PRO AGRO LECTORIUM

Sources and intensity of CH_4 emissions affected by iron oxides and microbial biomass changes

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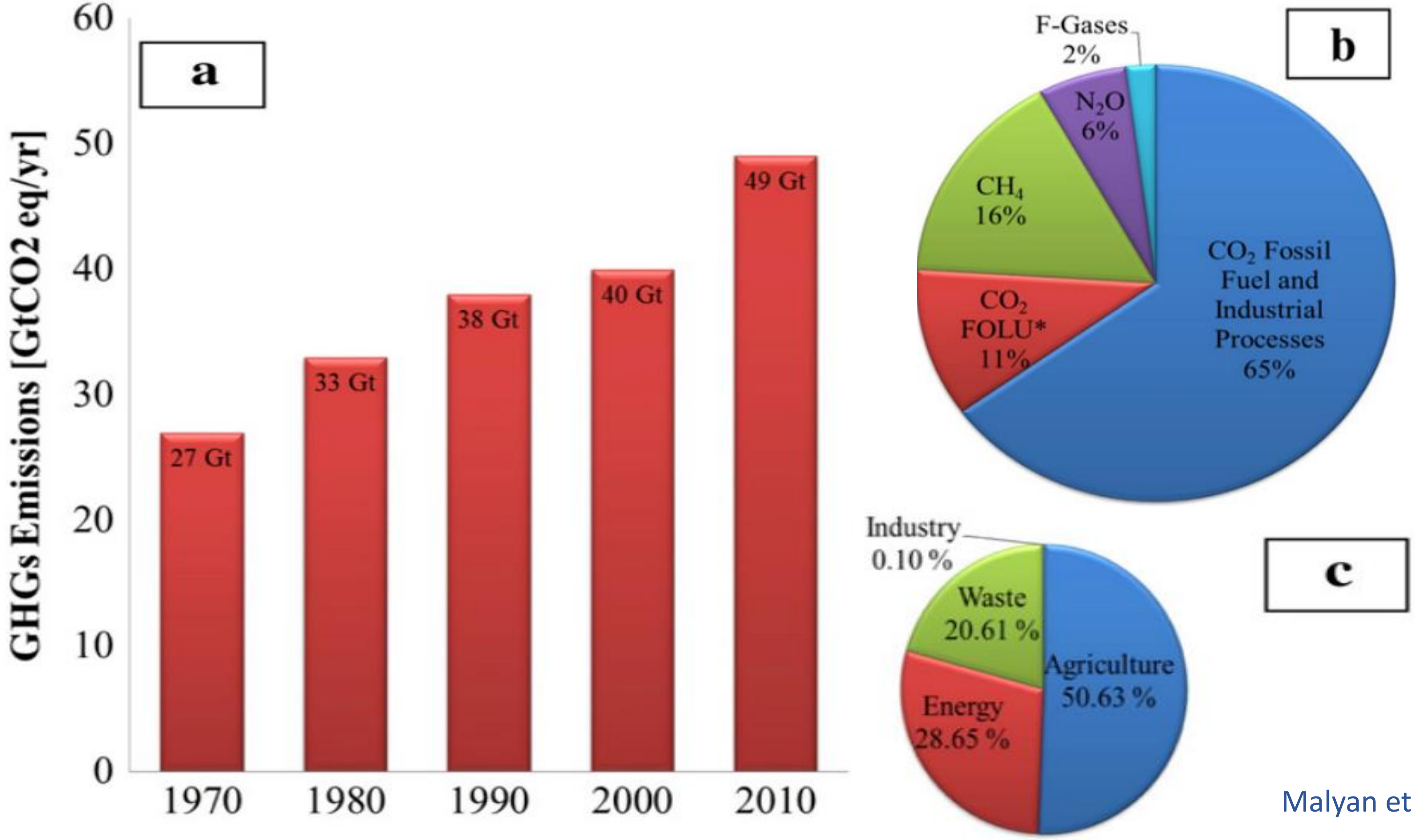
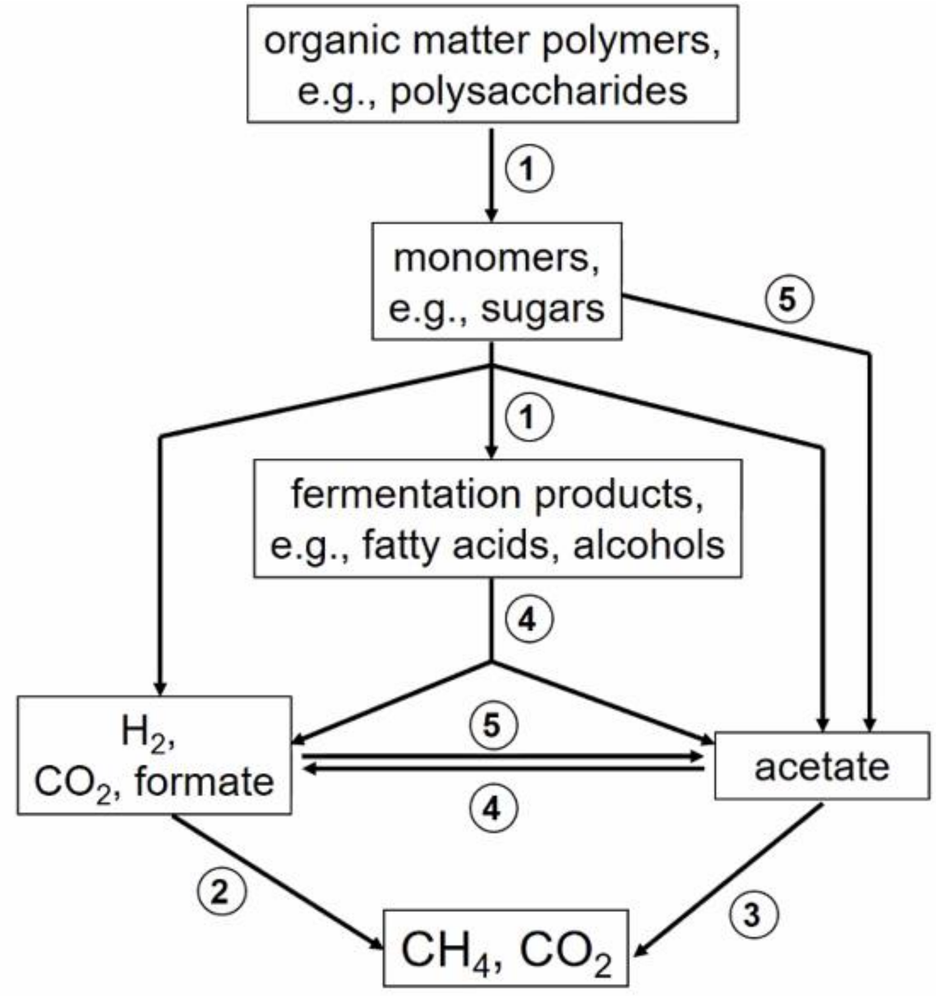
Contents

Global methane emission



Malyan et al., STE, 2016

Methane



- Primary fermenters (1)
- Hydrogenotrophic methanogens (2)
- Acetoclastic methanogens (3)
- Secondary fermenters, syntrophs (4)
- Homoacetogens (5)

R. Conrad, 1999

Free energy and representative methanogens in methanogenesis reactions

产甲烷反应 Methanogenesis reaction	$\Delta G^{'}$/kJ mol^{-1} CH_4	部分代表菌属 Representative methanogens
I. 还原CO_2途径 Hydrogenotrophic pathway		
$4H_2 + O_2 \rightarrow CH_2 + 2H_2O$	-135	*Methanothermus, Methanocaldococcus*
$4HCOOH \rightarrow CH_4 \rightarrow + 3O_2 + 2H_2O$	-130	*Methanobacterium, Methanothermococcus*
$4O + 2H_2O \rightarrow CH_4 + 3CO_2$	-196	*Methanothermobacter, Methanosarcina*
II. 甲基营养途径 Methylotrophic pathway		
$4CH_3OH \rightarrow 3CH_4 + CO_2 + 2H_2O$	-105	*Methanosarcina, Methanohalobium*
$CH_3OH + H_2 \rightarrow CH_4 + H_2O$	-113	*Methanomicrococcus blatticola, Methanosphaera*
$2(CH_3)_2 - S + 2H_2O \rightarrow 3CH_4 + CO_2 + 2H_2S$	-49	*Methanosalsum, Methanomethylovorans*
$4CH_3 - NH_2 + 2H_2O \rightarrow 3CH_4 + CO_2 + 4NH_3$	-75	*Methanococcoides, Methanosarcina*
$2(CH_3)_2 - NH + 2H_2O \rightarrow 3CH_4 + CO_2 + 2NH_3$	-73	*Methanococcoides, Methanosarcina*
$4(CH_3) - N + 6H_2O \rightarrow 9CH_4 + 3CO_2 + 4NH_3$	-74	*Methanosarcina, Methanohalobium*
$4CH_3NH_3Cl + 2H_2O \rightarrow 3CH_4 + CO_2 + 4NH_4Cl$	-74	*Methanosalsum, Methanohalophilus*
III. 乙酸途径 Aceticlastic pathway		
$CH_3COOH \rightarrow CH_4 + CO_2$	-33	Only *Methanosarcina* and *Methanosaeta*

