Electron Accepting Capacities of a wide variety of peat materials from around the Globe similarly explain CO2 and CH4 production

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November 24, 2022

Abstract

In organic soils the availability of electron acceptors determines the ratio of CO_2 to CH_4 formation under anoxic conditions. While typically only inorganic electron acceptors are considered, the importance of electron accepting capacities of organic matter is increasingly acknowledged. Redox properties of organic matter are yet only investigated for a limited set of peat and reference materials. Therefore, we incubated 60 peat samples of 15 sites located in five major peatland regions covering a variety of both bog and fen samples and characterized their capacities to serve as electron acceptor for anaerobic CO_2 production.

We quantified CO_2 and CH_4 formation, and changes in available EAC in anoxic incubations of 56 days. On the time scale of our experiment, on average 36.5 % of CO_2 could be attributed to CH_4 formation, assuming an CO_2/CH_4 ratio for methanogenesis of 1:1. Regarding the remaining CO_2 formed, for which a corresponding electron acceptor would be needed, we could on average explain 70.8 % by corresponding consumption of EAC from both organic and inorganic electron acceptors, the latter contributing typically less than 0.1 %. When the initial EAC was high, CO_2 formation from apparent consumption of EAC was high and outweighed CO_2 formation from methanogenesis. A rapid depletion of available EAC resulted in a higher share of CO_2 from CH_4 formation.

Our study demonstrates that EAC provides the most important redox buffer for competitive suppression of CH_4 formation in peat soils. Moreover, electron budgets including EAC of organic matter could largely explain anaerobic CO_2 production.

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Tags: Electron accepting capacity, Global, Peatlands, Bogs, Fens, Electrochemistry, Methane, Carbon Dioxide

Key Points

- Solid phase organic electron acceptors are yet poorly studied despite being abundant and important in peatland systems

- A set of 60 representative peat samples from 15 sites were analyzed in this study, spanning a range from fens to bogs

- Excess CO_2 in anoxic incubations could largely be explained with organic electron acceptors

Author Contributions: Conceptualization: Patrick Guth, Chuanyu Gao, Klaus-Holger Knorr; Data curation: Patrick Guth; Formal Analysis: Patrick Guth; Funding acquisition: Klaus-Holger Knorr; Investigation: Patrick Guth, Chuanyu Gao; Methodology: Chuanyu Gao, Klaus-Holger Knorr; Project Administration: Klaus-Holger Knorr; Supervision: Klaus-Holger Knorr; Validation: Patrick Guth, Chuanyu Gao; Visualization: Patrick Guth; Writing – original draft: Patrick Guth, Klaus-Holger Knorr; Writing – review & editing: Klaus-Holger Knorr, Chuanyu Gao

Abstract

In organic soils the availability of electron acceptors determines the ratio of CO_2 to CH_4 formation under anoxic conditions. While typically only inorganic electron acceptors are considered, the importance of electron accepting capacities of organic matter is increasingly acknowledged. Redox properties of organic matter are yet only investigated for a limited set of peat and reference materials. Therefore, we incubated 60 peat samples of 15 sites located in five major peatland regions covering a variety of both bog and fen samples and characterized their capacities to serve as electron acceptor for anaerobic CO_2 production.

We quantified CO_2 and CH_4 formation, and changes in available EAC in anoxic incubations of 56 days. On the time scale of our experiment, on average 36.5 % of CO_2 could be attributed to CH_4 formation, assuming an CO_2/CH_4 ratio for methanogenesis of 1:1. Regarding the remaining CO_2 formed, for which a

corresponding electron acceptor would be needed, we could on average explain 70.8 % by corresponding consumption of EAC from both organic and inorganic electron acceptors, the latter contributing typically less than 0.1 %. When the initial EAC was high, CO_2 formation from apparent consumption of EAC was high and outweighed CO_2 formation from methanogenesis. A rapid depletion of available EAC resulted in a higher share of CO_2 from CH_4 formation.

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Plain language Summary

For microbial respiration to CO_2 in absence of oxygen, alternative electron acceptors are needed. Typically considered inorganic electron acceptors, such as sulfate or iron, are usually low in organic soils, but an increasing number of studies has demonstrated the relevance of the organic matter itself as an electron acceptor in organic soils. Still, we lack information about typical ranges of microbially available electron accepting capacities of different, representative peat materials, as mostly only few samples or reference materials have been studied. In our study, we incubated in total 60 peat samples from 15 sites around the globe to quantitatively relate changes in electron accepting capacities of organic matter to observed CO_2 and CH_4 formation under anoxic conditions. Of all CO_2 formed for which a corresponding electron acceptor would be needed, we could on average explain 70.8 % or CO_2 formation. This demonstrated that the electron accepting capacities of organic matter provide the by far most important redox buffer in organic soils

Introduction

Peatlands are important carbon (C) storages with an estimated stock of 540 *Pg* C, while only covering about 3-4 % of the global land surface area (Yu Z., 2011; Gorham et al., 2012). They also emit an estimated contribution of 36 *Tg* CH_4-C (equivalent to approx. 10 %$_{Total}$) to the global atmospheric budget (Mikaloff Fletcher et al., 2004; Yu, 2011, Abdalla et al., 2016; Wuebbles & Hayhoe, 2002). This ambivalent role is due to fundamental differences in microbial decomposition in peatland ecosystems compared to mineralization in drained soils; still, decomposition happens to a large extent under aerobic conditions in the unsaturated layer of the acrotelm, but proceeds, albeit slowed, under waterlogged and therefore anoxic conditions in the catotelm, yielding CO_2 and potentially CH_4. Many controls on decomposition in peatlands have been identified, such as temperature, pH, as well as the availability of terminal electron acceptors (TEAs) for microbial processes that produce both, CH_4 and CO_2 as their end products of mineralization (Megonigal et al., 2014; Limpens et al., 2008; Conrad, 1998). As inorganic TEAs, such as nitrate, ferric iron or sulphate, are scarce in

peatlands, electron accepting capacities (EAC) of organic matter (OM) play a dominating role in the regulation of long-term peatland carbon storage, as well as greenhouse gas formation in the saturated peat (Gao et al., 2019; Lau et al., 2014; Keller JK & Takagi, 2013, Limpens et al., 2008). There is thus a need to improve our understanding of EAC_{OM} and to include EAC_{OM} into budgets of TEAs to explain CO_2 production under anoxic conditions (Lau et al., 2016 & 2017; Keller et al., 2019 & 2013; Gao et al., 2019).

Anaerobic decomposition proceeds via two major steps: i) After enzymatic cleavage of organic polymers, oligomers and monomers are fermented, yielding ii) a narrow range of fermentation products that ultimately get oxidized to CO_2 upon reduction of a respective TEA (Fenchel, Blackburn & King, 2012). Upon depletion of thermodynamically more favorable TEAs, methanogens, which utilize either acetate (acetoclastic methanogenesis), or CO_2 and hydrogen as major substrates, form CH_4 (hydrogenotrophic methanogenesis) (Fenchel, Blackburn & King, 2012; Conrad R, 1999; Blodau, 2011). Fermentation is stoichiometrically balanced in terms of redox equivalents (Conrad, 2005; Fenchel, Blackburn & King, 2012), resulting fermentation products are either oxidized upon reduction of a respective TEA, following a thermodynamically driven sequence (Blodau, 2011), or are, in absence of alternative TEAs, converted to CH_4. From a stoichiometric perspective, decomposition of a zerovalent carbon substrate, such as carbohydrates, would thus yield CO_2 and CH_4 at a 1:1 ratio in absence of TEAs (Yu Z-G et al., 2016; Blodau, 2011; Yavitt & Seidmann-Zager, 2006). Any formation of CO_2 during fermentation would not affect this ratio, as CO_2 formation in fermentation is balanced by a corresponding formation of more reduced compounds (such as hydrogen or alcohols) which would afterwards need correspondingly more electron acceptors for final oxidation. Assuming a representative nominal oxidation state of carbon thus allows to calculate electron budgets for anaerobic respiration (Yu Z-G et al., 2016; Gao et al., 2019).

As proposed earlier, a reasonable assumption to assess carbon mineralization in anoxic, organic rich systems is a nominal oxidation state of carbon (NOSC) of zero, assuming that carbohydrates are a dominant substrate. Existing studies determining NOSC in a range of DOM and OM samples from various environments confirmed that the NOSC is typically around zero also for complex and diverse DOM samples (Yu Z-G et al., 2016; Gao et al., 2019; Boye et al., 2017; Teickner et al., 2022; LaRowe DE et al., 2011). In peatland systems or generally waterlogged systems, a CO_2:CH_4 ratio of 1:1 would thus be expected, as soon as TEAs are depleted (Yavitt & Seidmann Zager, 2006; Gao et al., 2019; Yu Z-G et al., 2016).

