Science of the Total Environment 943 (2024) 173793

Contents lists available at ScienceDirect

Science of the Total Environment

journal homepage: www.elsevier.com/locate/scitotenv

Long-term paddy use influences response of methane production, arsenic mobility and speciation to future higher temperatures

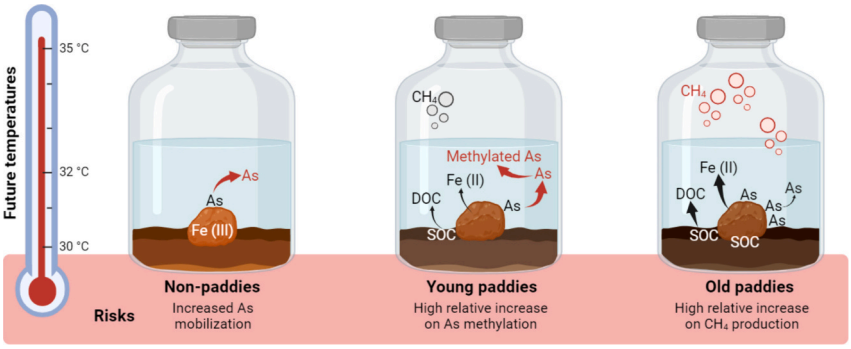
José M. León Ninin [a], Alejandra Higa Mori [a], Johanna Pausch [b], Britta Planer-Friedrich [a,*]

[a] Environmental Geochemistry, Bayreuth Center for Ecology and Environmental Research (BayCEER), University of Bayreuth, 95440 Bayreuth, Germany
[b] Agroecology, Bayreuth Center for Ecology and Environmental Research (BayCEER), University of Bayreuth, 95440 Bayreuth, Germany

HIGHLIGHTS

- Biogeochemical responses to higher temperatures differ between paddies and non-paddies.
- Paddies of long-term use show increased methane production at higher temperatures.
- Paddies of short-term use show higher arsenic mobility at higher temperatures.
- Higher temperatures increase arsenic methylation in all paddies, regardless of age.
- Higher temperatures increase dissolved iron, which limits arsenic thiolation.

GRAPHICAL ABSTRACT



ARTICLE INFO

Editor: Jan Vymazal

Keywords:
Soil development
Biogeochemistry
Chronosequence
Climate change
Methylation
Thiolation

ABSTRACT

Anaerobic microbial metabolisms make flooded paddy soils a major source of the greenhouse gas methane (CH_4) and mobilize toxic arsenic (As), threatening rice production and consumption. Increasing temperatures due to climate change enhance these microbially mediated processes, increasing their related threats. Chronosequence studies show that long-term paddy use ("age") changes soil properties and redox biogeochemistry through soil organic carbon (SOC) accumulation, its association to amorphous iron (Fe) phases, and increased microbial activity. Using paddy and non-paddy soils from a chronosequence as proxies of soil development and incubating them at different temperatures, we show that paddy soil age influences the response of paddies to changes in temperature. Older paddies showed up to a 6-fold higher CH_4 production with increasing temperature, compared to a 2-fold increase in young ones. Contrarily, changes in As mobility were higher in non-paddies and young paddies due to a lack of Fe-SOC-sorption sites. Temperature increased the formation of phytotoxic methylated As in all paddies, posing a risk for rice production. Mitigation strategies for future maintenance, abandonment, or management of paddy soils should include the consideration that history of use shapes the soils' biogeochemistry and microbiology and can influence the response of paddy soils to future temperature increases.

* Corresponding author.
E-mail address: b.planer-friedrich@uni-bayreuth.de (B. Planer-Friedrich).

https://doi.org/10.1016/j.scitotenv.2024.173793
Received 5 April 2024; Received in revised form 14 May 2024; Accepted 3 June 2024
Available online 6 June 2024

1. Introduction

Rice is a crop of global importance, feeding over half of the World's population. In contrast to other cereals, rice is cultivated under flooded conditions in paddy soils (Kögel-Knabner et al., 2010; Meharg and Zhao, 2012). Biogeochemically, these soils undergo strong redox fluctuations, since the standing water and active microbes deplete it from oxygen after flooding (Kögel-Knabner et al., 2010). This depletion creates an anoxic environment where microbial groups use alternative anaerobic respiratory pathways, such as sulfur (S) and iron (Fe) reduction, and methanogenesis (Kögel-Knabner et al., 2010; Sethunathan et al., 1982). In the long-term, the redox fluctuations associated with paddy use alter pedologic properties (Kalbitz et al., 2013; Kölbl et al., 2014; Wissing et al., 2014; Wissing et al., 2011), for example by storing carbon (C) as soil organic carbon (SOC), lowering soil pH, and increasing the share of amorphous Fe phases. In a recent study using a 2000-year old chronosequence we have shown that long-term paddy use (i.e., paddy soil "age") also influences redox biogeochemistry and the above-mentioned respiratory pathways, increasing, among others, the rates of soil respiration, methanogenesis, and Fe reductive dissolution (León Ninin et al., 2024). With increasing paddy soil age, amorphous Fe^{III} phases accumulate and stabilize SOC by mineral associations (Kölbl et al., 2014; León Ninin et al., 2024; Lalonde et al., 2012). The reductive dissolution of these Fe^{III}-SOC associations releases high amounts of Fe^{II} and dissolved organic carbon (DOC) into the aqueous phase, supporting an increased microbial activity (León Ninin et al., 2024).