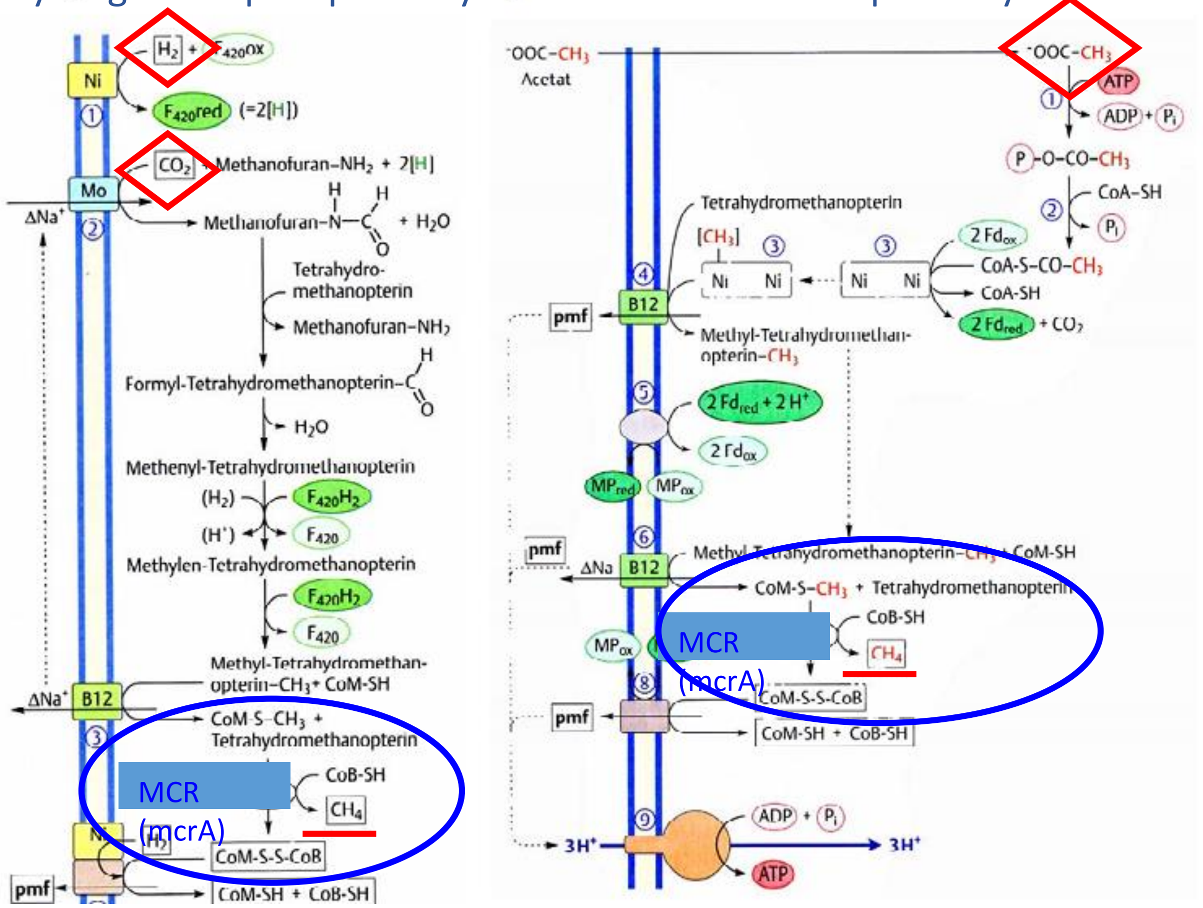
Hydrogenotrophic pathway: $4H_2 + CO_2 \longrightarrow 2H_2O + CH_4$ (30%)

Aceticlastic pathway: $CH_3COOH \longrightarrow CO_2 + CH_4$ (70%)

Methanogenesis

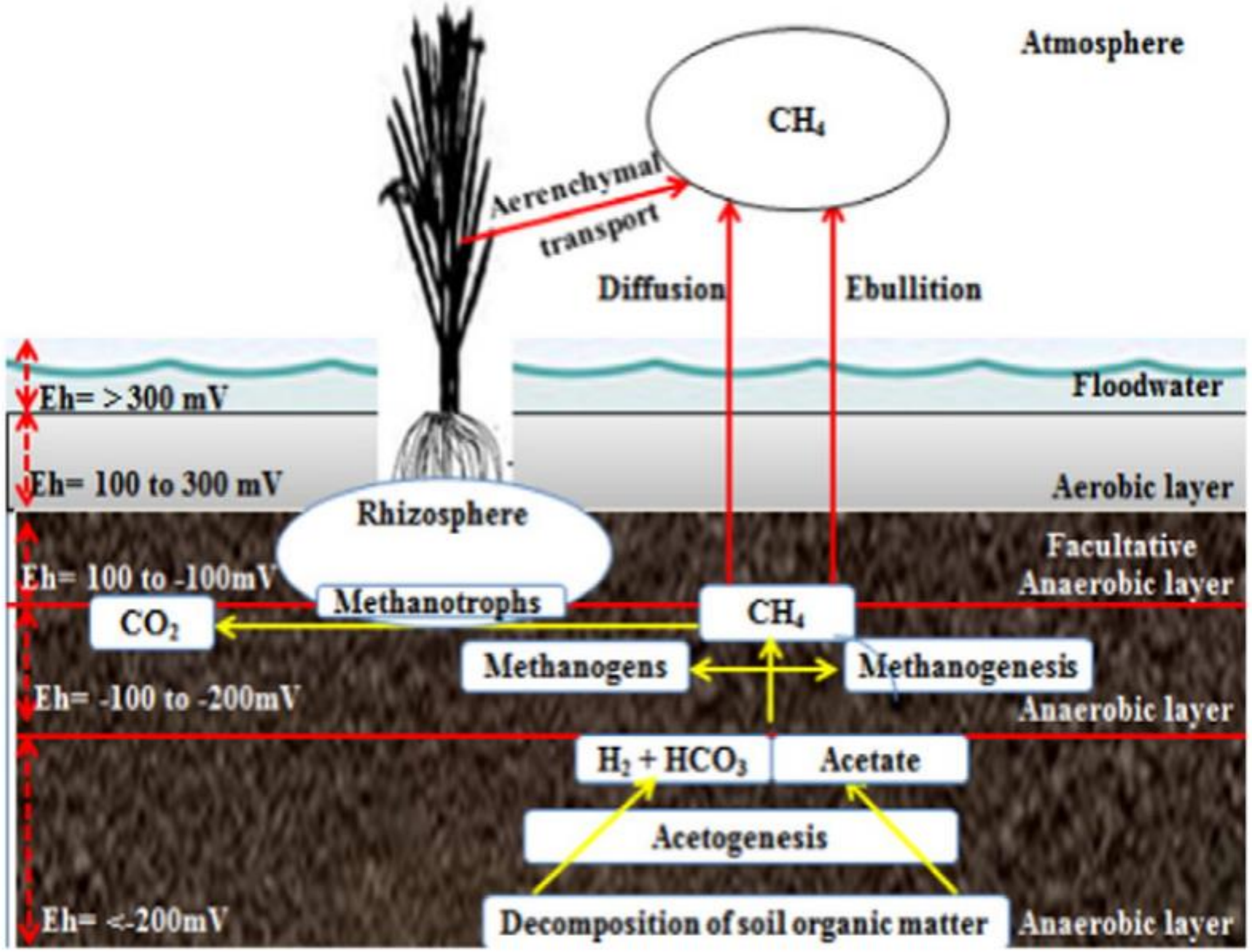
Hydrogenotrophic pathway

Aceticlastic pathway

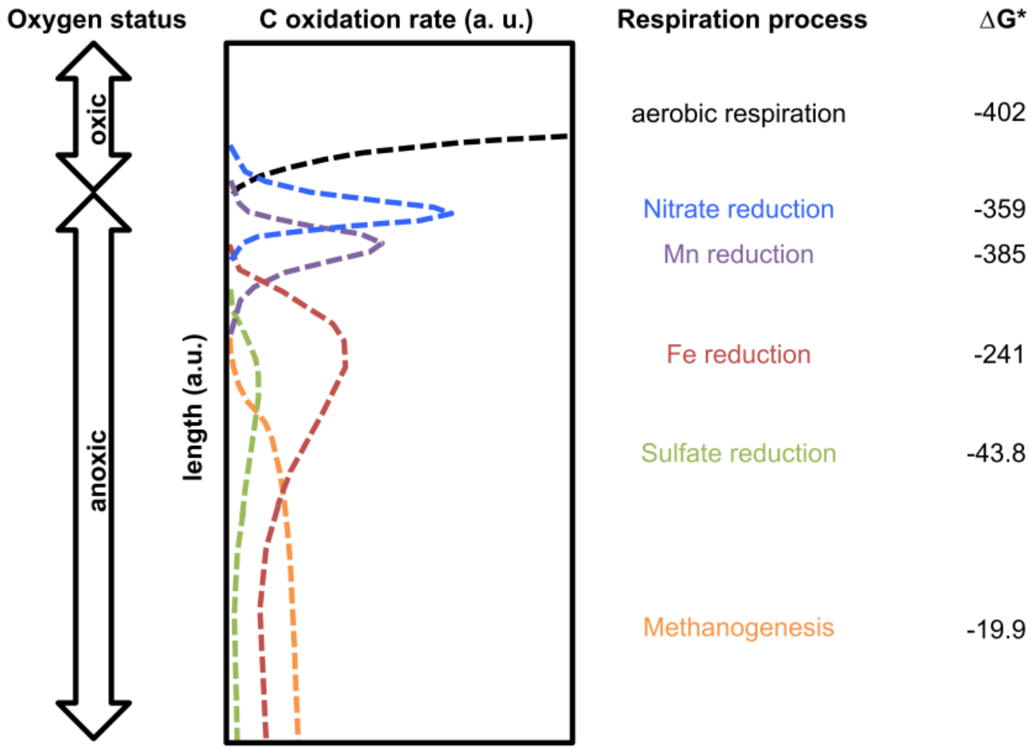


$$CH_3\text{-S-CoM} + \text{HS-CoB} \xrightarrow{\text{MCR (mcrA)}} CH_4 + \text{CoM-S-S-CoB}$$

