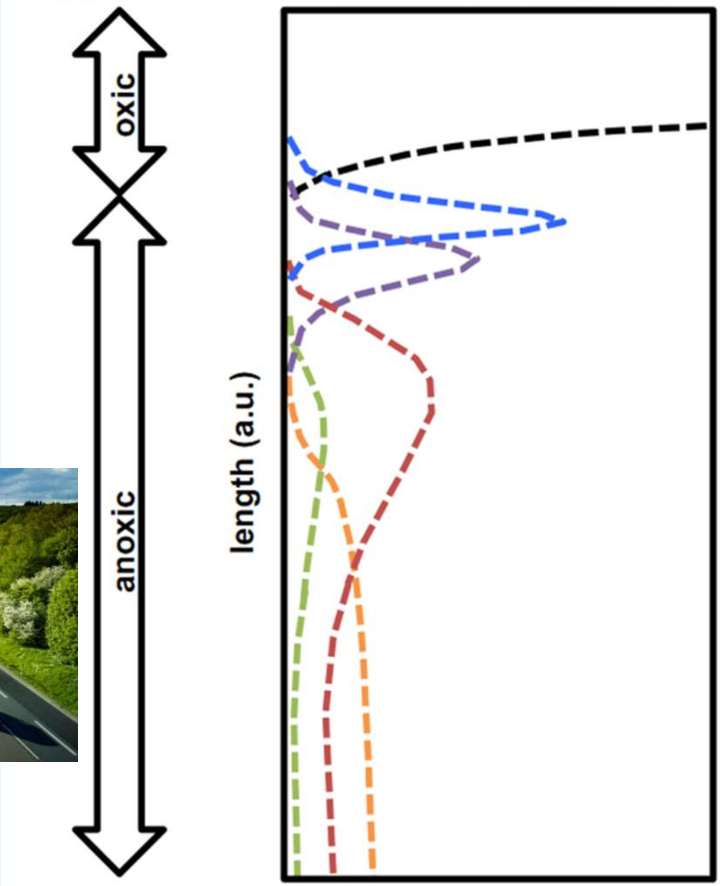


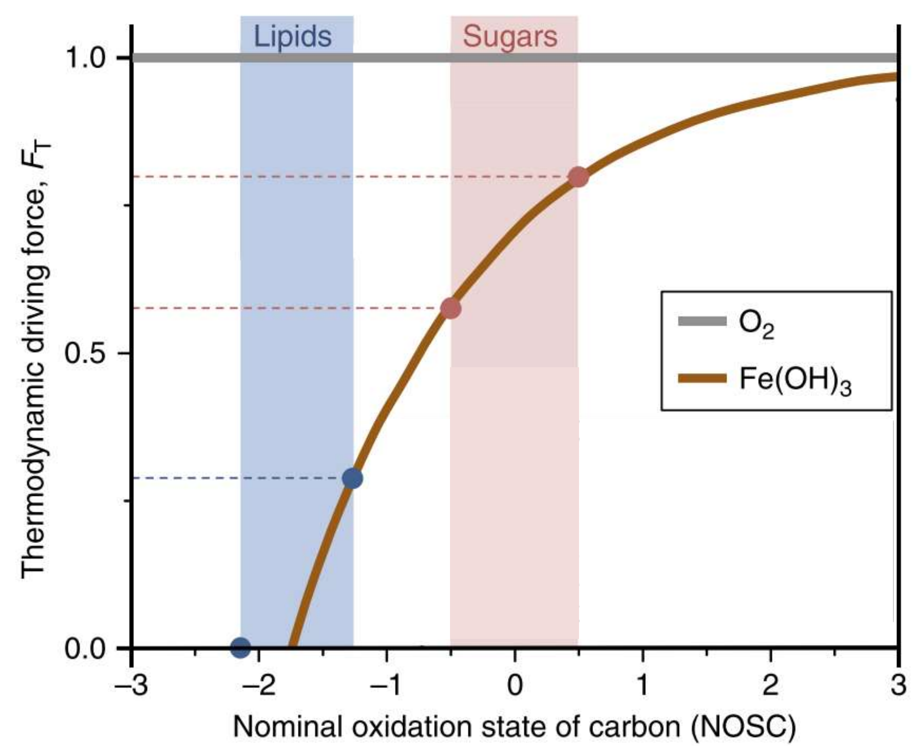

| Respiration process | ΔG* kJ |
|---|---|
| aerobic respiration | -402 |
| Nitrate reduction | -359 |
| Mn reduction | -385 |
| Fe reduction | -241 |
| Sulfate reduction | -43.8 |
| Methanogenesis | -19.9 |

Keiluweit et al. (2016)