The alternative respiratory pathways used by microbes under anoxic conditions are responsible for two main concerns related to paddy use. First, methanogenic archaea thrive in paddy soils and release methane (CH_4) as a metabolic by-product (Le Mer and Roger, 2001; Bridgham et al., 2013). Methane is a greenhouse gas with high relevance for climate change since, although it is produced in trace amounts, it has 27 times the warming potential of CO_2 over a 100 year time frame (Forster et al., 2021). Paddies are a major anthropogenic CH_4 source, responsible for the emission of 24 to 31 Tg $year^{-1}$ (11 % of annual agricultural CH_4 emissions) (Forster et al., 2021; FAO, 2022; Qian et al., 2023). Our previous study showed that long-term paddy use increases CH_4 production (León Ninin et al., 2024), due to SOC accumulation, increased microbial biomass and activity, and likely a well-established community of methanogens (Conrad, 2020; Ho et al., 2011).

Secondly, anaerobic microbial activity drives different aspects of the biogeochemistry of arsenic (As). Arsenic is a toxic trace element that accumulates in rice plants and grains, affecting plant yield and representing a risk of As exposure from rice consumption (Stone, 2008; Ma et al., 2008; Zheng et al., 2013). Iron reduction controls the availability of As in the porewater for plant uptake, since the reductive dissolution of As-bearing Fe minerals releases carcinogenic inorganic oxyarsenic species, arsenate and arsenite (Stone, 2008; Smedley and Kinniburgh, 2002; Zobrist et al., 2000). Sulfate reducing bacteria (Chen et al., 2019) (SRB) as well as other microbial groups (Reid et al., 2017) have been proposed as As methylators. Methylated As species (mono- and di-methylarsenate, MMA and DMA, respectively) represent a lower risk for humans but have been reported to cause plant sterility (Zheng et al., 2013; Zhao et al., 2013). The reduced S produced as a by-product of SRB respiration can thiolate As to form thioarsenates. Inorganic and methylated thioarsenates are usually-overlooked, highly mobile and cytotoxic As species that have been found in paddy soil porewater (León Ninin et al., 2024; Wang et al., 2020; Chen et al., 2021a), rice grains, and products (Colina Blanco et al., 2021; Dai et al., 2022; Colina Blanco et al., 2024). Lastly, methanogenesis also has been previously reported as a biogeochemical process affecting As speciation through de-methylation (Chen et al., 2019; Chen et al., 2022; Chen et al., 2023; Zhang and Reid, 2022). Our previous study in the chronosequence showed that long-term paddy use decreases As mobility due to the formation of amorphous Fe^{III}-SOC associations that act as effective sorption sites. Additionally, the increased microbial activity and SOC accumulation with increasing paddy soil age enhances As methylation, particularly during the first 300 years of paddy use (León Ninin et al., 2024). Regarding As thiolation, increased SOC and dissolved Fe^{II} with long-term paddy use scavenge reduced S, decreasing its availability for thioarsenate formation.

The rates of these microbially mediated processes are reported to be enhanced by temperature (Frey et al., 2008; Castro et al., 2010; Bradford et al., 2008). In the context of anthropogenic climate change, several studies have shown how higher temperatures could increase As mobility, methylation and thiolation (Chen et al., 2021a; Muehe et al., 2019; Farhat et al., 2021; Neumann et al., 2017; Müller et al., 2022), while the reports regarding CH_4 production are contradictory and depend on agricultural practices (van Groenigen et al., 2011; Cheng et al., 2006; Tokida et al., 2011; Gaihre et al., 2013). These observations have been partially attributed to SOC being an important factor determining soil responses to changes in temperature (Wei et al., 2019; Su et al., 2024). However, it remains unknown how the systematic accumulation of SOC as a cause of long-term paddy use can affect these temperature responses. More generally, a better understanding of how the pedologic and redox changes related to paddy soil aging could be influenced by increasing temperatures in the future is lacking.