Methane in rice paddy soil



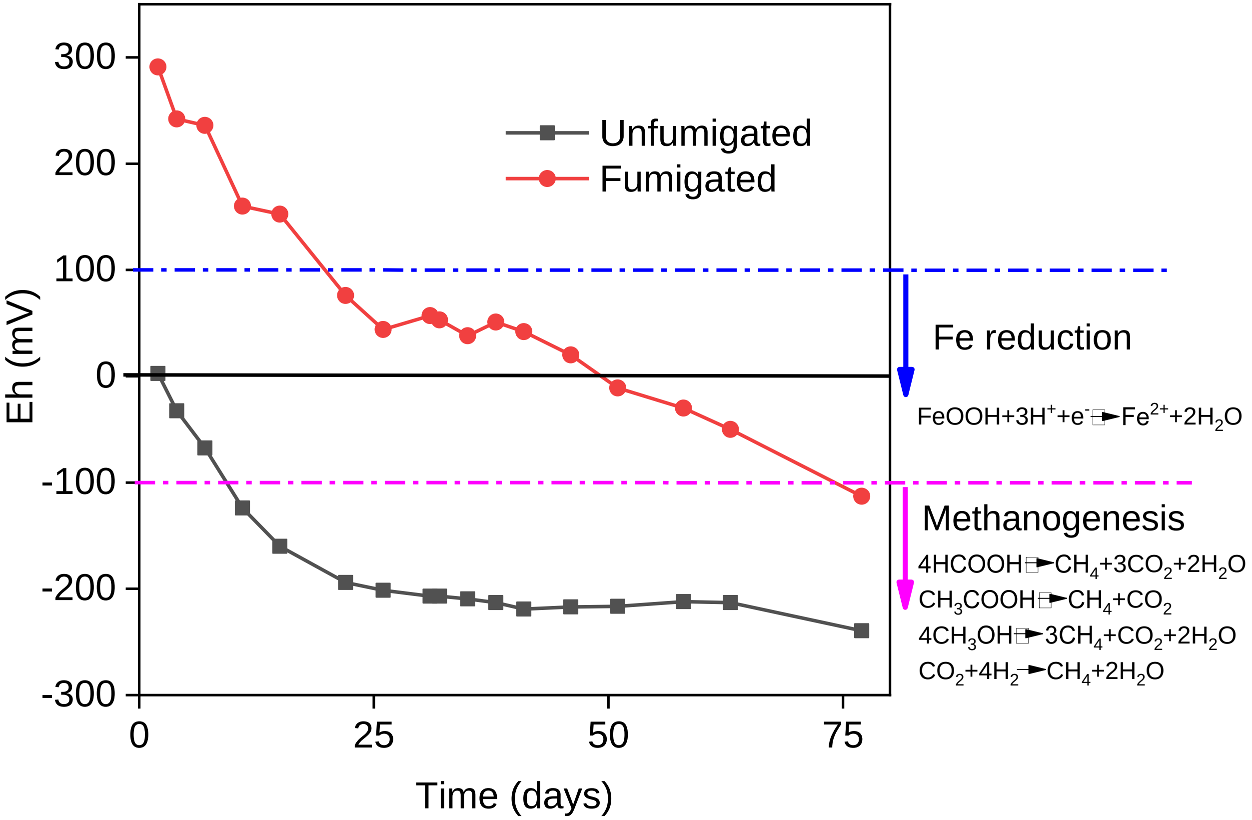
Redox ladder



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

According to the law of thermodynamics, electron acceptors with a higher redox potential are reduced preferentially, thus the iron-reducing bacteria usually outcompeted the methanogens in the microbiome.

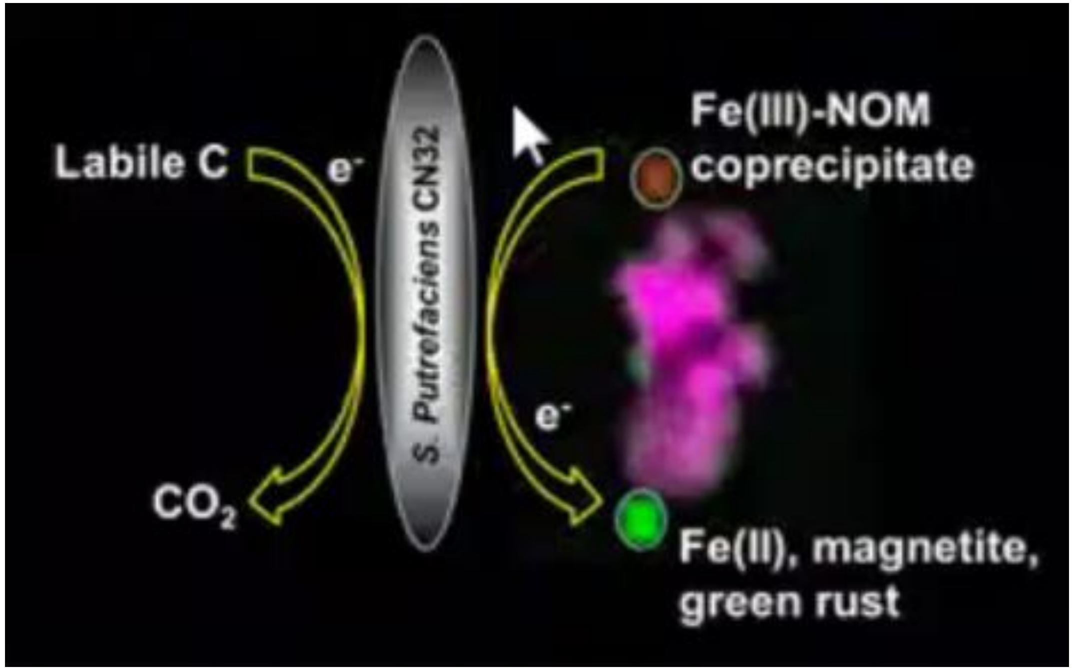
Competition between methanogenesis and iron reduction