Regarding peatlands and organic, waterlogged soils, OM was identified to be the most important EA with mostly negligible contribution of inorganic TEAs (Lau et al., 2014; Gao et al., 2019; Segers & Kengen, 1998; Keller et al., 2009). To assess the EAC of OM (EAC_{OM}) and the electron donating capacity EDC of OM (EDC_{OM}), different approaches have been employed. While microbially mediated or wet chemical approaches exist (Keller et al., 2009; Blodau et al.,

2009; Jiang J et al., 2008; Bauer M, et al., 2007), mediated electrochemical reduction (MER) and mediated electrochemical oxidation (MEO) directly target the reversible EAC_{OM} and EDC_{OM}, not affecting chemical structure or composition of OM (Aeschbacher et al., 2010, 2011 & 2012). This approach has recently also been applied to assess EAC and EDC of particulate organic matter (POM) (Gao et al., 2019; Lau et al., 2016; Lau et al., 2014). Only few studies, though, aimed at providing quantitative information on the contribution of OM as a major TEA its effects in suppressing CH_4 formation by stoichiometric comparison of TEAs and CO_2 and CH_4 being formed (Gao et al., 2019; Keller & Takagi, 2013).

Absolute quantities of EAC_{OM} have been proposed to depend on OM chemical properties, such as aromatic content and degree of decomposition (Aeschbacher et al., 2011; Teickner et al., 2022). However, despite few pioneering studies using a limited range of natural and reference materials (Gao et al., 2019), we are still lacking a broader overview of microbially available EAC in different peat materials to support anaerobic respiration and explain temporary suppression of methanogenesis. Typical, microbially available ranges of EAC_{OM} found in peat with different biochemical properties and origins are yet unknown but would be necessary to explain C mineralization under anoxic conditions, excess CO_2 production and onset of methanogenesis, and to quantify effects of water table fluctuations and EAC recharge (Lau et al., 2014; Keller & Takagi, 2013). We therefore aim to address these knowledge gaps, by quantitatively relating changes in OM redox properties in terms of EAC_{OM} to anaerobic CO_2 formation and the onset of CH_4 formation in a large set of different peat samples from some peatland regions around the globe, including ombrotrophic and minerotrophic sites. We wanted to identify typical ranges of EAC_{OM}, the general applicability of the proposed concept, and evaluate differences in potentials of CO_2 and CH_4 formation, as well as the role of EAC_{OM} and peat bulk properties in potentially explaining observed differences between sites. To this end we investigated most used bulk peat quality parameters, Fourier-Transform Infrared Spectroscopy (FT-IR), as well as elemental and stable isotope analysis (C, N, P, S, ^{13}C, ^{15}N) of all peat materials under study. We hypothesized that i) anoxic CO_2 production can largely be explained by changes of available EAC_{OM}, and ii) the time scales of competitive suppression of methanogenesis depend on available EAC_{OM} and the reactivity of the material itself (determining the rate of EAC consumption).

1.

Materials and Methods

(a)

Sampling and Site description

Peat samples from 15 sites of major peatland regions in North-western Europe, Western Siberia, Eastern Canada, Southern Patagonia, and North-eastern China (see Table 1) were collected and analyzed to determine redox properties in terms of EAC, comprising inorganic EAs and EAC_{OM}, and EDC_{OM}. This sample set was also described in Teickner et al. (2022). While this latter study focused on absolute values of measured EAC and EDC, our study here focused on microbially available ranges as assessed in incubations (Gao et al., 2019).

In brief, we sampled four depths at each site: 10-20 cm, 30-40 cm, and 60-70 cm below ground, as well as one deep sample of ~200 cm or at the peatland basis. This was intended to cover peat material from the acrotelm, as well as different ages and decomposition states of the catotelm. The sampled sites cover both, bogs and fens (see Table 1). Additional environmental data and information was either collected from respective studies describing the sites, or from a dataset of global, spatially interpolated climate data (Fick SE & Hijmans RJ, 2017). If no specific data was available for individual sites, the local average monthly temperature and annual precipitation were calculated with a global dataset (Fick et al., 2017) (Table 1).

Table 1. Location of sampling sites and basic climatic information of all study sites. MAP: mean annual precipitation; MAT: mean annual temperature

ID	Site Name	Short Form	Region	Peatland type	Vegetation
1	Beerberg	BB	Germany (Thuringia)	Bog	*Sphagnum*, shrubs
2	Degerö	DE	Sweden (Västerbotten)	Fen	*Sphagnum*, sedges, shrubs
3	La Tenine	LT	France (Vosges)	Bog	*Sphagnum*, shrubs
4	Martinskapelle	MK	Germany (Black Forest)	Bog	Shrubs, *Sphagnum*
5	Ishimbaevskoye	ISH	Russia (Oblast Tjumen)	Fen	Shrubs, *Sphagnum*
6	Kyzyltun Ryam	KR	Russia (Oblast Tjumen)	Bog	*Sphagnum*
7	Touxi	TX	China (Jilin Province)	Fen	Vascular plants, *Sphagnum*
8	Dongtu	DT	China (Jilin Province)	Fen	Vascular plants, *Sphagnum*
9	Lutose Bog	LB	Canada (Alberta)	Bog	*Sphagnum*, shrubs
10	Lutose Plateau	LP	Canada (Alberta)	Bog	*Sphagnum*, lichens
11	Mer Bleue	MB	Canada (Ontario)	Bog	Shrubs, *Sphagnum*
12	P. Brunswick	PBR	Chile (Patagonia)	Bog	*Sphagnum*, shrubs
13	Skyring I-1	SKY I-1	Chile (Patagonia)	Bog	Vascular plants (*Astelia pur*
14	Skyring I-6	SKY I-6	Chile (Patagonia)	Bog	*Sphagnum*
15	Skyring II	SKY II	Chile (Patagonia)	Bog	*Sphagnum*

Sample preparation and organic Matter characterization

Each individual peat material was homogenized by milling in a planetary ball mill (tungsten carbide cup, MM400, Retsch, Haan, Germany) to increase the surface area of the peat POM, which allows to determine electron transfer at rea-

sonable time scales. We are aware that this procedure can introduce differences between electron transfer capacities as assessed here and capacities available in-situ, yet the increase in surface area is needed for faster kinetics during the measurement and as for an accurate quantification of capacities a micropipette transfer of the peat POM in suspension to the MER/MEO cells is necessary. As discussed by Gao et al., 2019, benefits outweigh the downsides, and we see this as an initial step to compare different peat materials in a standardized way as currently no approaches exist to determine EAC under more natural conditions. Actual in-situ capacities may thus differ, we would expect somewhat lower capacities mostly due to slower kinetics in electron exchange for intact material but values approaching our standardized numbers on longer time scales. The reasonable electron budgets calculated in the latter study may be seen as a further support for our methodological approach.

To allow for comparison with other peat soils and to relate organic matter redox processes and properties to typically assessed peat chemical properties, we applied several common analytical techniques for peat chemical characterization (Biester et al., 2014). This was also intended to verify whether our peat samples represent a wide range of different peat qualities described in existing studies. C and N concentrations and stable isotopic composition, expressed as ^{13}C and ^{15}N, were measured with an elemental analyzer coupled to an isotope ratio mass spectrometer (EA-IRMS; ES-3000, Eurovector, Pavia, Italy & Nu Horizon, Nu Horizon Instruments, Wrexham, UK). Certified reference materials and certified standards were used to calibrate the measurements (IAEA-600 (Brand, Werner, MPI Biogeochemistry, Jena; Coplen et al., 2006), USGS-35 (Böhlke et al., 1993); certified wheat four standard and 2.5-Bis(5-tert-butyl-2-benzo-oxazol-2-yl)thiophen (BBOT), both HEKAtech Analysentechnik, Wegberg, Germany). Isotopic values are expressed in the delta notation, ^{13}C relative to V-PDB and ^{15}N relative to AIR. Further bulk elemental contents (Fe, Ca, S, P) were acquired using wavelength dispersive x-ray fluorescence spectroscopy (WDXRF, Rigaku ZSK Primus II, Rigaku, Japan), calibrated by a set of 16 reference materials of plants and peat material.

From elemental analyses we calculated the mass ratio of C/N as an indicator for the degree of decomposition (Kuhry P et al., 1996). Furthermore, the mass ratio of N/P may serve as valuable proxy to determine the nutritional status of the peat (Wang et al., 2015). Moreover, values of ^{13}C and ^{15}N have been proposed to serve as indicators for decomposition (Groß-Schmölders et al., 2020; Biester et al., 2014; Alewell et al., 2011).

To characterize major chemical structures in the peat, Fourier-Transform Infrared Spectroscopy (FT-IR; either Vector 22, Bruker Optik, Ettlingen, Germany, or Cary 660, Agilent, Santa Clara, USA) was applied on each peat sample to derive a humification index (HI) as proposed elsewhere (Biester et al., 2014; Broder et al., 2012). Spectra were recorded in absorption mode with subsequent baseline subtraction on KBr pellets consisting of 200 mg dry potassium bromide (KBr; IR-grade, Sigma Aldrich, St. Louis, USA) and 2 mg of ground

peat sample. All measurements were recorded from 4500 cm^{-1} to 300 cm^{-1} using a resolution of 2 cm^{-1}. 32 consecutive scans per sample were averaged. We normalized absorption intensities around 1650 cm^{-1} (1650-1600 cm^{-1}), indicative of aromatic structures (aromatic **C=C** stretching and/or asymmetric **C-O** stretching in **COO⁻**) by absorption around 1090 cm-1, indicative of polysaccharides, to provide an index HI of peat humification (Cocozza et al., 2003, Biester et al., 2014).