Here, we incubated soils from a well characterized 2000-year-old paddy soil chronosequence at different temperatures. The advantage of using selected soils of such a chronosequence is that they provide a range of stages in paddy development, which allow a broad understanding of paddy soil biogeochemistry. Our aim was to investigate whether there is a link between long-term paddy use and the degree to which CH_4 and As biogeochemistry are affected by increasing temperatures. In this sense, we are using this chronosequence as a tool to understand how intrinsic pedological changes associated with paddy management affect their response to increasing temperatures. We hypothesize that higher temperatures will accelerate microbial processes to a greater extent in older paddies, with more active microbes sustained by higher SOC, leading to increased methanogenesis and As methylation. However, we expect older paddies to remain unaffected by temperature increase in terms of As mobility due to abundant Fe^{III}-SOC sorption sites. Additionally, we used non-paddy soils to understand how the development of new fields could be affected by future warmer temperatures, as well as to determine if such a response to increasing temperatures is indeed related to long-term paddy use.

2. Materials and methods

2.1. Incubations from soil chronosequence

Incubation experiments were carried out with soils from a paddy soil chronosequence located around Cixi, in the delta of the Yangtze River in the province of Zhejiang, China (Kölbl et al., 2014; Cheng et al., 2009). Through sedimentation and dike building, land reclamation for agricultural purposes has been taking place from saltmarshes since approximately 2000 years. The building dates of the dikes allow an estimation of the age of the arable land and its management as paddies and non-paddies. For this study, the $\leq$2 mm fraction of the topsoil of the main sites described by Cheng et al. (2009) and Kölbl et al. (2014) were used, representing paddies (P) with ages of 50, 100, 300 and 2000 years. Two additional non-paddy soils (NP) from the same chronosequence, used for upland agriculture and with ages of 50 and 700 years, were also incubated as representatives of upland systems. The soils were characterized for As binding mechanisms by sequential extraction procedures (SEP), proposed by Fulda et al. (2013). A detailed description of the procedure can be found in the supporting information (supplementary methods, Table SI1). Selected soil properties can be found in Table SI2.

For the incubations, 10 g of soil and 20 mL of N_2-purged tap water were added into 120 mL septum vials in triplicate under anoxic conditions inside a glovebox (95 % N_2, 5 % H_2, COY). The vials were closed with butyl rubber stoppers and aluminum caps, shaken to mix the slurry and incubated standing at 30, 32, and 35 °C. While 30 °C represents the

average maximum temperature in Cixi during the cropping season between April and September, 32 °C and 35 °C correspond to +2 °C and + 5 °C increases in air temperature for IPCC scenarios SSP2–4.5 and SSP5–8.5 in the region, respectively (Muehe et al., 2019; Le Quéré et al., 2018). Data used in this publication for the paddy soils incubated at 30 °C has been previously published in León Ninin et al. (2024).

2.2. Sampling

The corresponding triplicate vials were sampled sacrificially after 1, 3, 5, 7, and 10 days of incubation. These days were selected based on the dynamics of redox processes that we described before in the chronosequence (León Ninin et al., 2024). The vials were removed from the water bath, shaken, and allowed to reach room temperature (20 °C) before measuring the inner pressure of the vials using a handheld pressuremeter (Greisinger GMH, 3100 Series), followed by sampling the headspace with a gas-tight syringe and needle. Approximately 5 mL of headspace were sampled from each vial and stored in evacuated glass vials until CH_4 and CO_2 determination using a gas chromatograph with a Flame Ionization Detector (GC-FID, SRI Instruments 8610C) equipped with a methanizer.

The vials were then brought into the glovebox and shaken to form a homogeneous slurry that was transferred into 50 mL centrifuge tubes. The tubes were closed and wrapped in Parafilm before being centrifuged for 10 min at 4000 rpm outside the glovebox. The tubes were brought back into the glovebox and the aqueous phase was separated from the soil with syringe and needle. The aqueous phase was split into different aliquots for different geochemical analyses described below.

2.3. Aqueous phase analyses

To measure dissolved organic carbon (DOC), 2 mL of aqueous phase were filtered through a 0.45 μm polyamide filter (Chromafil® Xtra), acidified with 40 μL of 6 M HCl and kept at 4 °C until analysis (Multi N/C 2100 S, Analytik Jena). For the rest of the analyses, the aqueous phase was filtered through 0.2 μm cellulose-acetate filters (Chromafil® Xtra). Inside the glovebox, a multiparameter (HQ40d, Hach) connected to the respective electrodes was used to measure pH (PHC301, Ag/AgCl electrode) and redox potential (MTC101).

Photometric determinations following the Ferrozine method (Stookey, 1970; Hegler et al., 2008) for total Fe and the methylene blue method (Cline, 1969) for sulfide were carried out. After stabilization, colorimetric reactions and measurements were done outside the glovebox. All photometric determinations were carried out in triplicate using a multiplate reader (Infinite® 200 PRO, Tecan). Samples were diluted, if necessary, with ultrapure deionized water (Millipore, 18.2 MΩ cm).