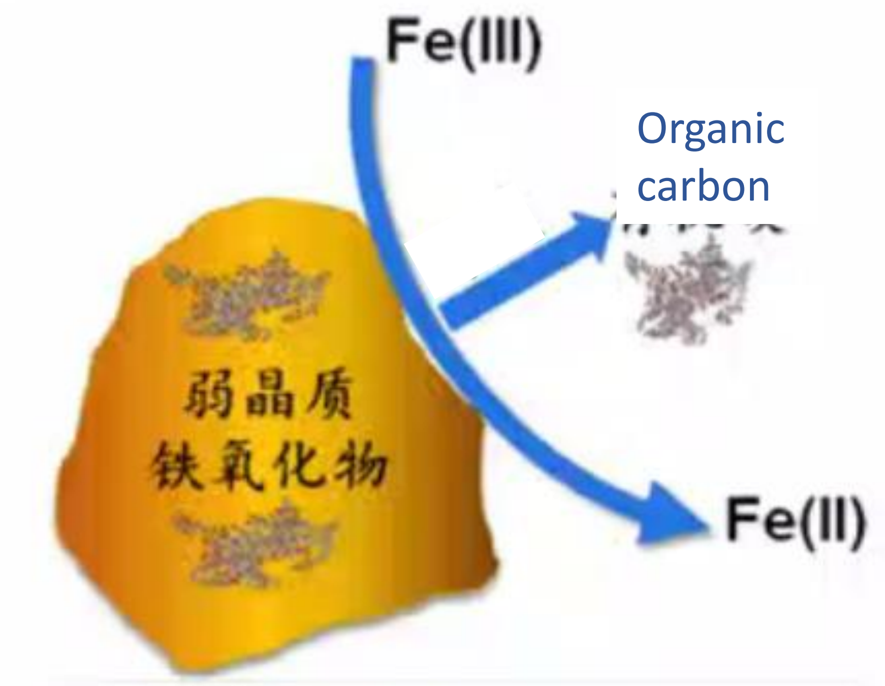


$8FeOOH+CH_3COOH+16H^{+} \rightarrow 8Fe^{2+} + 2CO_2 + 14H_2O$

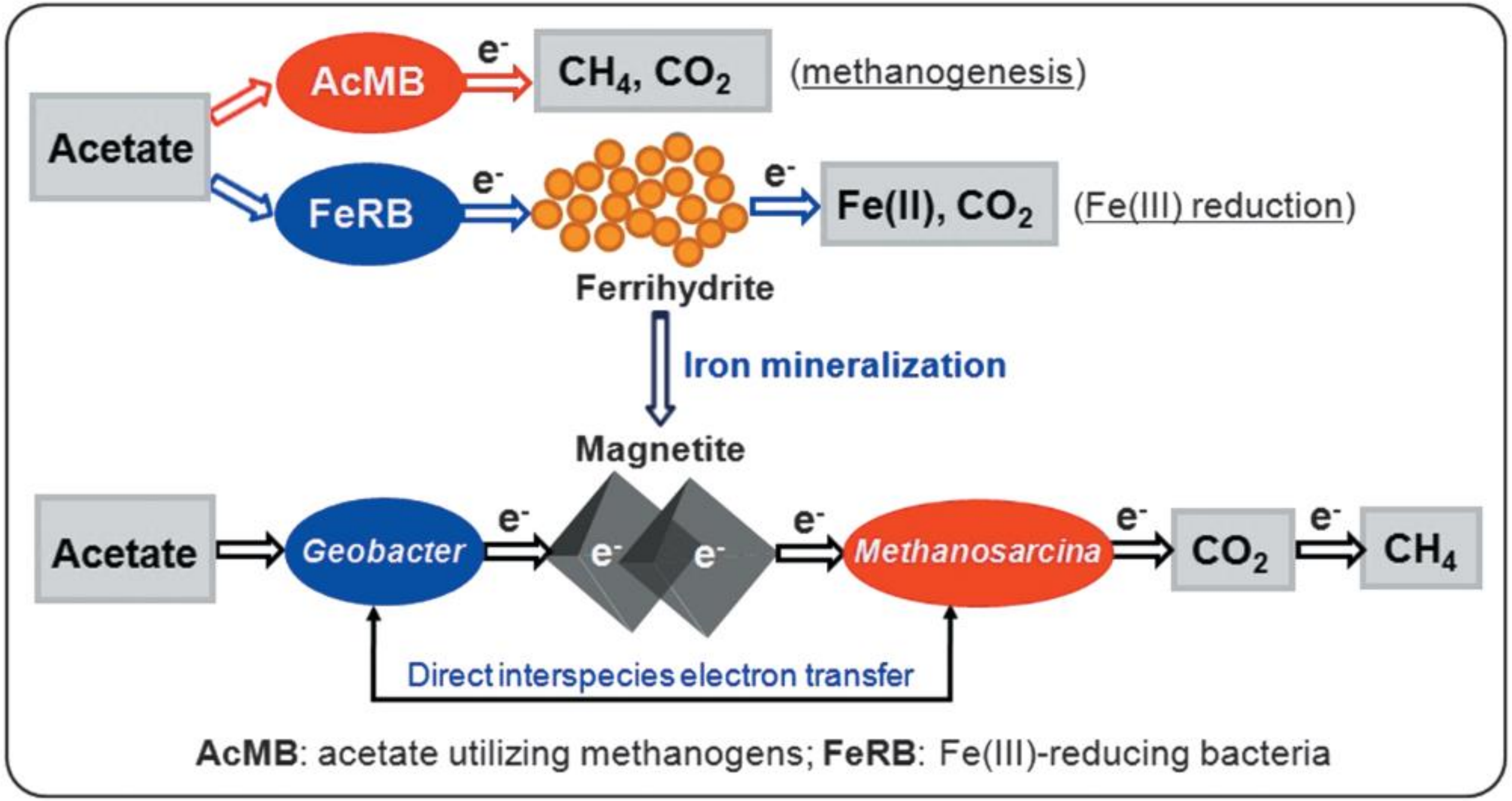
$CH_3COOH \rightarrow CO_2 + CH_4$

Iron reduction releases organic carbon that associated with iron oxides





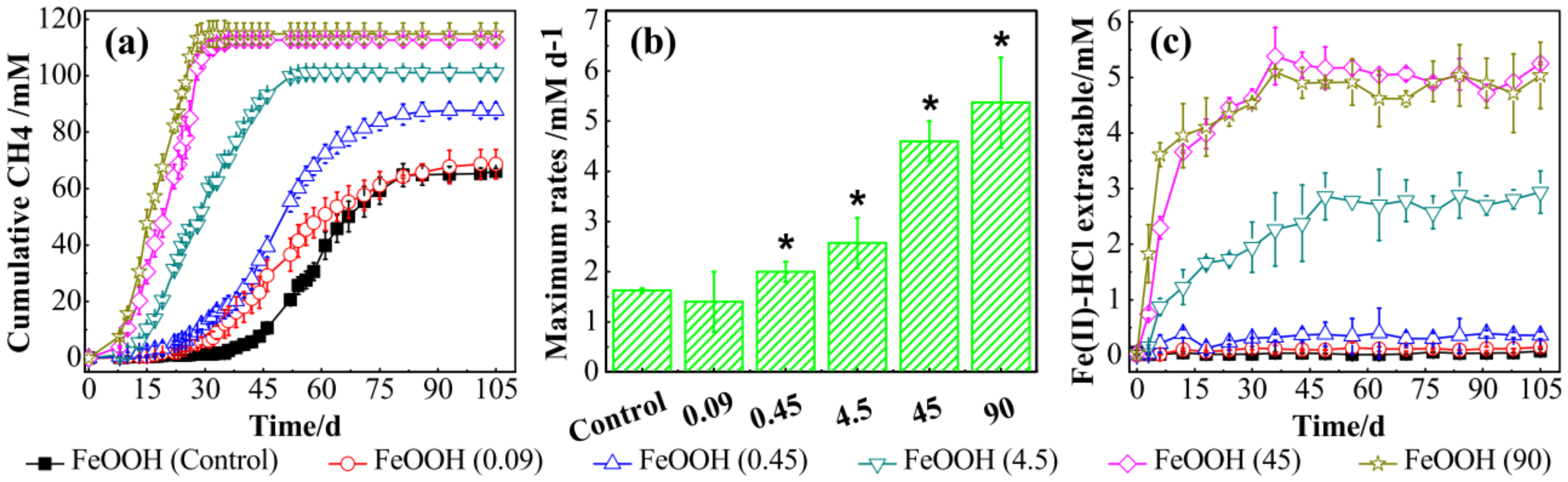
Acetate degradation and ferrihydrite biomineralization



Zhuang et al., JGR, 2015

Methanogenesis facilitated by electric syntrophy via (semi)conductive iron-oxide minerals

Methane generation and iron oxide reduction at various goethite dosages



- Iron is the component element of several enzymes in the methanogenesis
- The changes of both pH and ORP in cultures after the addition of goethite might be another reason for the promotion of methanogenesis

Yao et al., BEJ, 2017

Acetate-CH_4 emission with and without chloroform

ELSEVIER

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Turnover of glucose and acetate coupled to reduction of nitrate, ferric iron and sulfate and to methanogenesis in anoxic rice field soil

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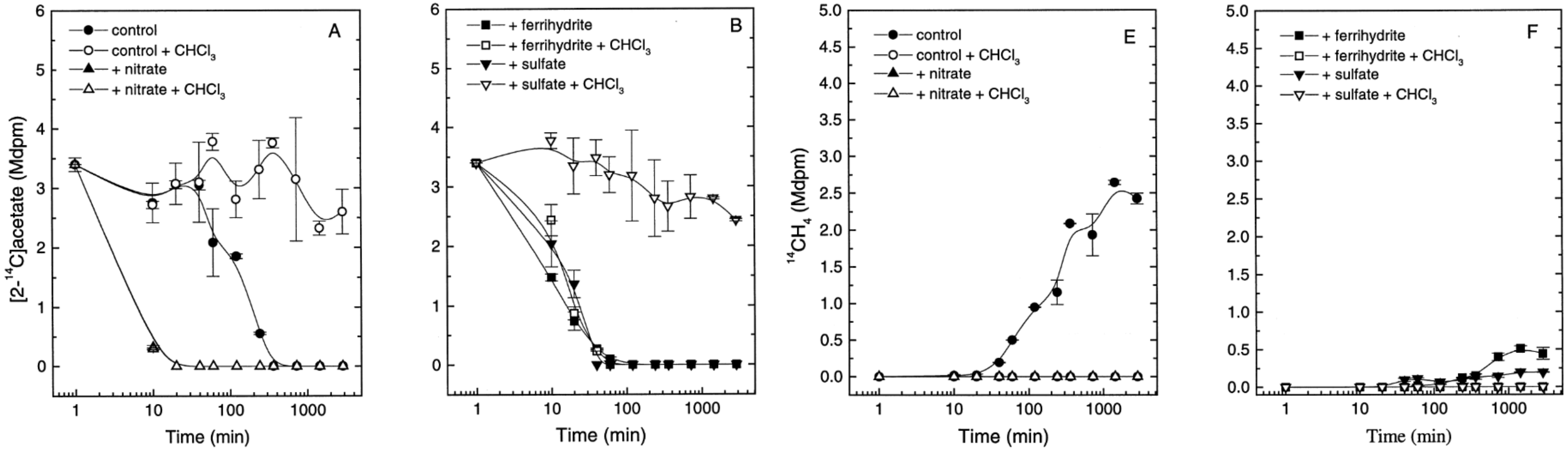


Hypotheses

- Iron oxides addition reduces CH_4 emissions by competing for electrons with methanogenesis, and by adsorbing substrates
- The effects of ferrihydrite and goethite on methanogenesis are different owing to crystallinity, specific surface area, and conductivity
- Strong reduction in microbial biomass (e.g., by fumigation) changes the contribution of CH_4 sources and alters the effects of iron oxides on CH_4 production

Materials and methods

Treatments

- ^{13}C-acetate
- No acetate

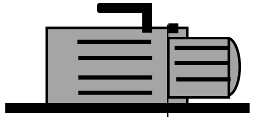
- Goethite
- Ferrihydrite
- No iron oxides