Incubation Setup

For each individual incubation, a 120 mL crimp-bottle was used to which 0.32 g (dry weight) of milled peat and 90 mL of deionized water were added. By doing so, no other solutes are added, and the deionized water would re-dissolve the DOM that was initially present in the peat material itself prior to peat drying.

Additionally, 0.2 g of fresh peat (equivalent to 0.01 g dry matter) from a restored peatland 'Neustaedter Moor' (Agethen et al., 2018) were added to each incubation as inoculum to introduce an active, near natural microbial community. This approach allowed us to compare primarily differences in redox properties of the peat materials, omitting differences related to different microbial communities. After sealing the bottles with butyl-stoppers, the solutions were purged with N_2 (5.0) for 90 minutes to achieve anoxic conditions. All bottles were incubated in the dark at 20 °C for a total duration of 56 days. Concentrations of CO_2, CH_4 and EAC in both POM and DOM were measured in the beginning of the incubation, after 3 days and again at the end. As the determination of EAC of POM required destructive sampling, we set up two sets of samples (sampling at begin/end) with each three replicates. Based on results from Gao et al. (2019), after an incubation time of 56 days at 20 °C, electron accepting capacities in the peat were expected to be fully depleted, and CH_4 formation was expected to have initiated. This was confirmed by the detection of CH_4 in the final sampling in each incubation.

Determination of CO_2, CH_4 formation

Headspace concentrations of CO_2 and CH_4 were measured by means of gas chromatography with flame ionization detection (FID) and methanizer (SRI 8619C, SRI Instruments, Torrance, USA). The intrusion of O_2 during headspace sampling was prevented by flushing both, syringes, and cannulas with N_2 (5.0) prior to sampling. Total amounts of CO_2 and CH_4 in each flask were calculated from headspace concentrations, considering the headspace volume, and by applying Henry's Law for dissolved species with temperature corrected coefficients (Sander, 2015). The formation rate of either gas was determined by linear regression of the slope of total amounts of CO_2 and CH_4 over time. After collecting headspace samples for gas analyses, all bottles were transferred into a glovebox (Innovative Technology, Inert Lab Glovebox, USA) and samples for electrochemical analysis were obtained via pipette, directly from the peat suspension. After

this step, pH was measured to account for pH-dependent speciation of CO_2 (Stumm and Morgan, 2012) (inoLab pH 730, WTW, Weilheim, Germany).

Electrochemical Analysis of electron accepting and donating capacities of organic and inorganic TEAs

Inside the glovebox (c_{O2} < 1 ppm; atmosphere = N_2 (5.0)) 8 mL of supernatant were obtained from each incubation bottle and filtered through 22 µm nylon luer-lock filters (BGB, USA), to determine EAC and EDC of DOM (EAC_{DOM}, EDC_{DOM}), as well as the total concentration of dissolved organic carbon DOC (TOC analyzer, Shimadzu, Kyoto, Japan), and dissolved inorganic electron acceptors (see below). The determination of EAC followed largely Lau et al. (2014), as also described in our earlier study (Gao et al., 2019). This approach utilizes a multichannel potentiostat (CH1000, CH Instruments, Austin TX, USA) and mediated electrochemical reduction (MER) and mediated electrochemical oxidation (MEO) for determination of EAC and EDC, respectively (Aeschbacher & Sander et al., 2010). Cylindrical glassy-carbon cells were used as working electrodes (Sigradur® G GAZ 6, HTW GmbH, Thierhaupten, Germany), a platinum wire (Sigma Aldrich, St. Louis, USA) that was separated from the cell by a semi-permeable glass frit (Glasgerätebau Ochs, Bovenden, Germany) served as counter electrode, and a silver/silver chloride (Ag/AgCl) electrode was used as reference electrode (RE-1B, ALS Co. Ltd., Tokyo, Japan. All cells contained a phosphate buffer to stabilize pH (pH = 7, 0.2 mol L^{-1} KH_2PO_4, 0.1 mol L^{-1} KCl) (Aeschbacher et al., 2010) and were stirred continuously. For MER a constant reduction potential of E_h = -0.49 V was applied; for MEO, E_h = +0.61 V were applied (reported against the H_3O^+/H_2-standard-electrode). Reductive and oxidative currents were recorded in 5 s intervals.

Prior to sample injection, 180 µL of a mediator solution were added to the cell, containing 6,7-dihydrodipyrido[1,2-a:2'.1'-c] pyraziniumdibromide monohydrate (aka 'diquat', DQ, with a single electron reduction potential of E^0_h = -0.36 V; Supelco, USA; purity: 99.5 %, c_{med_DQ} = 0.1 mol L^{-1}) in MER and 2,2-azino-bis-[3-ethylbenzthiazoline-6-sulfonic acid ammonium salt] (aka ABTS, with a single electron reduction potential of E^0_h = +0.68 V; Sigma Aldrich, St. Louis, USA; purity: 99.5 %; c_{med_ABTS} = 0.1 mol L^{-1}) in MEO (Aeschbacher et al., 2010).

A sample volume of 50-200 µL (depending on TOC concentrations, targeting 2-4 g C L^{-1}) of filtered sample for analyses of EAC_{DOM} and EDC_{DOM}, and of 100 µL of peat suspension for analyses of EAC_{OM} and EDC_{OM} was added to each cell and the reductive or oxidative current response signals in MER and MEO were recorded over time. Subsequently, currents were normalized to the total number of electrons (n_{e^-} (nmol e$^-$)) transferred to and from the added samples, as well as to the amount of carbon added to the cells. A total electron exchange capacity (EEC) was defined as the sum of EAC and EDC. This value describes the total number of electrons transferred to and from redox-active species in each sample (Lau et al., 2014).

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To determine the potential contribution of iron to the electrochemical current responses (1 mol e⁻ per (mol Fe^{3+})⁻¹ to the EAC and 1 mol e⁻ (mol Fe^{2+})⁻¹ to the EDC), total iron concentrations as well as iron speciation in the liquid phase were determined by spectrophotometric quantification using the phenanthroline method (Tamura et al., 1974). Moreover, to account for solid phase iron, concentrations in particulate peat were quantified after acidic extraction following Lau et al., 2014: 1 mL of peat suspension were acidified with 4 mL of 1 M HCl and extracted for 72 h in the dark at room temperature. Suspensions were filtered through 22 µm nylon Luer-lock filter tips and the eluates were analyzed like the liquid phase samples. We are aware that upon extraction, speciation of iron may change (Lau et al., 2014). Therefore, to determine potential contributions to EAC, we assumed all iron to be initially present as ferric iron and finally be reduced to ferrous iron. The contribution of iron to EAC_{OM} can thus be regarded as a potential maximum and is presented as total iron content (Fe_{TOT}).

As further potential inorganic electron acceptors, solute NO_3^- and SO_4^{2-} concentrations were determined in the filtered samples using ion chromatography (Basic IC 883 with chemical suppression, A-supp 4 column, Metrohm, Herisau, Switzerland).

Calculation of electron budgets & Statistical Methods

The total CO_2 and CH_4 formation were based on the total CO_2 and CH_4 in the incubations after 8 weeks minus the initial concentrations measured at the start of the incubation (day 3), considering pressure and temperature related solubility based on Henry's Law and the ideal gas law. For the total amount of CH_4 which formed during the experiment we assumed a ratio of CO_2:CH_4 formation of 1:1 in methanogenesis, as commonly accepted for methanogenesis in case of a (near) zero-valent carbon source (Yu Z-G et al., 2016; Conrad R, 1999). With this assumption, any excess amount of CO_2 not balanced by an equal amount of CH_4 could be attributed to a respective consumption of EAC. Total CO_2 was thus split into CO_2 stemming from methanogenesis and CO_2 stemming from consumption of an equivalent amount of EAC. The difference between initial ($EAC_{initial}$) and final EAC_{end} in each given incubation, ΔEAC, including EAC_{OM} and EAC of inorganic TEAs, should then be equal to the number of electrons transferred for all non-methanogenic CO_2 formed. The formation of a single molecule of CO_2 thereby consumes 4 e⁻ of available EAC, given the assumption of a zerovalent carbon source (Gao et al., 2019). Thus, the total amount of CO_2 should by balanced by a consumption of EAC as:

$$[n(CO_2) - n(CH_4)] \text{ x } 4e^- = \Delta EAC = EAC_{end} - EAC_{initial} \text{ (eq. 1)}$$

In which $n(CO_2)$ and $n(CH_4)$ is the total amount of CO_2 or CH_4 formed in the incubations, multiplied by 4 to yield the number of electrons to be transferred per CO_2 (assuming zerovalent carbon as a substrate), and EAC is the difference between initially available EAC ($EAC_{initial}$) and final EAC (EAC_{end}). Thereby,

$EAC_{initial}$ and EAC_{end} represent the sum of EAC provided by solid and dissolved OM (EAC_{OM}) and by inorganic electron acceptors (EAC_{inorg})such as NO3-, Fe^{3+}, and SO_4^{2-}. For NO_3^- we assumed a reduction to N_2 (5 e- transfer), for Fe_3^+ to Fe_2^+ (1 e- transfer), and for SO_4^{2-} to H_2S (8 e- transfer). Due to the small contribution of EAC_{inorg} to EAC_{total}, we did not further differentiate the individual inorganic electron acceptors. The overall electron transfer budget was then calculated including besides EAC of dissolved and solid organic matter also the inorganic TEA contribution. We want to note that fermentation reactions do not involve external e--transfer (Conrad, 1999) and oxidation of reduction equivalents from fermentation (mainly H_2 and low molecular weight organic acids) are included in this approach of budgeting TEA processes (Konhauser, 2009; Gao et al., 2019), therefore, CO_2 arising from fermentation does not have to be considered separately.