Total As and S were determined by Inductively Coupled Plasma-Mass Spectrometry (ICP-MS, 8900 Triple Quad, Agilent) in reaction mode with O_2. Arsenic was measured as AsO^+ (*m/z* 91) and S as SO^+ (m/z 48). Detection limits were 0.01 μg L^{-1} for As and 21 μg L^{-1} for S. For this analysis, a 2 mL aliquot was stabilized with 0.5 % H_2O_2 and 0.8 % HNO_3 and diluted before analysis. Rhodium was used as internal standard to compensate for signal drift and a certified reference material (TMDA 62.2, Environment Canada) was used for quality control.

For the determination of As speciation, a 700 μL aliquot was stabilized with 100 μL of hydroxybenzylethylenediamin (HBED, pH 7) (León Ninin et al., 2024). An HBED solution of 10 mmol L^{-1} was used to stabilize samples with Fe concentrations <1 mmol L^{-1} and a 59 mmol L^{-1} solution was used for those with higher Fe concentrations. Stabilized samples were frozen with dry ice and stored at −20 °C until analysis. Arsenic speciation was determined by ICP-MS after chromatographic separation by ion chromatography (IC, 940 Professional IC Vario Metrohm). The chromatographic separation was done using an AS16 column (Dionex AG/AS16 IonPac column), with a 2.5–100 mM NaOH gradient, 1.2 mL min^{-1} flow rate, and an injection volume of 50 μL (Planer-Friedrich et al., 2007). Samples were thawed inside the glovebox before analyses to avoid changes in speciation due to oxidation. Individual As species were assigned based on previously reported retention times (Wang et al., 2020; Wallschläger and London, 2008; Wallschläger and Stadey, 2007). Concentrations were calculated through a linear calibration containing arsenite (NaAsO2, Fluka), arsenate ($Na_2HAsO_4 \times 7H_2O$, Fluka), MMA ($CH_3AsNa_2O_3 \times 6H_2O$, Supelco), and DMA ($C_2H_6AsNaO_2 \times 3H_2O$, Sigma-Aldrich). Detection limit for As species was 0.02 μg L^{-1}. Because of the unavailability of commercial standards for thioarsenates, concentrations of thiolated As species were calculated based on their oxyarsenic homologues: inorganic thioarsenates (mono-, di-, and trithioarsenate) were calibrated through arsenate, monomethylated thioarsenates (monomethyl mono-, di-, and trithioarsenate) through MMA, and dimethylated thioarsenates (dimethyl mono- and dithioarsenate) through DMA. Throughout the following text, rather than describing the species individually, they will be grouped as inorganic oxyarsenic, oxymethylarsenates, inorganic thioarsenates and methylthioarsenates. An example chromatogram, names, abbreviations, and grouping can be found on Figure SI1.

2.4. Statistical analyses

Mean and standard deviation were calculated for each measured variable. Relative change of biogeochemical parameters with temperature was calculated by dividing the absolute difference of said parameter at both temperatures by the value of the parameter at the higher temperature. These values are shown in percentages throughout the text and figures. One- or Two-way-ANOVAs were used to determine the individual or combined effects of paddy soil age and incubation temperature (*P*-values are summarized in Tables SI 3 and 4, and additional statistical data can be found in the supplementary files). ANOVAs were carried out using the "Analysis ToolPak" Add-In for Microsoft Excel. Pearson correlation coefficients were used to assess the significance of the presented correlations, and done using RStudio (R Development Core Team, 2008).

3. Results and discussion

3.1. Temperature effect on general redox (biogeo)chemistry

Previous studies have established that increases in temperature enhance microbially mediated processes in redox dynamic soils (Weber et al., 2010). The results of our incubations using the 2000-year-old paddy soil chronosequence revealed that the magnitude of such enhancement is strongly influenced by soil age. Fig. 1a and b show dissolved Fe concentrations at 30 °C versus 32 °C (from now on referred as 30–32 °C), and 32 °C versus 35 °C (32–35 °C), respectively. Concentrations of dissolved Fe increased from non-paddies to paddies with increasing age as reported before (León Ninin et al., 2024). Moreover, deviations from the 1:1 line indicate that there was a temperature effect on Fe reductive dissolution. These deviations are presented as relative change in Fig. 1c for 30–32 °C and Fig. 1d for 32–35 °C. Fig. 1c shows that non-paddies had a negative relative change, indicating an average decrease on dissolved Fe concentrations, while the positive relative change in paddies indicates enhanced Fe reductive dissolution. Furthermore, the relative change in dissolved Fe concentration in paddies increased with soil age. Relative change was larger between 30–32 °C (Fig. 1c) than between 32–35 °C (Fig. 1d). Two-way ANOVA confirmed that paddy soil age and incubation temperature had a significant individual effect on dissolved Fe concentrations, as well as a significant interaction between both factors ($p < 0.05$). Dissolved Fe concentrations over incubation time (Fig. SI2a-d), were enhanced both in magnitude (higher peaks) and kinetics (earlier peaks) at the higher temperatures. Across the non-paddy incubations there was a constant increase of dissolved Fe concentrations with incubation time (Fig. SI3a, b), opposite to the bell-shape observed in paddy soils (Fig. SI2a-d).