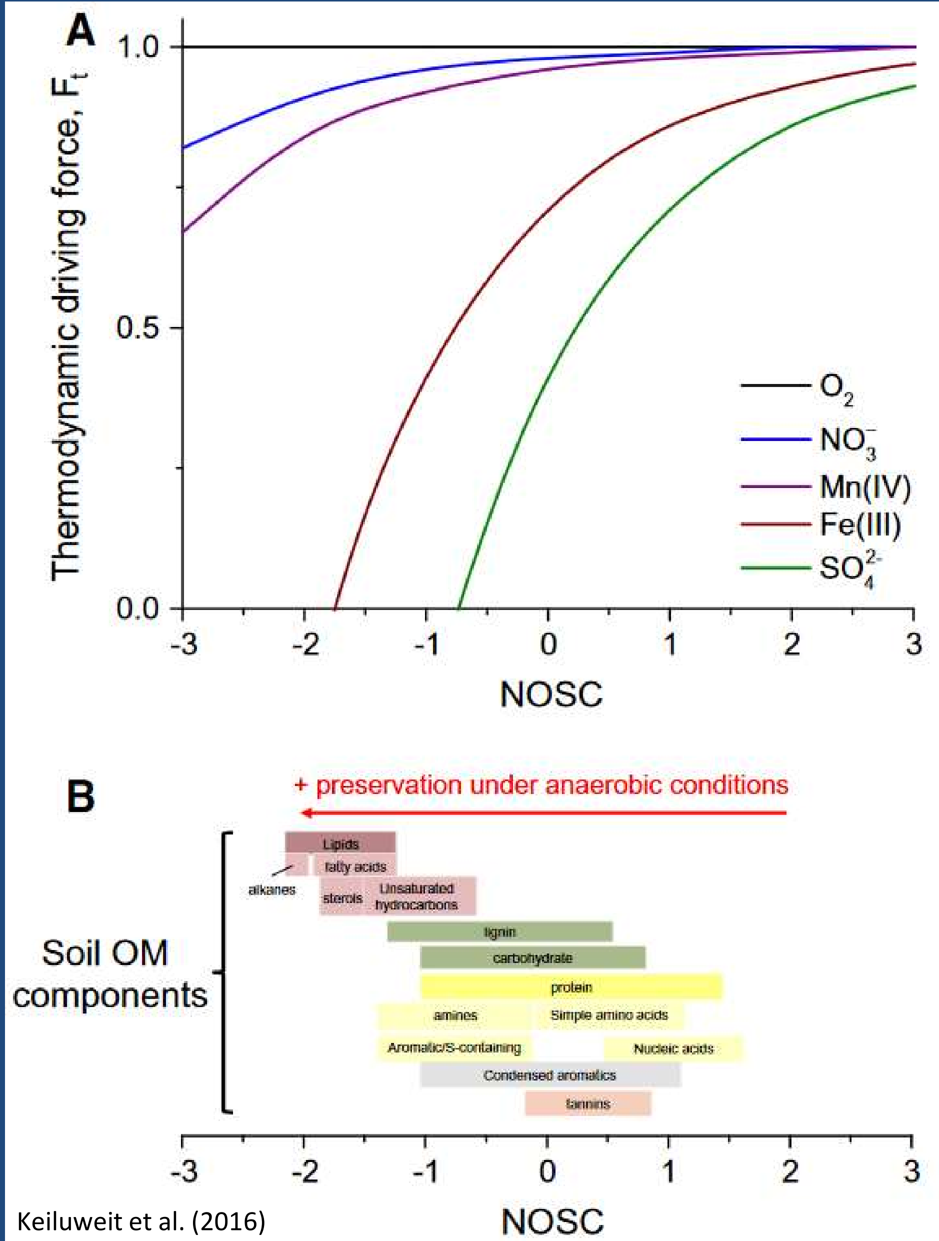
*Standard Gibbs free energy with acetate as an electron donor (kJ per reaction, ΔG)

Keiluweit et al. (2016) *Biogeochem.* 127

# Thermodynamic constrains of metabolism



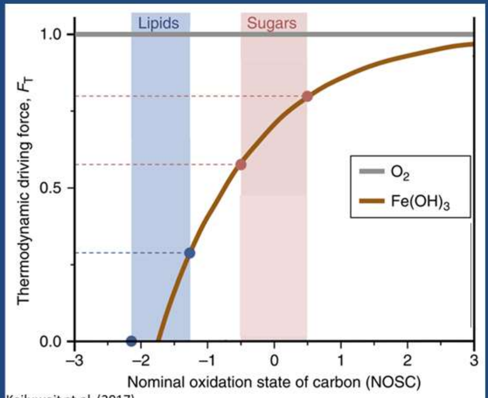

Keiluweit et al. (2017)