Prior to further calculations, the entire dataset was scrubbed using Knime 4.4 (KNIME - the Konstanz Information Miner: Version 4.4 (Berthold et al., 2008)) and Orange Data Mining (Demsar et al., 2013), to test for data distribution, outliers and other data biases. All peat quality indices, peat elemental composition, and elemental ratios were used in a correlation analysis to reveal potential impacts of basic peat chemistry and properties on CO_2 and CH_4 formation, available EAC_{OM} and EDC_{OM}, and the total mineralization during the incubation experiment. We also report the adjusted coefficient of determination (adj. R^2), which corresponds to the R^2 values based on the degrees of freedom of the respective model (adjusted for regressors, as well as sample size). Whenever needed, we also report FDR values for type 1 errors in null hypothesis testing when conducting multiple comparisons.

1.

RESULTS

(a)

General Chemical Properties of the Individual Peat Soils Investigated

Absolute C contents in samples ranged between a minimum of 24.64 % (SKY l-1 Deep) and a maximum of 56.71 % (MB Deep) and were in median average slightly higher in bogs, than in fens: In bogs the median C content was 51.62 ±3.2 %, in fens it reached 47.96 ±4.02 %. Median N-contents were 0.95 ±0.27 % for bogs and 1.25 ±0.58 % in fens. Especially two fen sites in China, impacted by a nearby volcano (TX and DT), had significantly higher N-contents (+~150 %, compared to all other samples). Overall lowest C/N ratios were thus measured for these samples (24.17 ±1.73), whereas the site classes bog, and fen showed median C/N mass ratios of 64.22 ±18.19 in bogs and 44.29 ±16.15 in fens. Mass ratios of N/P ranged from 33.09 in samples from MK to 222.20 in a deep sample

from China, DT. The median for bogs was 76.71 ±24.00, the median for fens was 84.18 ±19.67. C/S ratios ranged from a median of 746.75 ±594.93 in fens to 1257 ±556.50 in bogs. The lowest value of 218.31 was measured in the upper peat layer of BB, Germany. The deepest samples from DT, China showed the highest value with 4506.67, while at both sites from China, DT and TX, C/S ratios were otherwise low. Overall, neither for C/N, N/P or C/S we could find statistically significant differences for site types (i.e., bog or fen), even though they show minor differences.

Regarding depth trends, for C/N mass ratios, values around 59.68 ±27.67 in the upper depth class (10-20 cm layer) did not differ significantly from values of 66.85 ±28.87 in the medium and lower depth class (30-40 cm and 60-70 cm) and thus only a slight trend was apparent. The class 'deep' (representing 150-200+ cm) showed decreasing mass ratios as expected from increasing decomposition, ranging around 60.92 ±22.75, but this was also not significant. Also, for ratios of N/P or C/S, no significant depth trends were observed except a in general lower N/P ratio in the uppermost depth class due to less mineralization of peat material of younger age. A low C/N value in the context of this study represents a highly decomposed peat and a high value represents a lower grade of decomposition.

Regarding FTIR derived humification indices, the average 1650/1090 cm^{-1} ratio in the upper depth class was 0.60 ±0.19 and values were increasing with depth, reaching 0.72 ±0.23 in the deepest depth class, as expected, indicative of a higher relative content of aromatics in these more decomposed peats; On average, the ratio was 0.64 ±0.21. When comparing bogs and fens, the indices for bogs were slightly lower (0.63 ±0.22), than for fens (0.68 ±0.14), indicating higher aromatic-structural contents in fens, than in bogs.

Results of stable isotopic composition of the peats, i.e., values of ^{13}C, ^{15}N and ^{34}S, are in detail provided in the online dataset (Guth et al., 2022), while aggregated values are displayed in Table 2. Values of ^{13}C ranged from -28.19 ‰ in MBs upper depth class -23.6 between 20 and 40 cm depth in LB (lower depth class). The median ^{13}C value for bogs was -25.76 ±0.81 and -26.56 ±0.80 for fens (including all depth classes). In total, sites with predominance of Sphagnum and/or lower average temperatures showed lower values, than sites with more herbaceous species, or higher average temperatures (Table 1). Values of ^{15}N values were on average lowest (0.89 ±1.76 ‰) in the 10 – 20 cm layer and on average highest (1.87 ±1.28 ‰) in the deepest layer when comparing depth classes over all sites. Isotope values are reported in delta notation against the standards mentioned in the materials and methods section. C/N, C/S and N/P are mass-based ratios.

FTIR peak ratios are calculated as described in the materials and methods section.

Table 2: General chemical properties of peat for all depth classes, as well as both categories bog and fen (see methods section for details). HI is the FTIR-based

humification index (1650 cm^{-1}:1090 cm^{-1} ratio, see methods section). Ratios of C/N, C/S and C/P are mass based ratios. Values are presented as median values together with their respective median absolute deviation (MAD).

	Total	Upper (10-20 cm)	Medium (30-40 cm)	Lower (60-70 cm)	Deep (70+
	Mean	MAD	Mean	MAD	Mean
HI	0.64	0.21	0.60	0.19	0.65
^{15}N	-26.12	1.07	-26.64	1.03	-25.80
^{13}C	1.37	1.52	0.89	1.76	1.43
C (%)	49.42	5.36	49.47	4.77	50.47
N (%)	1.14	0.53	1.18	0.53	1.26
C/N	61.18	25.93	59.68	27.67	57.25
C/S	1159.7	614.1	1086.4	693.4	1124.6
N/P	28.32	34.02	147.19	43.60	200.22
Grouped by Site Class					
	Bogs	Fens			
	Median	MAD	Median	MAD	
HI	0.53	0.10	0.53	0.10	
^{13}C	-25.76	0.81	-25.76	0.81	
^{15}N	1.78	1.31	1.78	1.31	
C (%)	51.62	3.20	51.62	3.20	
N (%)	0.95	0.27	0.95	0.27	
C/N	64.22	18.19	64.22	18.19	
C/S	1257.94	556.50	1257.94	556.50	
N/P	76.71	24.00	84.18	19.67	

CO$_2$ and CH$_4$ Formation

All anoxic incubations initially showed high net CO$_2$ formation rates. Net CH$_4$ formation rates varied slightly between the peatland classes bog and fen, as well as between different sites and depths but were overall consistent within sites. CH$_4$ formation in the peat soils ranged from 1.97 $\pm$1.72 µmol (g C)$^{-1}$, equivalent to 0.003 $\pm$0.007 µmol (g C)$^{-1}$ day^{-1} in KRs uppermost depth class to a maximum of 609.48 $\pm$290.68 µmol (g C)$^{-1}$, equivalent 10.88 $\pm$5.19 µmol (g C)$^{-1}$ day^{-1} in TX uppermost depth class. Both values represent extremes, while the median of CH$_4$ formation was 43.39 $\pm$37.5 µmol (g C)$^{-1}$ in bogs and 94.41 $\pm$88.50 µmol (g C)$^{-1}$ in fens, which is equivalent to 0.78 $\pm$0.66 µmol (g C)$^{-1}$ day^{-1} in bogs and 1.69 $\pm$1.58 µmol (g C)$^{-1}$ day^{-1} in fens. In general, there was more methane being formed in samples from fens (median 42.03 $\pm$11.82 µmol (g C)$^{-1}$) than in samples from bogs (37.57 $\pm$14.65 µmol (g C)$^{-1}$).

CO$_2$ formation ranged from 59.89 $\pm$6.0 to 855.79 $\pm$365.17 µmol (g C)$^{-1}$, with a median of 277.36 $\pm$111.12 µmol (g C)$^{-1}$ in fens, equivalent to 4.95 $\pm$2.4 µmol

(g C)$^{-1}$ day^{-1} and in 194.61 ±86.94 µmol (g C)$^{-1}$ equivalent to 3.47 ±0.04 µmol (g C)$^{-1}$ day^{-1} for bogs. The highest CO_2 formation occurred in samples from TX, China (855.79 ±365.17 µmol (g C)$^{-1}$) and KR, Russia (600.63 ±92.48 µmol (g C)$^{-1}$), a fen and a bog site, respectively, lower rates were found for samples from LP (Canada), LT (France) and MK (Germany) representing bogs, or DE, Sweden, representing a fen.