Similar to what was observed for Fe, DOC concentrations increased

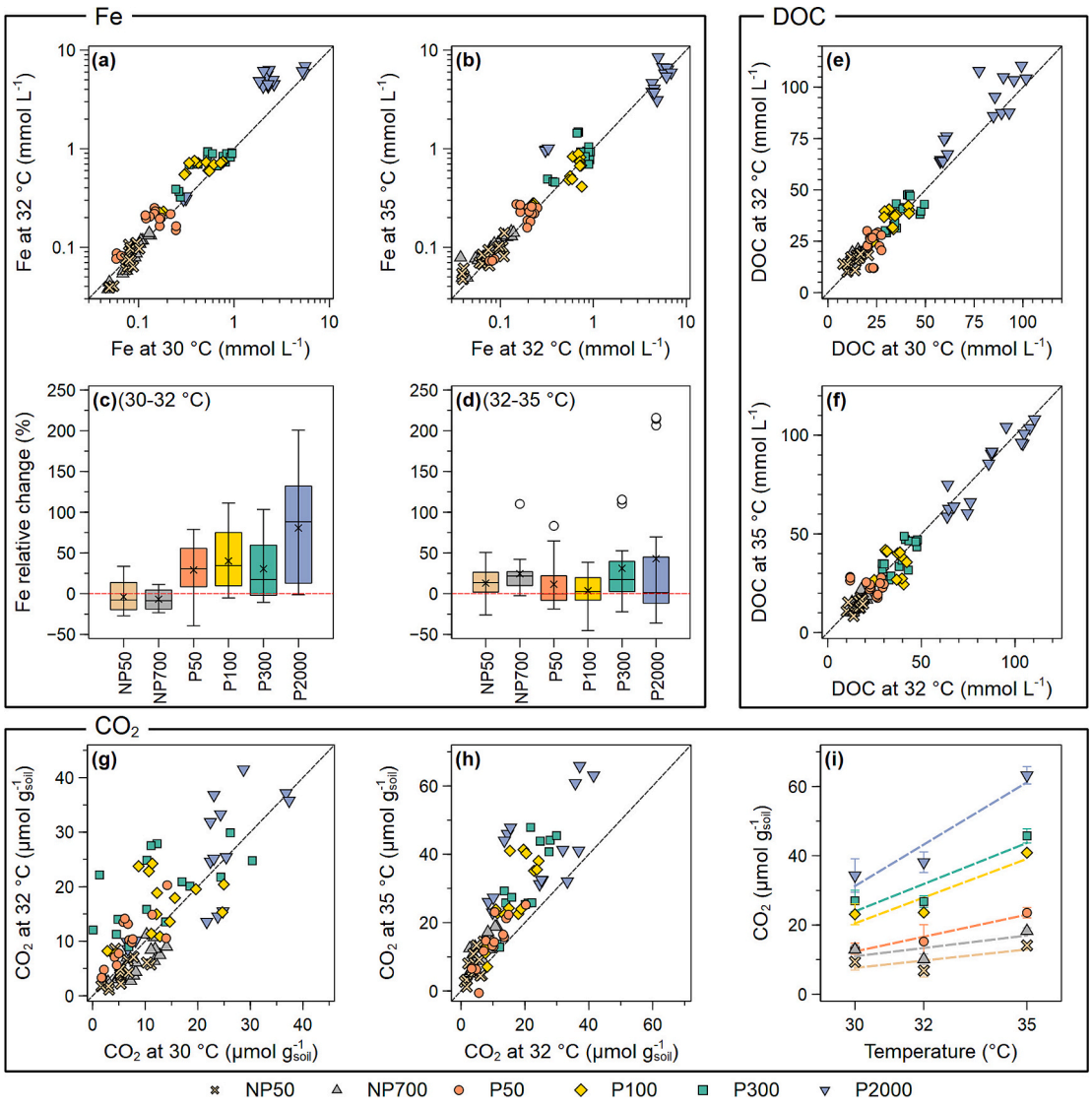


Fig. 1. Changes in selected biogeochemical parameters through the chronosequence with increasing temperature. Comparison of dissolved Fe concentrations between 30–32 °C (a) and between 32–35 °C (b). Relative change in dissolved Fe concentration, integrated over all incubation times, based on both temperature comparisons (c, d). Comparison of DOC concentrations between 30–32 °C (e) and between 32–35 °C (f). Comparison of CO_2 production between 30–32 °C (g) and between 32–35 °C (h). Effect of incubation temperature on CO_2 production by the end of the experiment (day 10) (i). For c and d, each box summarizes the results of triplicates through the incubation time ($n = 15$), with "x" showing the mean value and white circles showing outliers (1.5 IQR). For i, data points represent averaged results and error bars show standard deviation ($n = 3$). For the rest of the plots, data is displayed as individual results of experimental triplicates from all 5 incubation times (n = 15), color-coded per soil. The black dotted line represents a 1:1 line. Note logarithmic scale for (a) and (b).