Crystallinity

- Chloroform Fumigation
- Unfumigation

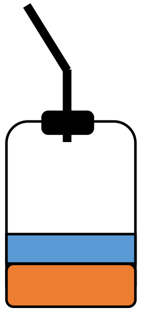
MBC

Anoxic incubation



Air pump

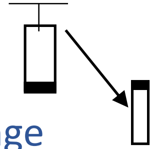
Exchange headspace gas with N_2



Flooding
3cm
Soil 20 g

Sampling

Gas



Syringe 30ml

Evacuated bottle 12ml

Destructive soil sampling
Chloroform fumigation
K_2SO_4 extraction

Analysis

CH_4
$^{13}CH_4$

- DOC
- MBC
- $DO^{13}C$
- $MB^{13}C$

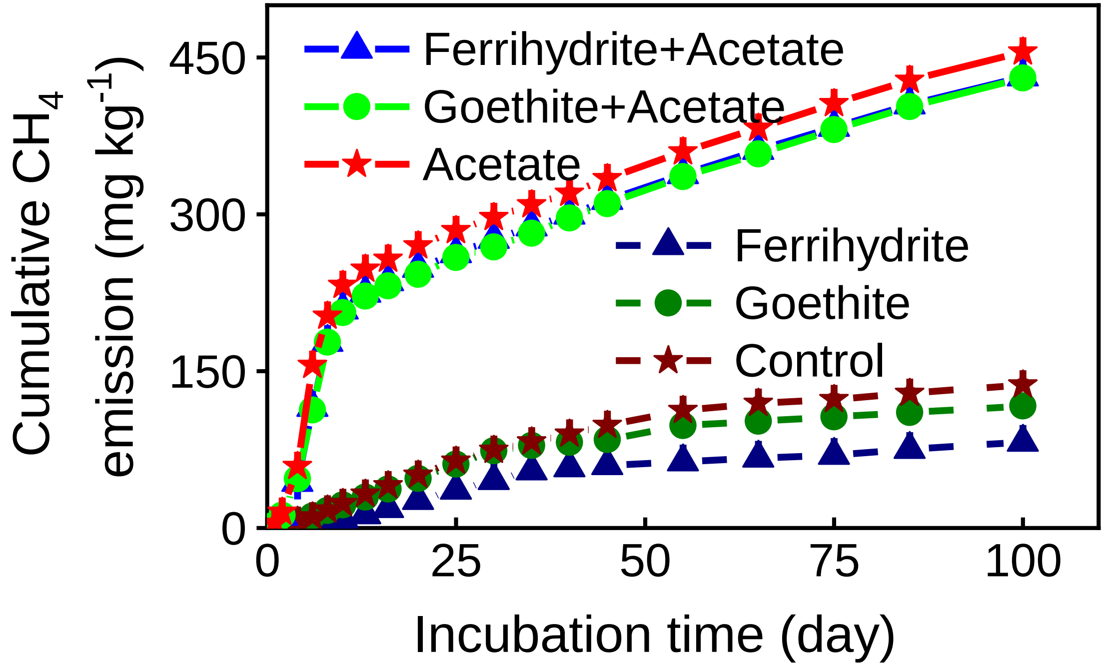
Gas Chromatograph

Isotope ratio mass spectrometer

Results. Effect of iron oxides

Unfumigated soil

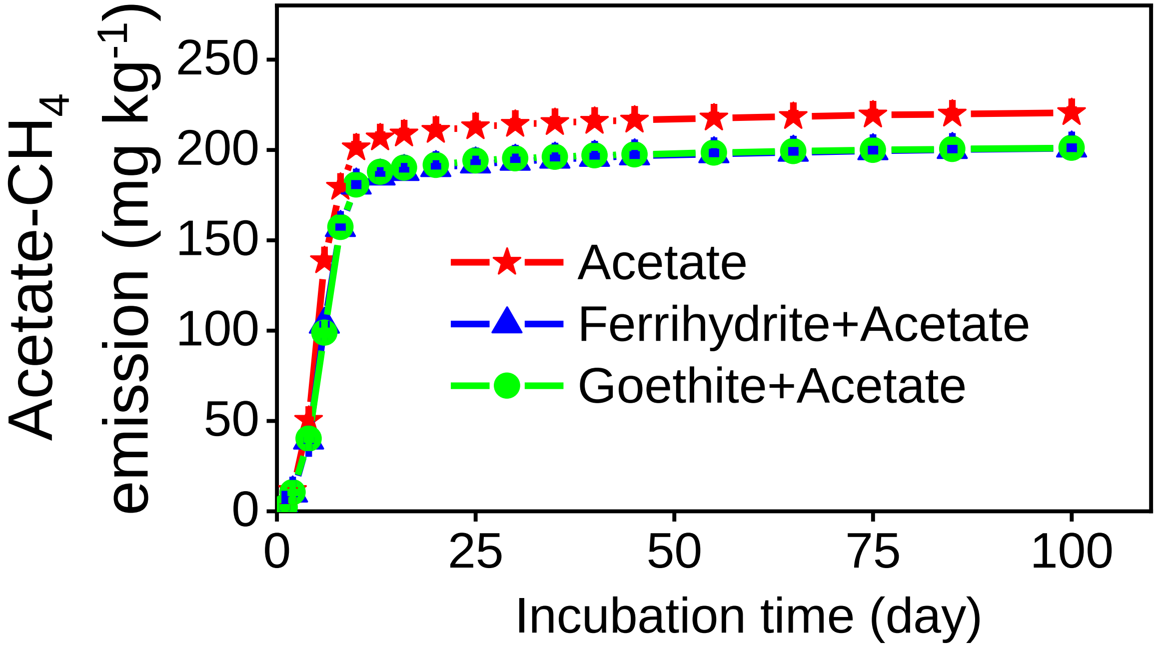
Total CH_4 emission



- Iron addition with and without acetate decreased CH_4 emission.
- Without acetate, the reduction effect of ferrihydrite was stronger than goethite.
- With acetate, ferrihydrite and goethite showed no difference.

Unfumigated soil

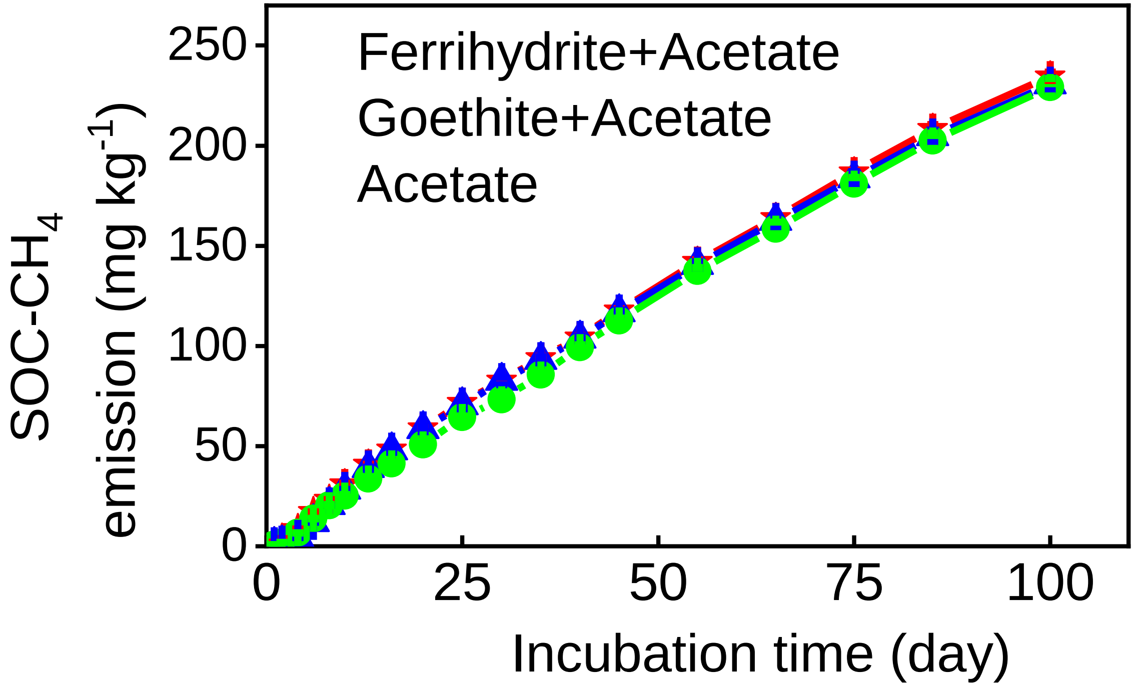
Acetate-CH_4 emission



- Most Acetate-CH_4 was emitted in the first 10 days.
- Ferrihydrite and goethite equally reduced acetate-CH_4 emission.

Unfumigated soil

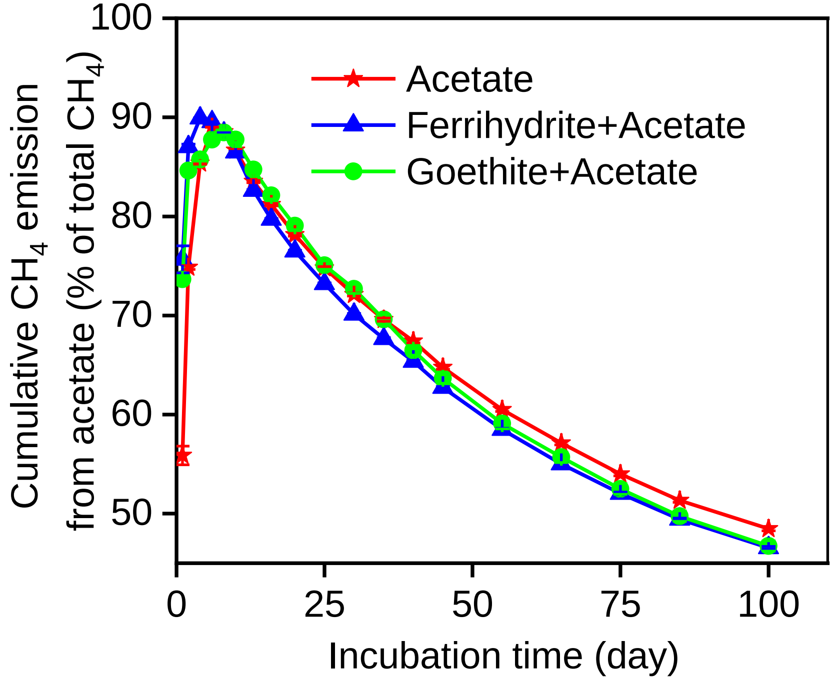
SOC-CH_4 emission



- Acetate-CH_4 emission was larger than SOC-CH_4.
- Acetate-CH_4 reduction (mg kg-1) by ferrihydrite and goethite was larger than SOC-CH_4 reduction.