Subtracting CO_2 stemming from methanogenesis from total CO_2 formation, assuming equimolar CH_4:CO_2 formation in methanogenesis (see methods section), yielded CO_2 not formed by methanogenesis. For this non-methanogenic CO_2, a corresponding transfer of electron equivalents of 4 moles e$^-$ per mole CO_2 would be required, see equation 1. Non-methanogenic CO_2 formation ranged from 40.21 µmol (g C)$^{-1}$ to 598.66 µmol (g C)$^{-1}$, corresponding to 58 to 100 % of total CO_2 formed in the incubations. Site KR produced the highest amounts of non-methanogenic CO_2, while producing the least amount of CH_4 (18.60 µmol (g C)$^{-1}$ on average), site DE had lowest amounts of non-methanogenic CO_2, whilst also producing only low amounts of CH_4 (36.18 µmol (g C)$^{-1}$ on average). To investigate final contributions of non-methanogenic respiration to total respiration, we calculated an apparent final CO_2:CH_{4_FINAL} formation ratio by using following equation:

$$CO_2 : CH_{4FINAL} = \frac{(CO_2\left(mol*gC^{-1}\right)+\frac{EAC}{4})}{CH_4(mol*gC^{-1})} \text{ (eq. 2)}$$

In which CO_2:CH_{4FINAL} represents the apparent final ratio of CO_2 to CH_4 production, CO_2 (µmol gC^{-1}) and CH_4(µmol gC^{-1}) the final amounts of CO_2 and CH_4, respectively after 56 days of incubation, and EAC the detected change in total EAC in the incubation in these 56 days (divided by 4 electrons to represent CO_2 equivalents). This ratio should decrease towards 1 the closer we get to truly methanogenic conditions, after all EAC available to microbes has been depleted. Median values of these ratios at the end of the experiment were 1.46 ±2.37 for bogs and 2.07 ±0.63 for fens; both classes moving between minima and maxima of 0.74 and 26.69. A ratio of 1 was thus not overall reached, but lowest ratios occurred in samples from bogs, especially MB (Canada): 0.95 in 'deep', DE (Sweden): 1.15-1.26 through all depth classes and LT (France): 1.20-1.44 through all depth classes where we observed higher C/N ratios, lower Si and lower S contents. Most of these sites showed both, low CO_2 and low CH_4 production. Fens on the other hand, and especially those from China show both, very high CO_2 production as well as very high CH_4 production. These sites show the highest C-mineralization and very narrow C/N ratios indicating very decomposed peats. It can be noted that volcanic dust deposition on the sites TX and DT located in China led to very high Si-, P and S concentrations, elevating the share of inorganic electron acceptors in the peat. Also, in fen peat from Russia, high mineral contents increased the share of inorganic TEAs along with high C-mineralization. In fact, those ratios are in line with others already published (Hornibrook et al., 2000; Heitmann et al., 2007; Biester et al., 2014).
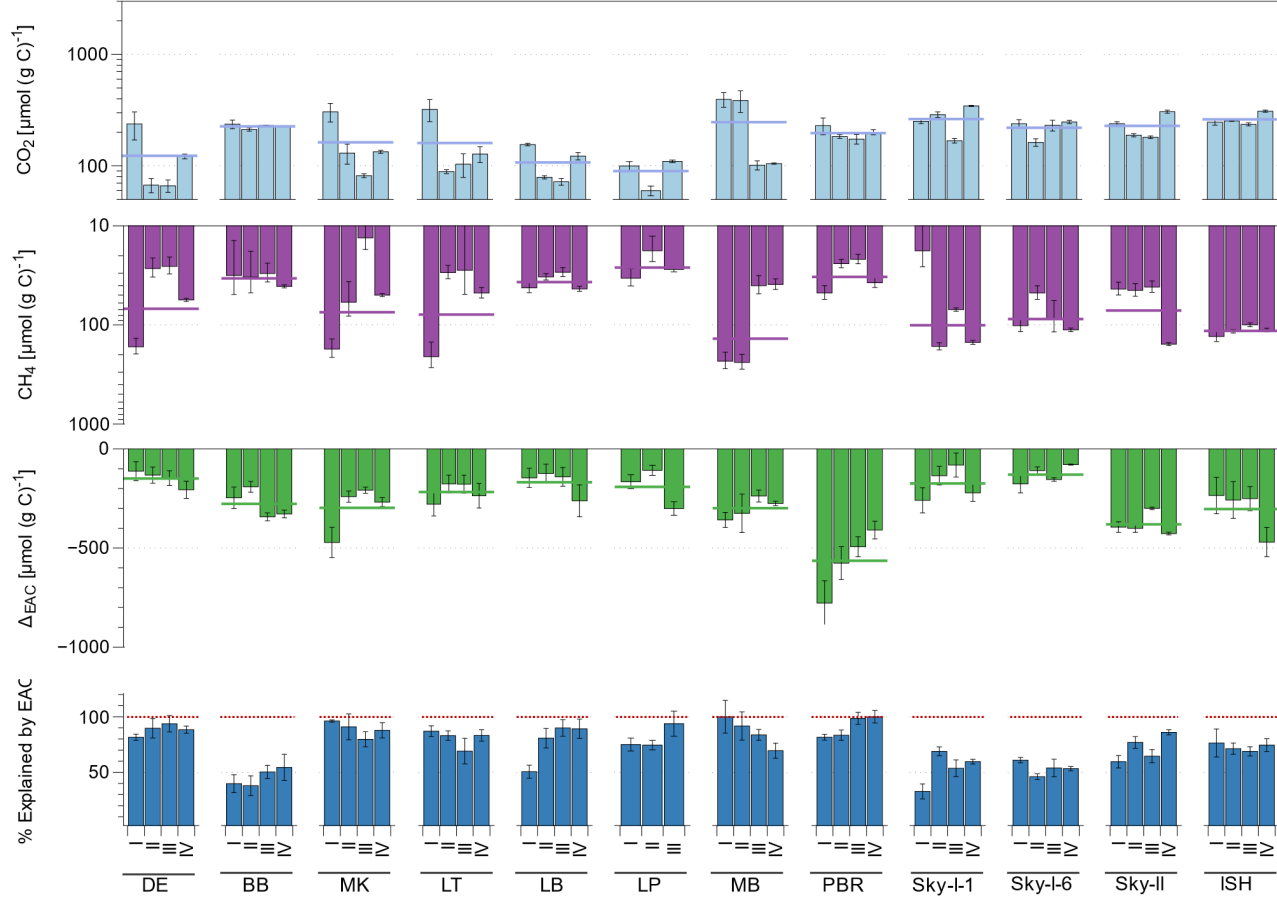
Figure 2: Upper panels: Absolute amounts of CO_2 (bright blue) and CH_4 (purple) per gram of carbon (C) after 56 days for all 15 sites and their respective depths. Not that both values in many cases approach a ratio of 1:1. Center: the delta in EAC (green) between the beginning and the end of the experiment. Bottom: Share of the excess CO_2 explained by EAC_{TOT}

Relation between Peat Chemistry and CO_2/CH_4 Formation

Within the investigated peat properties, spearman correlation analysis revealed a strong positive correlation between aromaticity of the peat and the sulfur content in bogs (0.664, FDR = 4.83 * 10^{-5}) (as calculated via the FTIR-ratio of

1650/1090 cm^{-1}) . Moreover, C/N ratios and aromaticity were negatively correlated (-0.582, FDR = 2.66 * 10^{-5}), as expected from patterns of peat decomposition. In fens, strongest negative correlations were found between aromaticity and C/N (as in bogs) (-0.565, FDR = 8.0 * 10^{-3}) and -0.415, FDR = 0.50 in fens. Overall, we found a positive correlation between aromaticity and rising N-content (0.482, FDR = 0.390), but in fens the correlation between aromaticity and nitrogen content was stronger (0.594, FDR = 0.122) than in bogs. We also found a strong negative correlation of ^{13}C (-0.714, FDR = 0.026) and the totally explained fraction of CO_2 (-0.774, FDR = 9.00 * 10^{-3}) with aromaticity.

CO_2 and CH_4 formation correlated with peat quality indices, such as positive with N and Si content, and negative with C content, C/N ratios, ^{15}N and ^{13}C. This was broadly reflected in the observation that fen peats had higher C mineralization (CO_2 and CH_4 formation), higher N and Si contents, but lower C/N ratios, ^{15}N and ^{13}C values compared to bog peat. Total C-mineralization (CO_2 + CH_4) ranged between 77.73 and 1465.26 µmol (g C)$^{-1}$ with a median of 235.75 ±114.02 in bogs and 386.09 ±176.89 in bogs. Interestingly, on average, fen peat had initially higher CO_2/CH_4 formation ratios, but narrower CO_2/CH_4 formation ratios at the end of the incubations, albeit this was not statistically significant. This trend suggests that some peat materials consumed their available EAC pool much quicker than others, producing relatively more CH_4, whilst other samples had initially slower rates of CO_2 production. The general timing of the onset of methanogenesis was not related to the fraction of CO_2 that could be explained by available EAC and methanogenesis, suggesting that neither an increased fraction of CO_2 from available EAC nor from methanogenesis would improve the explained fraction of overall CO_2 production; overall, CO_2 production could be explained well (see below). Moreover, EAC_{OM} was only weakly correlated to bulk chemical properties of the peat (for example weakly positive with aromaticity (0.086, FDR = 0.664).