from non-paddies to paddies with increasing age (Fig. 1e,f). Temperature showed only small effects on DOC concentrations, slightly enhancing them for a 2 °C increase (30–32 °C) (Fig. 1e, Fig. SI4), while for a further 3 °C increase (32–35 °C) the relative change was around the zero % line (Figs. 1f, SI4). Looking at the temporal resolution (Fig. SI2e-h for paddies, Fig. SI3 c,d for non-paddies), higher temperatures slightly increased DOC release in early days in the incubation, but also caused a stronger and earlier decrease.

Higher incubation temperature also caused an increased CO_2 production in all paddies (Fig. 1g,h), especially when incubated at 35 °C (Fig. SI5). A two-way ANOVA confirmed that the CO_2 production by the end of the experiment (day 10) was significantly ($p < 0.05$) affected individually by paddy soil age and temperature, and by the interaction of both factors. When plotting the final CO_2 produced by day 10 against the incubation temperature (Fig. 1i), all paddies showed a positive slope which increased with paddy soil age, indicating that older soils with higher soil C stocks have a greater response on CO_2 production at high temperatures. Soil respiration in non-paddies was only half of the values observed in paddy soils. Temperature had contrasting effects on the CO_2 production in non-paddies, with 32 °C causing generally lower respiration and being distinctively different from the effect of temperature in paddy soils, and with 35 °C enhancing it (Fig. SI5). For non-paddies, a two-way ANOVA showed that temperature and age had individual significant effects ($p < 0.05$) on the final CO_2 production but no significant interaction between both factors.

The above-described observations can be explained when considering paddy soil development. Increased Fe dissolution with paddy soil age is related to the formation of amorphous Fe^{III} phases with SOC accumulation, which changes the structure of Fe oxyhydroxides upon reprecipitation (Kölbl et al., 2014). These Fe^{III}-phases are known to be more easily reduced at higher temperatures (Schwertmann, 1991), explaining why the magnitude of the increase of dissolved Fe is higher with increasing temperature and age. A significant Pearson correlation between dissolved Fe and DOC (r: 0.9, $p < 0.0001$; Fig. SI6), as well as

their similar temporal dynamics (Fig. SI2) suggests that DOC is mainly released from the reductive dissolution of Fe-SOC mineral associations. However, this could also indicate that the increased availability of DOC with increasing soil age enhances Fe reductive dissolution. The effective removal of DOC from the paddy incubations with increasing time at higher temperatures suggests effective microbial consumption of organic substrates, supported by the increased CO_2 production. Increased soil respiration in paddies indicates that their role as C sinks (Kögel-Knabner et al., 2010; Chen et al., 2021b) could be negatively affected by increasing temperatures, particularly in older paddies where more SOC is stored.

Non-paddy soils are subject to different agricultural practices like tillage, which aerates the soil releasing accumulated SOC as CO_2 into the atmosphere, lowering the SOC pool and hampering the formation of amorphous Fe^{III} phases (Kölbl et al., 2014; Rhoton et al., 2002) (Table SI2). Non-paddy soils are thus generally less dynamic systems once they are flooded and exposed to different temperatures. The constant increase of Fe concentrations in the aqueous phase of the non-paddy incubations can be explained when considering that the main mechanism removing reduced Fe from solution is the precipitation of Fe–S phases (Xu et al., 2019; Saalfield and Bostick, 2009), once SRB perform dissimilatory sulfate reduction (DSR). A decrease of total aqueous phase S with incubation time in paddies and non-paddies (Fig. SI7) indicates effective DSR. The amount of S in non-paddies was lower than in paddies, meaning that there was less reduced S available to precipitate dissolved Fe and remove it from the aqueous phase. This lower availability of reduced S in non-paddies explains the constantly increasing dissolved Fe concentrations in these soils, compared to the bell-shaped curve described for paddies (Figs. SI2a-d and SI3a,b). Furthermore, the lower DOC concentrations in non-paddies, as well as a different microbial community which is likely not adapted to anoxic and suboxic environments, decreases microbial activity under flooded conditions in comparison to paddies (Wei et al., 2022). The lower microbial activity in the incubations of flooded non-paddies was reflected in lower