Keiluweit et al. (2016)

Keiluweit et al. (2016) *Biogeochem.* 127
Keiluweit et al. (2017) *Nat. Commun.* 8

# Thermodynamic constrains of metabolism



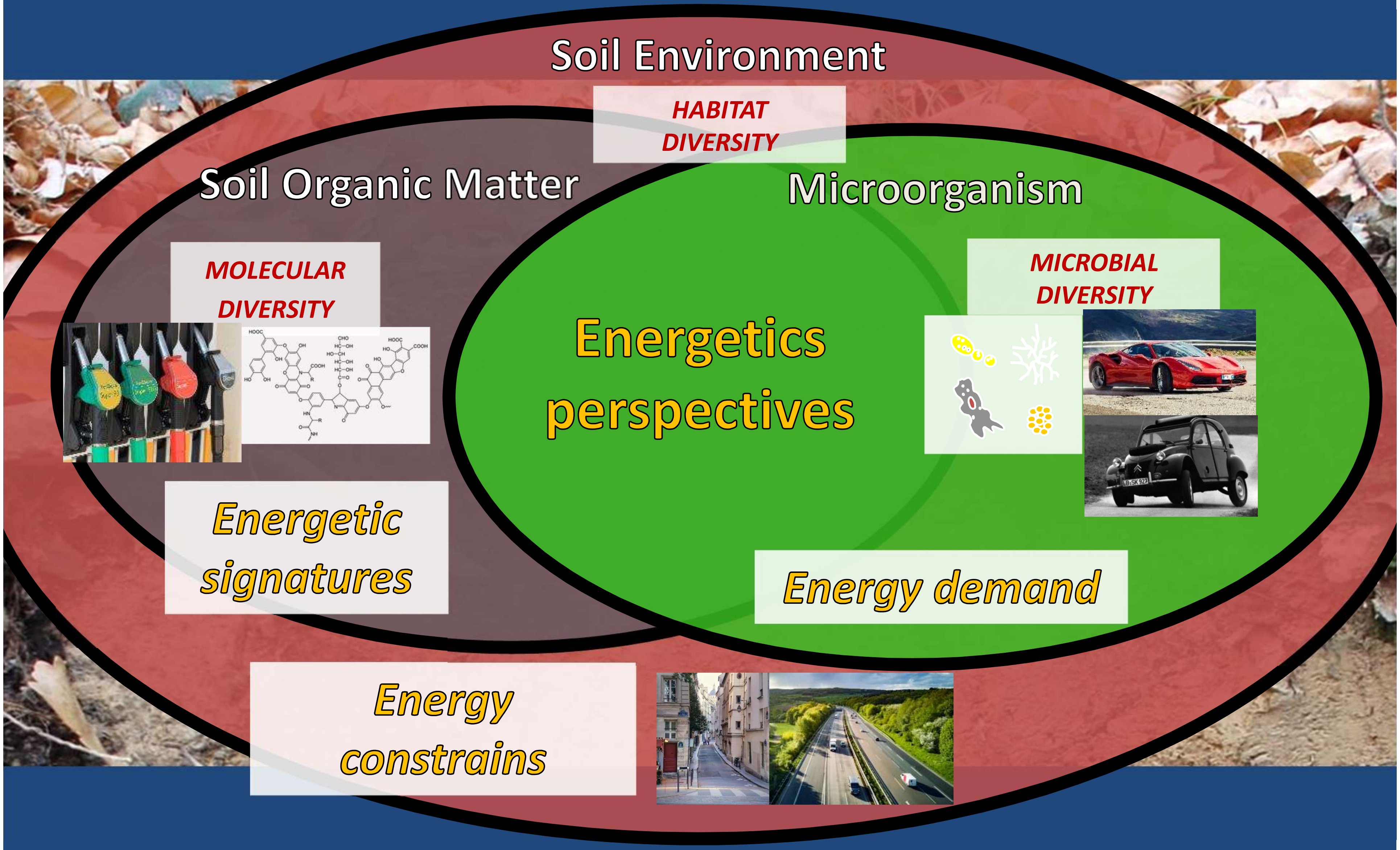
Keiluweit et al. (2017)

**Anaerobic conditions can hamper the decomposition of certain SOM substrates due to thermodynamic limitations.**

**The environment (road network) prevents the microbial engine to run – properly or at all – on certain fuel.**


Keiluweit et al. (2016) *Biogeochem.* 127
Keiluweit et al. (2017) *Nat. Commun.* 8

# The microbial engine



# THANK YOU FOR YOUR ATTENTION!

# Resources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