General e^--Exchange Capacities of the Investigated Peat Soils

Given that the total electron exchange capacity, EAC_{TOT}, is the sum of inorganic electron acceptor capacities (EAC_{Inorg}) and organic electron acceptor capacity (EAC_{OM}), EAC_{Inorg} was negligible even for minerotrophic sites, ranging between 0.05 and 0.41 µmol (g C)$^{-1}$. Bogs provided on average 0.11 ±0.13 µmol (g C)$^{-1}$ whilst fens provided on average 0.13 ±0.04 µmol (g C)$^{-1}$. That is approximately 1/1800 (0.06 %) of the available EAC_{TOT} range observed during the experiment. Therefore, when aiming to explain CO_2 produced during the incubations with EAC_{TOT}, we did include EAC_{Inorg}, yet its contribution was near zero, so all described effects could primarily be attributed to the EAC of the organic matter (EAC_{OM}). Initial EAC (EAC_{Init}), varied strongly among sites and depths but no significant correlation of EAC_{Init} and peat quality indices could be identified. EAC_{Init} itself ranged from 267.7 to 1096.63 µmol e$^-$ (g C)$^{-1}$ and was on average 547.28 ±171.09 µmol e$^-$ (g C)$^{-1}$, 565.52 ±171.96 µmol

e$^-$ (g C)$^{-1}$ in bogs and 498.25 $\pm$169.77 µmol e$^-$ (g C)$^{-1}$ in fens. At the end of the 56-days incubation period, final EAC (EAC$_{End}$) had decreased to 293.78 $\pm$87.60 µmol e$^-$ (g C)$^{-1}$ in bogs and to 268.7 $\pm$96.51 µmol e$^-$ (g C)$^{-1}$ in fens (overall range 78.91 to 777.51 µmol e$^-$ (g C)$^{-1}$; average 260.31 $\pm$131.52 µmol e$^-$ (g C)$^{-1}$).

Considering the observed decreases in EAC$_{TOT}$ during the incubation, i.e., on average 46.25 $\pm$12.70 % of this initially measured EAC$_{TOT}$ was available to microbes and consumed in incubations of bog peats, compared to 44.48 $\pm$7.49 % available EAC$_{TOT}$ in fen peats. In general fens provided slightly less microbially available EAC$_{TOT}$ (229.56 $\pm$108.82 µmol e$^-$ (g C)$^{-1}$), than bogs (271.75 $\pm$138.44 µmol e$^-$ (g C)$^{-1}$), albeit this was not significant. In line with this, fen sites produced considerably more CH$_4$, but also more CO$_2$ (see above). Corresponding with observed changes in EAC$_{TOT}$, the average values for EDC$_{TOT}$ increased from 310.80 $\pm$114.50 to 470.80 $\pm$120.50 µmol e$^-$ (g C)$^{-1}$. Their minimum and maximum were 91.00 and 598.00 µmol e$^-$ (g C)$^{-1}$ and increased to 228.10 and 790.80 µmol e$^-$ (g C)$^{-1}$ during the anoxic incubations. EDC$_{TOT}$ itself showed only a weak correlation with EAC$_{TOT}$, though. The ratio of EAC$_{TOT}$ and EEC$_{TOT}$ was initially up to 0.80 for the original peat soil samples, while the average ratios of EAC$_{TOT}$:EEC$_{TOT}$ decreased from 0.64 $\pm$0.10 to 0.38 $\pm$0.08 and . After the incubation period of 56 days this ratio ranged between 0.57 $\pm$0.02 and 0.24 $\pm$0.01. EEC$_{TOT}$ slightly decreased during the incubation and was in the end approximately 9.70 $\pm$12.70 µmol e$^-$ (g C)$^{-1}$ lower than in the original samples. Prior to the incubation, EAC$_{TOT}$ was lower in samples from minerotrophic sites TX and DT in North-Eastern China, while site PBR, an ombrotrophic, Sphagnum and dwarf-shrub dominated site in south America showed distinctly higher initial EAC$_{TOT}$ values. Nevertheless, these EAC$_{TOT}$ values approached each other and got more similar during incubation and thus ongoing reduction of the peat soil. Overall, during incubation, site specific as well as depth specific differences between all samples decreased. On average less than half (45.8 %) of the measured EAC$_{TOT}$ seemed to be available to microbes and got depleted during the incubation while still explaining on average 70.77 % of all excess CO$_2$ (see below).

Figure 3: Peat chemical properties, C/N, and N/P mass-based ratios, concentrations of Fe, Ca, S, and Si, and values of ^{13}C and ^{15}N. The color-coded bar in each subplot is the arithmetic average value over all depth classes.

Calculated Electron Budgets for CO$_2$ Formation

Assuming *zerovalent* carbon as substrates (see methods section), we set up an electron transfer budget aiming to explain the observed CO$_2$ production in our incubations. Budgeting the electron transfer including available EAC consumption to explain CO$_2$ formation from a reduction of a corresponding electron acceptor (subtracting EAC$_{END}$ from EAC$_{Init}$) and including CH$_4$ formation to

explain CO_2 stemming from methanogenesis, explained total CO_2 formation in the incubations to a large extent (Figure 2): On average (all sites and depth classes) measured changes in EAC_{TOT} (EAC) could explain 70.8 $\pm$20.6 % of the total CO_2 formation in our incubations. There were few exceptions in which CO_2 production could not be well explained, such as in **KR** (uppermost depth class), 13.2 $\pm$3.9 % and **KR** (medium depth class), 22.3 $\pm$2.8 %. In contrast, for other sites such as **PBR** (uppermost depth class), CO_2 production could be fully explained by available EAC_{TOT} (106.2 $\pm$14.7 %). Nevertheless, due to a different reactivity of the peats under study, the fractions of CO_2 stemming from either consumption of a TEA or of methanogenesis varied considerably. Fractions and total amounts of CO_2 formation from either consumption of EAC_{TOT}, or from CH_4 formation are given in Table 3, along with fractions of total CO_2 explained. $CO_{2(EAC)}$ for which we could assign a corresponding consumption of electron acceptors, was on average 34.3 $\pm$19.0 % of total CO_2, spanning a wide range between 8.0 $\pm$3.3 and 85.0 $\pm$12.4 %. $CO_{2(CH4)}$ stemming from methanogenesis was on average 36.5 $\pm$17.8 % but also varied strongly between the peats under study, ranging from 0.4 $\pm$0.3 to 70.5 $\pm$7.3 %. For samples with high CH_4 formation, i.e., with a high share of methanogenic CO_2, CO_2 formation could be apparently better explained, while if most CO_2 stemmed from reduction of TEAs, generally less CO_2 production could be explained.

1.

DISCUSSION

(a)

Peat Chemistry and observed CO_2 and CH_4 formation

Peat quality as reflected in commonly assessed indicators (C/N, C-content, degree of decomposition) is driven by the peat parent vegetation (Wang et al., 2014) and pathways or extent of decomposition (Mathijssen PJH et al., 2019; Wang et al., 2015; Biester et al., 2014). The chosen samples thus represent a wide range of peat properties and degrees of decomposition, as found in sites from mid to high latitudes. Sphagnum peat from all bog sites was comparable in terms of carbon content and bulk chemical properties, and element ratios fell within ranges previously reported (Leifeld et al., 2020; Moore et al., 2018; Wang et al., 2015; Hornibrook et al., 2000; Biester et al., 2014; Berger et al., 2017). Nevertheless, the peat materials varied considerably in CH_4 formation, CO_2 formation (and therefore also CO_2:CH_4 ratio), available EAC_{TOT} and range of available EAC. Our dataset therefore provides estimates for available EAC_{TOT}, basically representing EAC_{OM}, in a wide selection of representative peat samples. Moreover, we propose that the presented approach with one common inoculum for all peats is suitable in determining the available EAC as far as possible independent of the peat material chosen (Gao et al., 2019). A higher amount of

vascular plant material in fen peats, as well as its more minerotrophic chemistry were reflected in lower C/N ratios, and, albeit not significant, more negative ^{13}C values and a higher aromatic content as indicated by the 1610/1090 FTIR peat ratio (Broder et al., 2012). In contrast, bog peat samples showed considerably wider C/N ratios, less negative ^{13}C values, in general lower CO_2 formation and lower CH_4 formation. We thus cover most of the transition from bog to fen peat (Gałka M et al., 2019; Wang M et al., 2015; Jones MC et al., 2010; Mathijssen PJH et al., 2019). As further examples, carbon contents in Alaskan permafrost peats ranged from 16.8 % to 44.8 % with a C/N ratio of 23.3 to 89.5 (Treat et al., 2014), in boreal peat from eastern Finland from 44.8 % to 56.8 % with a C/N ratio of 34.9 to 115.3 (Lozanovska et al., 2016) and in alpine peat from the Quinghai-Tibetan Plateau from 10.0 % to 39.0 % (Chen et al., 2014). N/P ratios have been reported to cover ranges from 10 to 70 in peat from bogs and fens with no specific differences between peatland types, but more narrow ratios near the surface, increasing with depth (Wang et al., 2015), as also true in our sample set: N/P ratios were on average 37.2 ±15.4 (range 15-100; no difference between bogs and fens) and mostly increasing ratios with depth. Low ^{15}N values correlated with peat material long-term under anoxic decomposition (deeper layers), whereas high values were predominantly related to materials from upper layers with predominantly oxic decomposition (Groß-Schmölders M et al., 2020). Also, lower depth classes showed high ^{15}N values and N enrichment, due to intense recycling during decomposition e.g., in initial fen stages (Jones MC et al., 2010).