Unfumigated soil

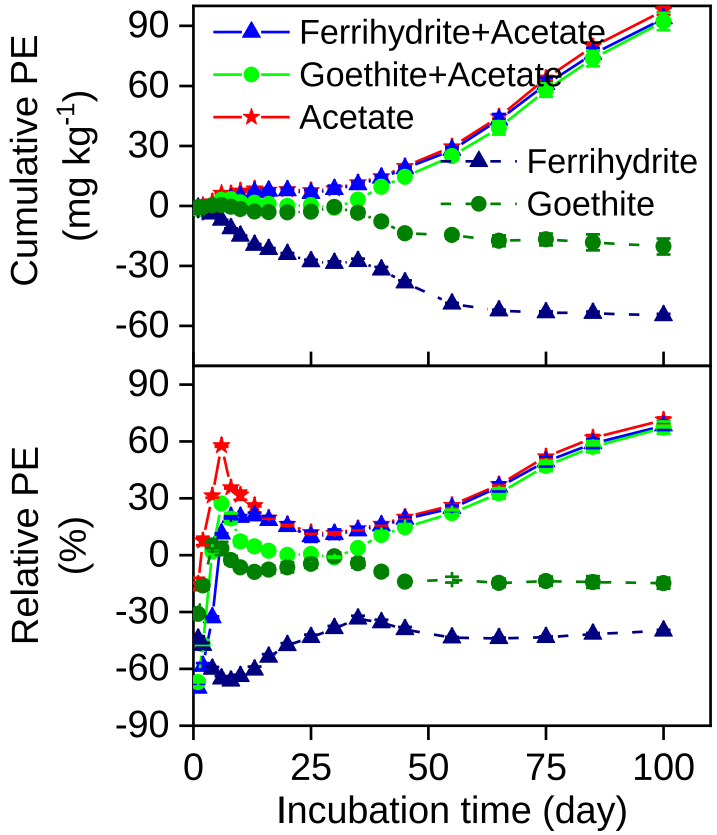
Acetate-CH_4 proportion in total CH_4 emission



- The proportion of acetate-CH_4 in total CH_4 emission was high in the early stage. This proportion decreased gradually and SOC-CH_4 dominated.
- On 100 day, the acetate-CH_4 proportion was smaller in Fh+Acetate and Goe+Acetate than Acetate.

Unfumigated soil

CH4 priming effect



- Sole ferrihydrite and goethite addition caused negative priming. Priming effect of ferrihydrite was stronger than goethite.
- Ferrihydrite and goethite addition with acetate and sole acetate addition caused equally positive priming effect.

Unfumigated soil

Lable C pool size (%) and mean residue time (MRT) for CH_4 emission from SOC and acetate

$$y=b(1-\exp(-kx))$$

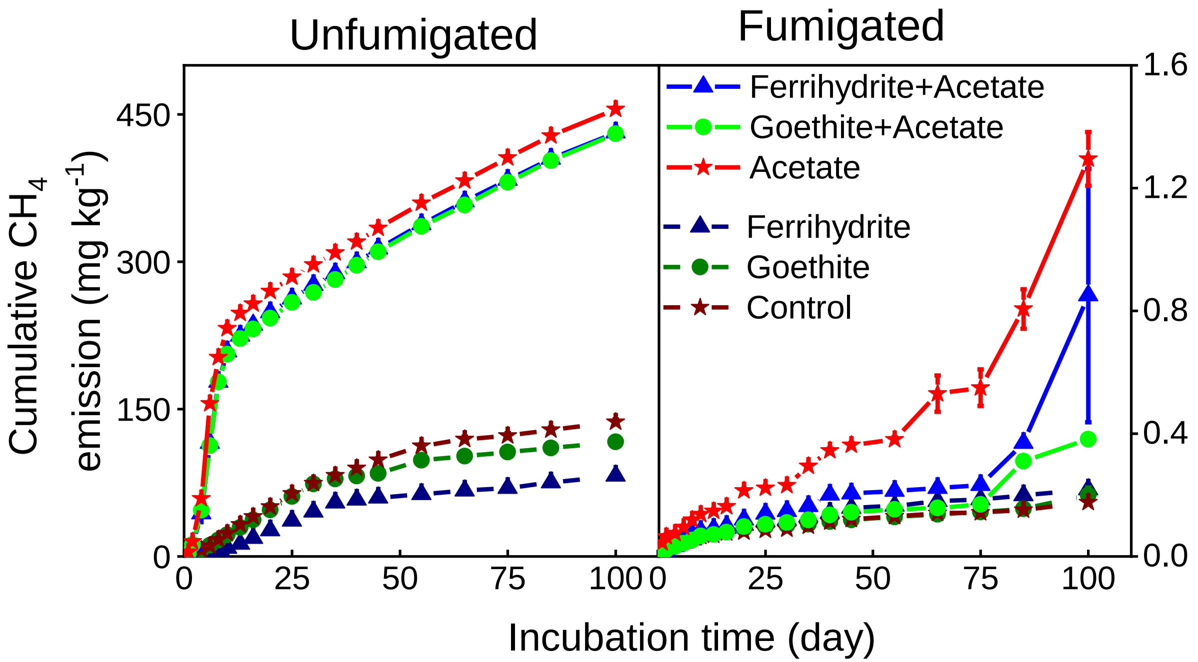
Treatment	SOC		Acetate	
	C pool size (%)	MRT (day)	C pool size (%)	MRT (day)
Ace	0.9 b	113.2 b	33.8 a	6.8 b
Fh+Ace	1.0 ab	120.4 b	30.7 b	7.4 a
Goe+Ace	1.3 a	185.9 a	30.9 b	7.5 a

Ferrihydrite and goethite reduced labile pool size of acetate and increased MRT for CH_4 emission

Effect of microbial biomass change

Fumigated soil

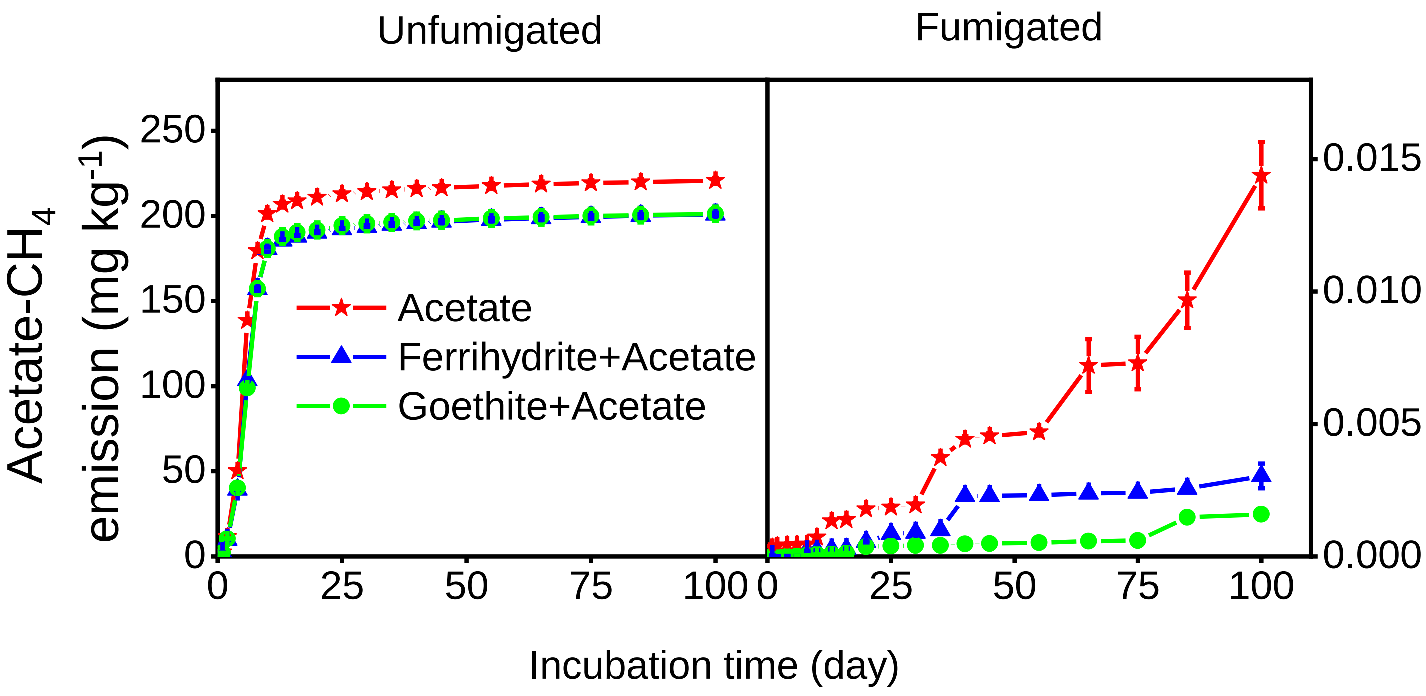
Total CH_4 emission



- Acetate addition increased CH_4 emission in both unfumigated and fumigated soils.
- The absolute increase (mg kg-1) was much smaller in fumigated soil.
- The relative ratio of the increase was larger in fumigated soil.