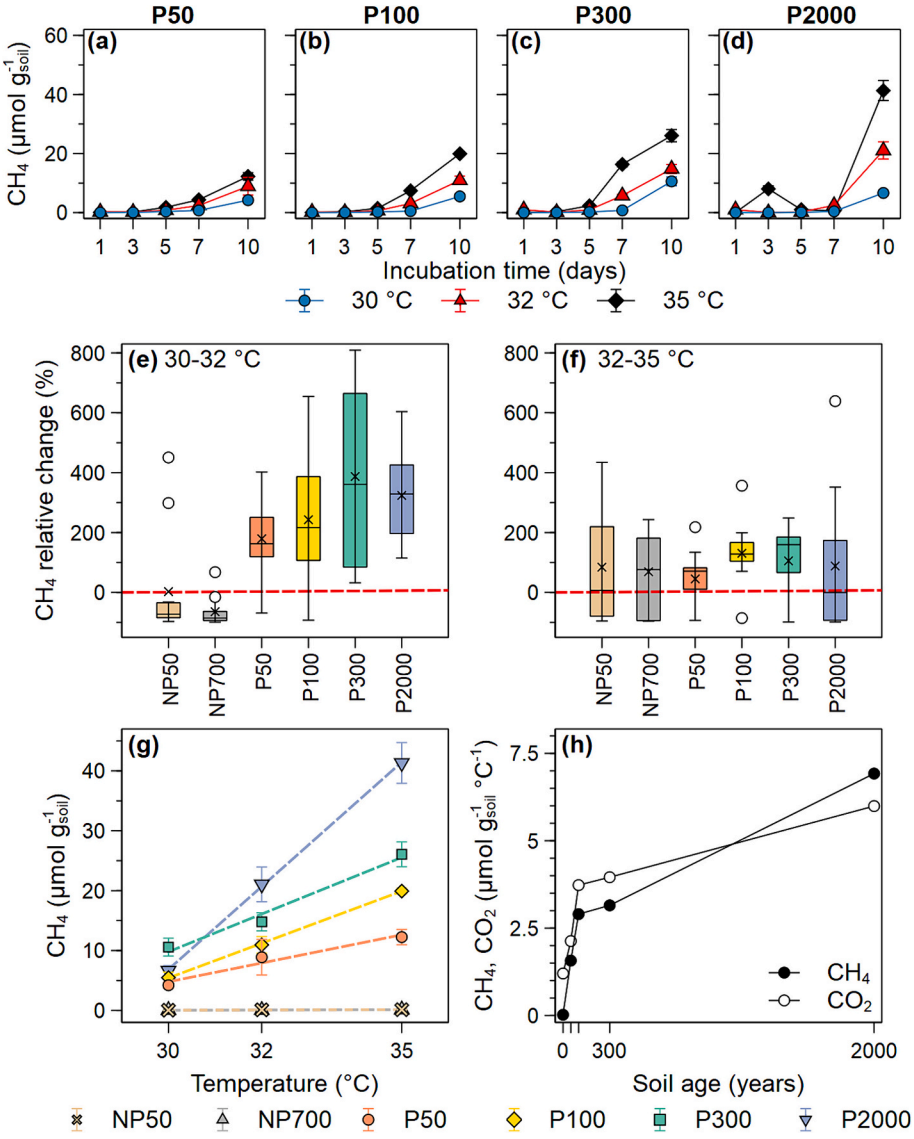


Fig. 2. Methane production in the paddy soils at different temperatures over time (a-d). Relative change in the CH_4 production between 30–32 °C (e) and between 32–35 °C (f), integrated over all incubation times. Effect of incubation temperature on CH_4 production by the end of the experiment (day 10) (g). Response of CH_4 and CO_2 production to changes in temperature in paddy soils (h), based on the slopes of (g) and Fig. 1i. Averaged values of NP50 and NP700 are used in (h) to represent a paddy soil of 0 years. For a-d, and g, data points represent averaged results and error bars show standard deviation ($n = 3$). For e and f, each box summarizes results of triplicates through the incubation time ($n = 15$), with "x" representing the mean value and white circles showing outliers (1.5 IQR). Data for CH_4 production in non-paddies is found in Fig. SI9.

CO_2 production and in higher Eh values, when compared to those in paddies (Fig. SI8).

Considering that increased temperature had stronger effects on the biogeochemistry of Fe and C in paddy soils than in non-paddies, we suggest that it is long term paddy management that creates the temperature-induced differences under flooded conditions. In the following sections, we will describe how these differences in biogeochemistry with long-term paddy use also influence the response of CH_4 production, As release, and affect As speciation to changes in temperature.

3.2. Temperature effect on methane production

Increasing incubation temperature caused higher CH_4 production in all paddies (Fig. 2a-d). The relative magnitude of this increase depended on the age of the paddies when considering 30–32 °C (Fig. 2e). Non-paddies showed a much lower CH_4 production than paddies (Fig. SI9) and even a negative relative change in CH_4 production at 30–32 °C (Fig. 2e). Further increasing the incubation temperature to 35 °C enhanced CH_4 production in all soils (Fig. 2f), including non-paddies, but overall showing a lower relative change when comparing 32–35 °C to 30–32 °C and not being systematic with paddy soil age.