CO_2 formation increased strongly at the beginning of the incubations and subsequently decelerated, as repeatedly observed (Gao et al., 2019; Keller & Takagi, 2013). Only after on average 21 days had passed, CH_4 formation started. The mean rates of anoxic CH_4 and CO_2 formation rates in our incubation experiment were 1.6 µmol (g C) day^{-1}, equivalent to 19.2 µg CH_4-C (g C)$^{-1}$ day^{-1}, and 4.2 µmol (g C)$^{-1}$ day^{-1} equivalent to 50.4 µg CO_2-C (g C)$^{-1}$ day^{-1}. The CO_2 formation rates were thus like those presented in other studies, while CH_4 formation rates mostly exceeded those previously presented (Moore & Dalva, 1997; Glatzel et al., 2004): We attribute this to the longer time scale of our anoxic incubation. Ranges of peat CH_4 formation were en-par with the median of maximum CH_4 formation in an incubation of northern permafrost zone soils across 54 sites as presented by Treat et al., 2015. Their results show a net CH_4 formation of 0.6 µg CH_4-C (g soil)$^{-1}$ day^{-1} which normalized per g carbon results in 3.2 µg CH_4-C (g C)$^{-1}$ day^{-1} and a net CO_2 formation of 18.0 µg CO_2-C (g soil)$^{-1}$, which normalized per gram carbon results in 58.3 µg CO_2-C (g C)$^{-1}$ day^{-1}. With regards to previous studies, we explain the initially high CO_2 production by anaerobic respiration utilizing the sum of inorganic and organic TEAs – as the reduction of those is energetically more favorable than methanogenesis (Lau et al., 2014; Blodau & Deppe, 2012; Knorr & Blodau, 2009; Gao et al., 2019; Teickner et al., 2022). as After depletion of these (in-)organic TEAs, methanogenesis set in and was expected to result in an equimolar formation of both, CO_2 and CH_4

(Conrad et al., 2011; Yavitt & Seidmann-Zager, 2006).

Changes in available Electron Accepting Capacities

Peatlands are ecosystems with very low mineral matter contents, so that OM represents the most important redox buffer in those systems and plays a key role in the competitive suppression of CH_4 formation (Gao et al., 2019; Klüpfel et al., 2014; Lau et al., 2014). As reported in previous studies, the EAC in humic acid standards and fulvic acid standards (DOM) ranged from 1300-3500 µmol e$^-$ (g C)$^{-1}$ and EDC typically ranged from 900 to 4900 µmol e$^-$ (g C)$^{-1}$ (Aeschbacher et al., 2010; Aeschbacher et al., 2012) (Table 3). These reported capacities for DOM-standards are thus higher than those found in this study, even when considering DOM only. Nevertheless, our reported ranges for DOM of original peat soils at the beginning of the incubation coincided with those reported for bulk peat and DOM in our earlier study (Gao et al., 2019). After the long-term anaerobic incubation, observed values of total EDC corresponded well with reported ranges (Gao et al., 2019; Walpen et al., 2018; Tan et al., 2017; Klüpfel et al., 2014; Lau et al., 2014; Heitmann et al., 2007).

For solid phase EAC_{TOT} and EDC_{TOT}, much less data is available. Reported ranges of EAC_{TOT} and EDC_{TOT} in bog peat were 900-1600 and 2800-3500 µmol e$^-$ (g C)$^{-1}$, thus higher than in this study, yet this was determined with another methodology (Walpen et al., 2018). Nevertheless, EAC_{TOT} in the original peat of this study here at the begin of the incubations coincided well with ranges of our previous study (Gao et al., 2019) and as reported elsewhere (Lau et al., 2014; Lau et al., 2016). Moreover, as EAC_{TOT} decreased, values of EDC_{POM} on the other hand increased, as expected and previously described (Keller JK & Takagi KK et al., 2013; Klüpfel L et al., 2014).

Besides the absolute values of EAC and EDC, as determined elsewhere (Gao et al., 2019; Walpen et al., 2018; Tan et al., 2017; Klüpfel et al., 2014; Lau et al., 2014; Heitmann et al., 2007) and as also determined for our peat materials not subjected to incubations (Teickner et al., 2022), the difference of initial and final EAC_{TOT}, herein termed EAC, in the incubations is particularly interesting, as it does not reflect a material property but indeed the microbially available fraction of EAC in an incubation (Gao et al., 2019). For our incubations, the observation that CH_4 was formed in all peat samples during the 56-day incubation was a clear indicator that long-term anoxic conditions depleted microbially available electron acceptor pools, including the largest pool, available EAC_{TOT} which we measured as EAC. Therefore, the observed EAC, predominated by EAC_{TOT}, could be seen as the relevant pool of readily available EAC for microorganisms in peat under anoxic conditions.

The remaining EAC_{OM} at the end of our incubation may likely not be available for anaerobic microbial respiration, even under prolonged incubation conditions. This is confirmed by the observation that ratios of CO_2:CH_4 formation reached values close to 1 (0.74 to 26.69), which would be the theoretical ratio of methanogenesis given a zerovalent substrate and thus absence of a TEA (Yu Z-G et al.,

2016; Gao et al., 2019; Conrad 1999). Still, in peats with higher final ratios of CO_2:CH_4, available EAC may even not have been fully depleted and available ranges may be larger. This finding of a remaining quantity of EAC yet underlines the necessity to analyze microbially available ranges of EAC to understand TEAs as a control on anaerobic respiration and methanogenesis (Gao et al. 2019), while total EAC as determined on bulk samples may rather represent an inherent material property (Teickner et al., 2022; Lau et al. 2016; Lau et al., 2017; Aeschbacher et al., 2011). Our data confirmed an earlier study on a limited dataset (Gao et al., 2019) that this utilizable share of EAC was on average only around 46 %, yet highly variable (25-73 %). Considering absolute measured values of EAC and EDC for peat may thus largely overestimate redox buffer capacities. Similarly, to EAC_{OM}, also EDC_{OM} of the initial sample peat material likely reflects a share of EDC_{OM} that remains untouched even under oxidized conditions and is thus not part of the actively cycled capacities of EAC_{OM} and EDC_{OM} – the available EEC. In an ecological context, our study thus calls for a necessity to assess ranges of available EAC and EDC rather than absolute values. Quite a few studies did not reach a 1:1 ratio of CH_4 and CO_2 formation (i.e., Yavitt JB & Seidmann Zager M, 2006), presumably due to too short incubation times, which led to a large part of the EAC pool staying untouched. In our studies, first peats became methanogenic after 25 days but most of them needed more than 50 days, hence our incubation time of 56 days. Typical incubation times therefore should exceed at least 50 days (at 20°C) in order to give the microbiome enough time to deplete EAC and reach methanogenic conditions.

However, the available range of EAC_{OM} was in our study unrelated to any of the investigated peat quality indices except for a weak correlation with values of ^{13}C and ^{15}N, possibly related to pathways of decomposition (Drollinger S et al., 2019; Groß-Schmölders et al., 2020). While existing studies (Aeschbacher et al, 2010, 2011 & 2012) reported a positive correlation with indices representing aromaticity of the sample, we could not confirm such a relationship. In contrast, we found a weakly negative correlation (not significant) of aromaticity, i.e., humification, as determined by FTIR spectroscopy and EAC_{Init}. We explain this lack of or inverse correlation with the fact that we investigated bulk peat but not DOM. While aromatics in DOM may be associated with phenolic and quinone moieties in DOM, as such functional moieties increase solubility, aromatics in POM do not necessarily have to be associated with increased contents of phenolics and quinones (Teickner et al, 2022).

The observed increase in EDC_{TOT} reflected the inverse pattern of EAC_{TOT}, as the process of electron transfers in a redox system should be reversible as per definition (Klüpfel et al., 2014). Nevertheless, changes in EDC were less consistent, presumably as the determination of EDC in MEO is potentially biased, as it may include oxidation of EDC of phenols, which would ideally not be considered as reversible EDC (Aeschbacher et al., 2010; Walpen et al., 2016 & Walpen et al., 2018). In existing studies, also EDC_{DOM} was strongly correlated with aromaticity, as determined by ^{13}C-NMR ($R^2 = 0.88$), whereas EDC

of terrestrial DOM showed weaker statistical correlation to this variable (R^2 = 0.32) (Walpen et al., 2016 & Walpen et al., 2018). Concerning EAC in all 15 different peat sampling locations in this study presented a high correlation with aromaticity (R^2 = 0.85), which is consistent with a high abundance of aromatic structures/moieties (Aeschbacher et al., 2012). A high phenolic and low aromatic content in polyphenolic or lignin-like structures in DOM extracted from peatlands would therefore explain the observed high EDC and low EAC values (Aeschbacher et al., 2012). Such high EDC values may have high ecological relevance, acting as redox buffer upon exposure of previously anoxic peat to atmospheric oxygen (Walpen et al., 2018) The rather weak correlations of peat chemistry with observed bulk peat EAC and EDC may additionally be explained by the observation that the variety of functional moieties along with the difficulties in their assessment in solid phase OM may mask clear relationships (Teickner et al., 2022); Moreover, per gram of carbon EAC_{DOM} and EDC_{DOM} are typically higher than for EAC_{POM} and EDC_{POM} (Aeschbacher et al., 2012, Lau et al., 2014). Moreover, particle size, molecular size and structures of higher complexity in POM limiting accessibility of redox active moieties and affecting their electron exchange kinetics, as hypothesized in Gao et al. (2019) would further weaken statistical relationships of EAC_{OM} and EDC_{OM} to bulk OM quality.