Fumigated soil

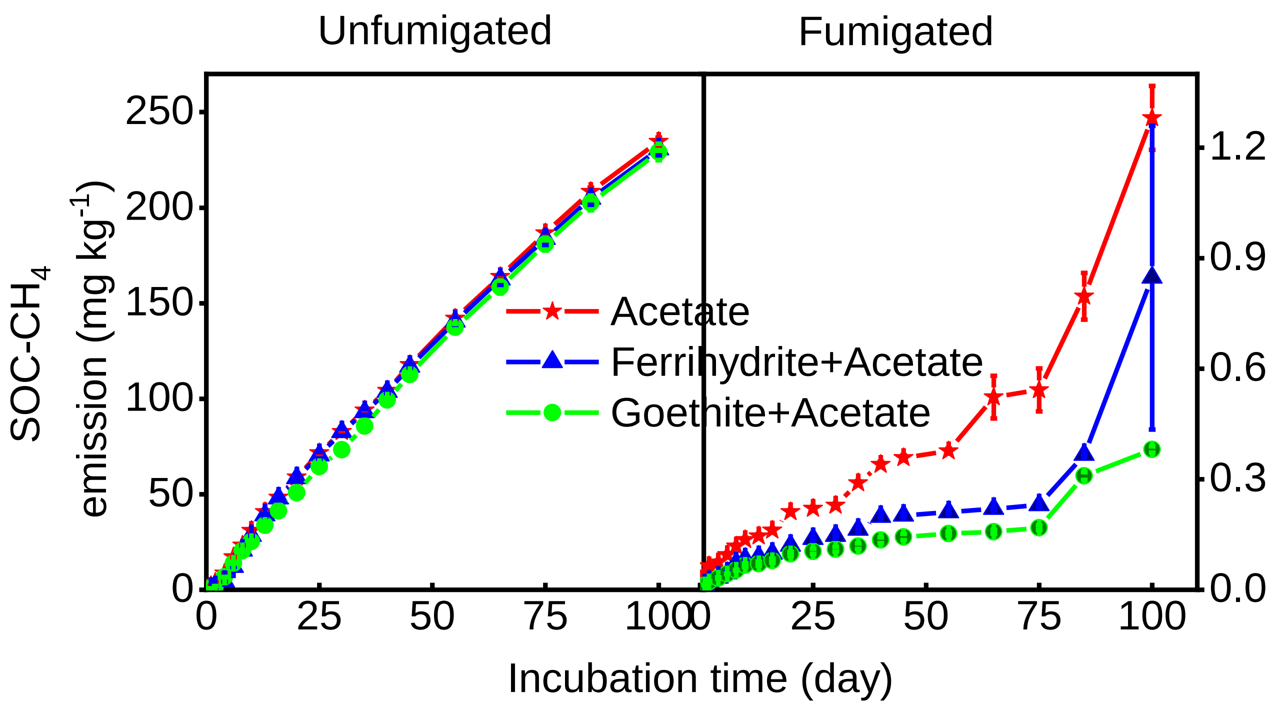
Acetate-CH_4 emission



- Fumigation reduced acetate-CH_4 emission.
- Dislike unfumigated soil, the acetate-CH_4 emission rate gradually increased in Ace.

Fumigated soil

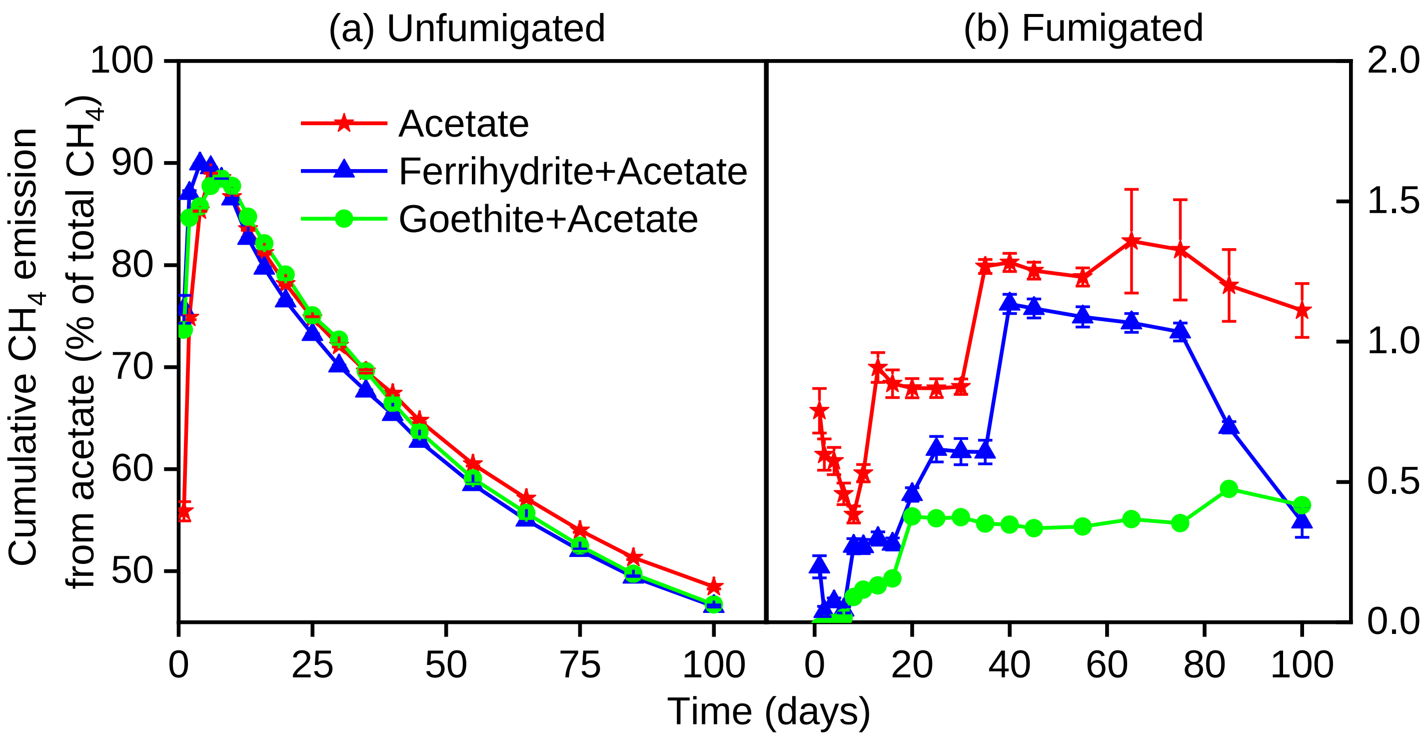
SOC-CH_4 emission



- Fumigation reduced SOC-CH_4 emission.
- SOC-CH_4 emission rate gradually increased in Ace.
- The acetate-CH_4 emission was much smaller than SOC-CH_4 emission.

Fumigated soil

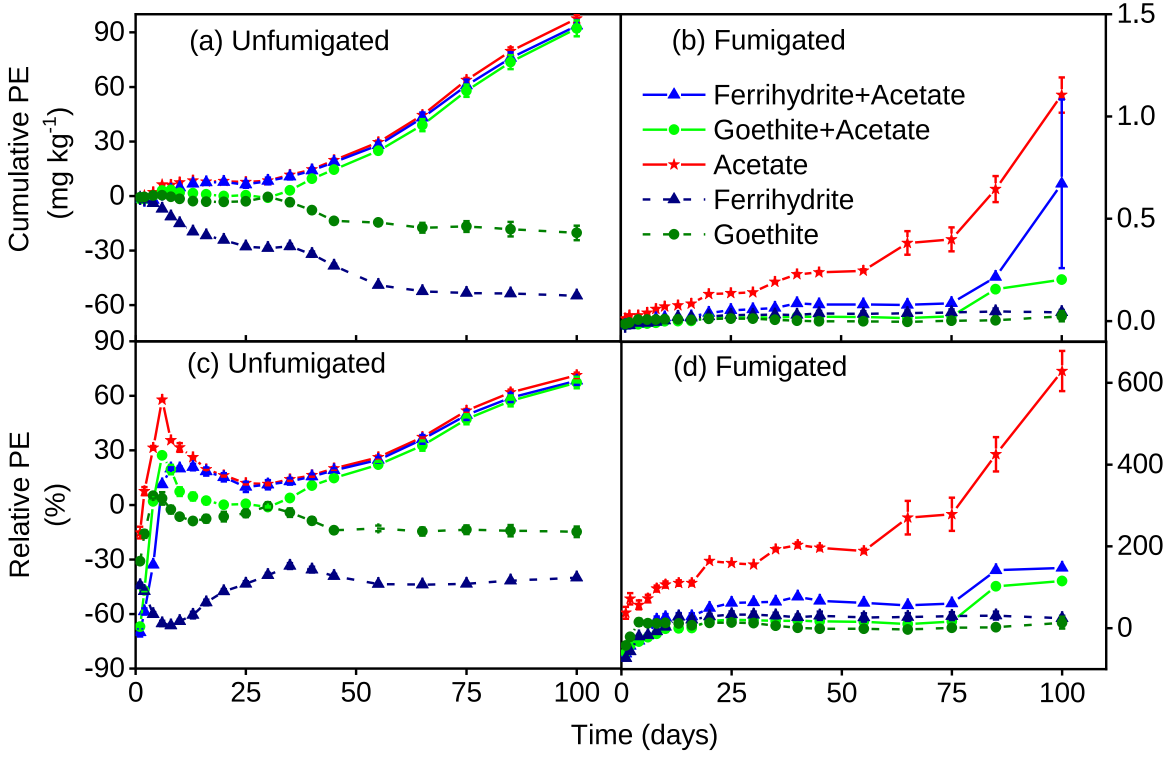
Acetate-CH_4 proportion in total CH_4 emission



- The acetate-CH4 emission was much smaller than SOC-CH_4 emission in fumigated soil. The acetate-CH_4 proportion was only <2% of total CH4 emission.