Results presented earlier (Aeschbacher et al., 2010) and results in this study indicate that the chemical composition of the observed bulk peat OM, especially its contents in aromatic and phenolic structures, as well as its quinone contents still play a key role in providing EAC_{OM} and EDC_{OM} pools in peat soils, although relationships are not straight forward to interpret across such a diverse set of peat samples (Teickner et al., 2022). Therefore, solid phase EAC_{OM} and EDC_{OM} apparently need to be determined individually by measurement. While from observed CO_2 and CH_4 formation the necessary electron equivalents needed to budget the non-methanogenic CO_2 formed ranged from -777.51 to -78.91 µmol e^- (g C)$^{-1}$, the corresponding decrease in EAC values, EAC, of dissolved and particulate TEAs was indeed observed for all incubations (see below).

Table 3: Previously reported typical values for EAC, EDC and EEC in different DOM and POM samples measured with comparable and different approaches:

Materials	EAC mol e^- (g C)$^{-1}$	EDC mol e^- (g C)$^{-1}$	EEC mol e^- (g C)$^{-1}$	Methods	Reference
DOM					
Original peat, globally	-2100 606±230	-2700 1303±470	-3821 1910±597	Electrochemical	This study
Reduced peat, globally	-850 433±126	-4400 1794±714	-5000 2227±758	Electrochemical	This study

Materials	EAC mol e⁻ (g C)⁻¹	EDC mol e⁻ (g C)⁻¹	EEC mol e⁻ (g C)⁻¹	Methods	Reference
Highly decomposed bog peat, Germany	-600	-2800	-3300	Electrochemical	(Gao et al., 2019)
Weakly decomposed bog peat, Germany	-450	-1700	-2100	Electrochemical	(Gao et al., 2019)
Long-term oxidized bog peat, Germany	-750	-2200	-2800	Electrochemical	(Gao et al., 2019)
Bog peat, Canada	-6100	-1400	-6100	H_2S and Fe^{3+}	(Heitmann et al., 2007)
Bog peat, Sweden	-1600	-3500		Electrochemical	(Walpen et al., 2018)
Standard humic and fulvic acids[a]	-3500	-4900	-5800	Electrochemical	(Aeschbacher et al., 2012; Aeschbacher et al., 2010)
	-1000	-	-	Fe^{3+}-citrate	
Standard humic acids[a]	-3600	-6400	-7300	Electrochemical	(Klüpfel et al., 2014)
Humic and fulvic acids, Loess Paleosoil, China [a]	-3100	-1500	-3500	Electrochemical	(Tan et al., 2017)
POM					
Original peat, globally	-1260 535±190	-675 274±128	-1585 809±252	Electrochemical	This study
Reduced peat, globally	-640 278±95	-976 407±150	-1467 685±207	Electrochemical	This study

Materials	EAC mol e⁻ (g C)⁻¹	EDC mol e⁻ (g C)⁻¹	EEC mol e⁻ (g C)⁻¹	Methods	Reference
Highly de-composed bog peat, Germany	-700	-440	-1200	Electrochemical	(Gao et al., 2019)
Weakly de-composed bog peat, Germany	-300	-550	-800	Electrochemical	(Gao et al., 2019)
Long-term oxidized bog peat, Germany	-450	-550	-900	Electrochemical	(Gao et al., 2019)
Fen peat, Germany	-1400	-600	-1450	Electrochemical	(Lau et al., 2014)
Lake sediment, Germany	-700	-700	-900	Electrochemical	
Bog peat, U.S.[b]	-53	-	-	(Fe(III)-nitriloacetic acid	(Keller and Takagi, 2013)
Lake sediment, Germany	-1600	-500	-1900	Electrochemical	(Lau et al., 2016)

[a] Ranges of EAC, EDC, and EEC of humic substances per g carbon were recalculated based on the reported data and assuming an average carbon content in humic substances of 55%

[b] Ranges of EAC, EDC, and EEC of POM were recalculated based on the reported data and assuming an average carbon content of peat of 50%.

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2.

Electron Budgets in Anoxic CO_2 Formation

On average, 36.5 ± 17.8 % (7.9-85 %) of the CO_2 formed over the entire incubation period of 56 days could be explained by methanogenesis, assuming a

CO$_2$:CH$_4$ ratio of 1:1 (Yavitt JB & Seidmann-Zager M (2006); Conrad R (1999). A share of on average 34.34 ± 19 % (0.4-70.5 %) of total CO$_2$ formation could be explained by electron transfer to detected EAC, including EAC$_{OM}$. In total, we could on average explain 70.8 ± 20.6 % of anaerobic CO$_2$ production for all ... peats under study, originating from 15 sites around the globe. This supports our earlier results of Gao et al., (2019) who assessed only 3 different peat types. While there were few exceptions, such as the uppermost depth of site KR (13.2 ± 3.9 % of explained CO$_2$) up to 100 ± 14.7 % of the CO$_2$ formed could be explained in our approach.

The results in this study therefore support the general applicability of the concept of electron transfer budgeting to explain anaerobic CO$_2$ production and suppression of methanogenesis (Gao et al., 2019; Yu Z-G et al., 2016). Furthermore, we could confirm the key role of EAC$_{OM}$ in the competitive suppression of methanogenesis, potentially explaining the frequently observed high ratios of CO$_2$:CH$_4$ in anoxic peat soils (Gao et al., 2019; Yavitt JB & Seidmann-Zager M (2006). Importantly, this study shows that after the onset of methanogenesis, molar formation ratios of CO$_2$:CH$_4$ were close to the theoretically expected 1:1 ratio. This raises the question, if previously reported higher ratios may in part be due to a remaining EAC in the peats under study, e.g., due to too short time scales of incubation. Assuming an NOSC of zero and thus a 4 mol e$^-$ transfer per mol CO$_2$ formed seemed plausible, given the high share of explained CO$_2$ and CH$_4$ production in our study compared to early conceptual work not considering EAC$_{OM}$ (Segers R & Kengen SWM, 1998). Moreover, the results in this study show that fermentation likely plays a negligible role for unexplained CO$_2$ formation, as it is conceptually included in our approach (Gao et al., 2019; Conrad R., 1999), given that fermentation does not involve any electron transfers to external electron acceptors. Fermentation is indeed a series of disproportionation reactions, which would imply that notable CO$_2$ production from fermentation not balanced by a corresponding TEAs would lead to a high share of fermentation products (H$_2$, Acetate) to accumulate in the incubations (Yu Z-G et al., 2016; Conrad R, 1999), yet this was not detected in our earlier study (Gao et al. 2019).

CONCLUSION

As hypothesized, the consumption of EAC$_{OM}$, the detected change EAC, in peat soils could explain most of the anaerobic CO$_2$ formation in a wide range of representative peat materials as used in this study. While we could not predict absolute values of EAC or available ranges of EAC by common peat quality indicators, we observed for example that with increasing aromaticity, such as in fen peats, the share of CO$_2$ stemming from EAC$_{OM}$ decreased, as in such OM a high share of CO$_2$ formation could be explained by methanogenesis. More CO$_2$ formed from methanogenesis was further linked to low mass ratios of C/N and N/P. Therefore, EAC plays a major role in suppression of CH$_4$ formation as also previously suggested for comparable systems (Teickner et al, 2022; Lau et

al., 2014; Gao et al., 2019), while the reactivity of the peat material determines its rate of consumption and thus time scales until onset of CH_4 production. We were able to show that our concepts are plausible: assuming carbohydrates as the main substrate with a nominal oxidation state of carbon of zero, a CO_2:CH_4 formation ratio of 1:1 indeed is what we found, when total EAC organic matter in peat soils, including that of organic matter, was ultimately depleted. Interestingly, however, only 24 to 71 % of the measured EAC were apparently available to microbes for anaerobic respiration, indicating that the sole assessment of absolute values of EAC and EDC may not suffice to understand anaerobic CO_2 and CH_4 formation.

Moreover, based on our survey of the redox properties in global peat soils collected from major peatland regions around the globe, we propose that this covers the basic characteristics of the redox properties in typical peatlands and its potential impact on CO_2 and CH_4 formation therein. Most of the EAC of the peat soils existed in POM, acting as major redox buffer in CH_4 formation that can be effectively renewed by oxygen under a low water table, as previously demonstrated.

Acknowledgements

Data Availability Statement

All data used in this study is available online on Zenodo (Guth et al., 2022) under CC BY 4.0 license. All software used to analyze the data is also open source (Knime, Orange).

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