Fumigated soil

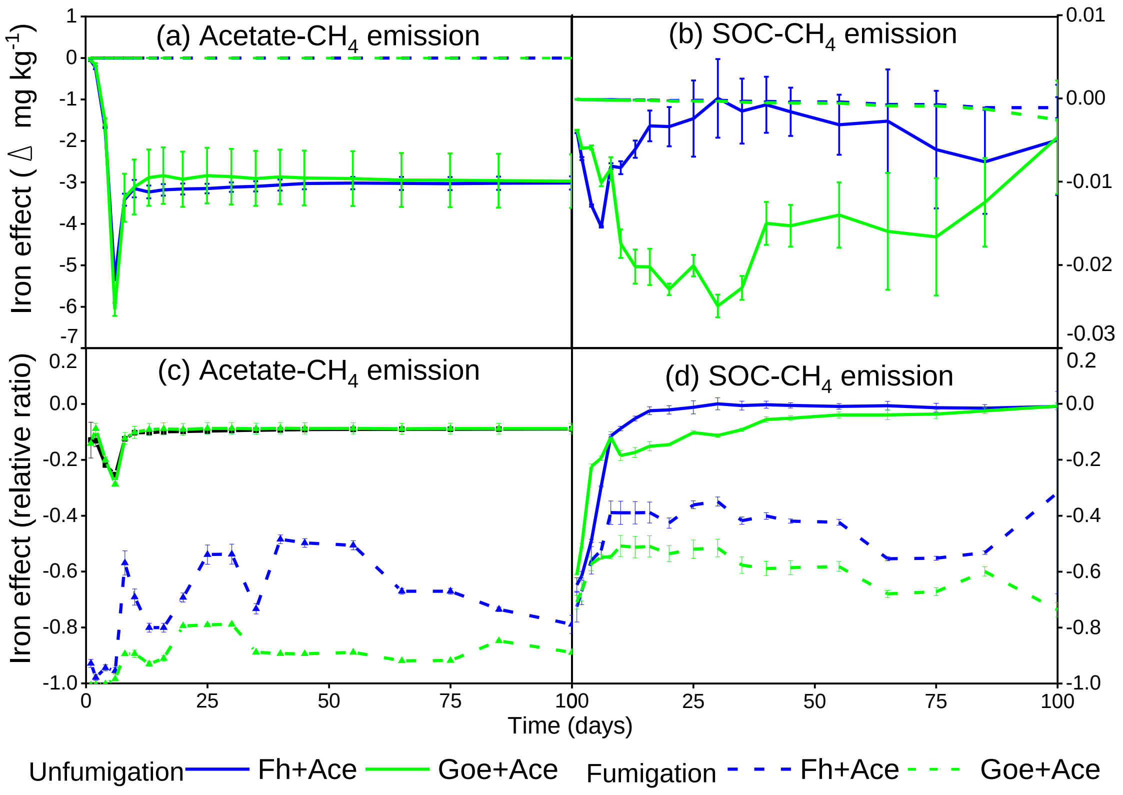
CH_4 priming effect



- In fumigated soil Fh and Goe addition with and without acetate and sole acetate addition caused greater positive priming effect than unfumigated soil.

Fumigated soil

Iron oxides effect



- In unfumigated soil, acetate-CH_4 reduction (mg kg-1) by Fh and Goe was larger than SOC-CH_4 reduction.
- In fumigated soil, the reduction by Fh and Goe was similar between acetate-CH_4 and SOC-CH_4.
- The reduction effect (relative ratio) in fumigated soil was much stronger.
- In unfumigated soil, the effect (relative ratio) of Fh and Goe on acetate and SOC was similar. In fumigated soil, Goe effect was stronger than Fh.

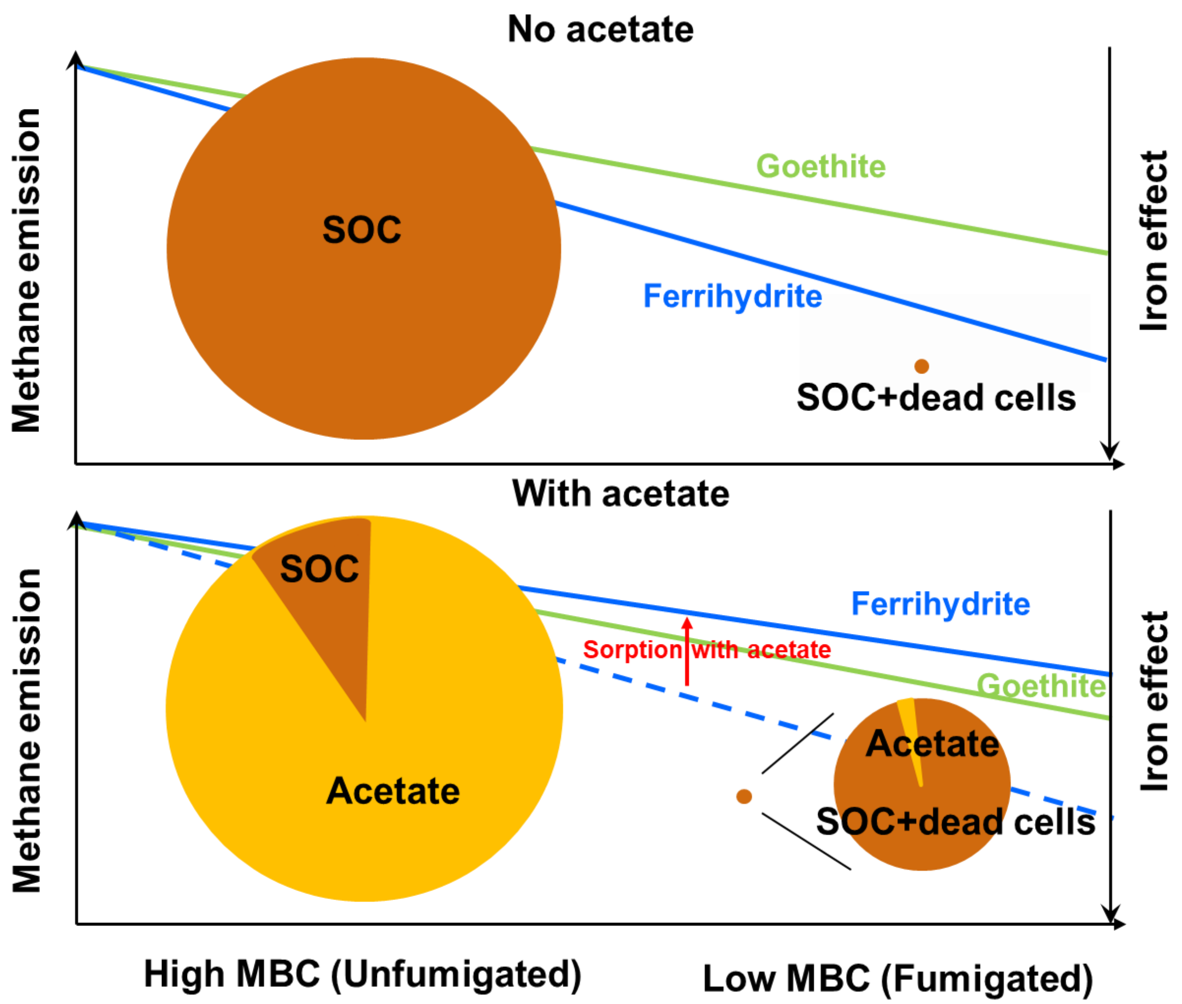
Fumigated soil

Lable C pool size (%) and mean residue time (MRT) for CH_4 emission from SOC and acetate

Soil	Treatment	SOC		Acetate	
		C pool size (%)	MRT (day)	C pool size (%)	MRT (day)
Unfumigation	Ace	0.9 b	113.2 b	33.8 a	6.8 b
	Fh+Ace	1.0 ab	120.4 b	30.7 b	7.4 a
	Goe+Ace	1.3 a	185.9 a	30.9 b	7.5 a
Fumigation	Ace	-	-	-	-
	Fh+Ace	0.0014	85	0.0007	101
	Goe+Ace	0.2407	28111	0.3714	188732
Iron oxides		***	***	***	n.
Fumigation		***	***	***	n.
Iron oxides*Fumigation		n.	***	n.	n.

- Fumigation largely reduced pool size and increased MRT of both SOC and acetate.

C sources of CH_4 emissions in anaerobic paddy soil depending on microbial biomass C levels and its response to iron oxides addition



Conclusions

- Microbial biomass reduction largely influences the sources and pathways of methanogenesis.
- Acetate-derived CH_4 accounted for a major proportion of total CH_4 emissions. The strong decrease in microbial biomass caused by $CHCl_3$-fumigation decreased this proportion.
- In soil without acetate, ferrihydrite has a larger surface area than goethite, resulting in a stronger reduction effect on CH_4 emissions.
- In soil with acetate, ferrihydrite had the same effect on acetate-sourced CH4 emissions as goethite, and had a weaker effect on SOC-CH_4 emissions. This was mainly because the high affinity between acetate and ferrihydrite.
- The relative effects of iron oxides were higher in the fumigated soil than the unfumigated soil, indicating that iron reduction became more competitive with methanogenesis for electrons after fumigation.

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Thank you!