A two-way ANOVA showed that the amount of CH_4 produced by day 10 was significantly influenced by paddy soil age and incubation temperature, as well as by the interaction of both factors ($p < 0.05$). Non-paddies showed no significant difference in their final CH_4 production with increasing temperature. Methane produced by day 10 showed a positive correlation with incubation temperature for all paddies (Fig. 2g), with slopes increasing with paddy soil age (Fig. 2h), indicating that the magnitude of the response to produce more CH_4 per increasing °C is highly dependent on soil age. This age-related trend was also found for CO_2 (based on results from Fig. 1i).

The increased response with paddy age to produce more CH_4 and CO_2 could have several explanations. Long-term paddy use enhances microbial biomass (Table SI5) and activity, meaning that older soils generally have a higher microbial activity that could respond to changes in temperature (Ho et al., 2011; Wang et al., 2021; Wang et al., 2015; Bannert et al., 2011; Liu et al., 2023). Increased microbial activity with paddy soil age can be observed in our experiments when comparing CO_2 production (as a proxy of microbial respiration) at a fixed temperature across paddy soil ages (Fig. SI2). It has been separately reported that long-term paddy use (Conrad, 2020; Ho et al., 2011) and increased temperature (Zhang et al., 2023; Mohanty et al., 2007; Lee et al., 2014) promote CH_4 production through enhanced activity of methanogens. To the best of our knowledge, this is the first time that both these parameters have been studied together. Older paddies also have a bigger pool of organic substrates that can support higher microbial activity, including that of methanogens (Table SI2, Fig. 1e,f). The importance of labile organic substrates regarding soil response to increased CH_4 and CO_2 production with temperature changes has previously been studied in batch experiments amended with C sources (Wei et al., 2019), where it was shown that the effect of temperature change is limited by labile C availability. The labile DOC from P50 may have been consumed rapidly by microorganisms with increasing temperature, before redox conditions for methanogenesis were reached, leading to a lower CH_4 production and lower relative change to increased CH_4 production. In contrast, we have previously reported (León Ninin et al., 2024) that P2000 has a high amount of labile organic C. This pool of labile C was likely still available for methanogens once other preferred metabolic pathways were exhausted. Additionally, we had previously reported that the high availability of Fe^{III} (oxy)hydroxides with increasing age delayed the start of methanogenesis at 30 °C (León Ninin et al., 2024; Luo et al., 2023; van Bodegom et al., 2004). Under higher temperatures, an accelerated reductive dissolution of Fe^{III} phases shortened this inhibition period. For non-paddies, it is likely that there is no established methanogenic community to be affected by changes in temperature (Liu et al., 2018). Furthermore, non-paddies also showed lower levels of DOC, which as mentioned above, is a limiting factor on how sensitive soils are to show changes in CH_4 production at different temperatures (Wei et al., 2019).

Moreover, according to the Carbon-Quality Temperature (CQT) hypothesis, recalcitrant C compounds have a higher sensitivity to changes in temperature, based on their activation energies (Craine et al., 2010; Davidson and Janssens, 2006). Previous studies carried out in the Cixi chronosequence focused on SOC accumulation and soil development, with contrasting reports regarding SOC quality. While some studies report no significant difference in C quality across the chronosequence (Hanke et al., 2013; Zhou et al., 2014), others find accumulation of lignin phenols and humic substances (Wang et al., 2015; Liu et al., 2023). A recent study from Su et al. (2024) determined that, in paddy soils, the effects of the CQT hypothesis are more relevant with increasing depth, as recalcitrant compounds become more abundant. In the topsoil of paddies (like the ones used in our study), the degradation of labile organic matter was the determining factor increasing the response of CH_4 production with higher temperatures.

The effect of long-term paddy use on the response of CH_4 production to increased temperature can be linked to previous contrasting results. While some studies have shown none (Wang et al., 2022), slightly positive (Yun et al., 2012), or negative (Ziska et al., 1998) effects on CH_4 production when exposing paddy soils to higher temperatures, most studies have reported increases (Pereira et al., 2013; Tokida et al., 2010; Xu et al., 2020). Although cropping systems and climate have been proposed as reasons for these contrasting responses (Zhang et al., 2023), we suggest based on our results that paddy soil age can also be a contributing factor since it is directly reflected in methanogenic communities, SOC as substrate and Fe^{III}-phases as a possible inhibitor of methanogenesis. It must be noted, however, that although paddy soil development is a general process for all flooded rice fields, the rates at which changes take place also depend on climate and cropping practices.

Our results show that as paddy soils develop, the accumulated C and increased microbial activity increases CH_4 production in paddies compared to non-paddies with lower SOC contents. The C accumulated through long-term paddy use provides methanogens (and other bacterial groups) with substrates, increasing their response to changes in temperature, and thus, soil response to CH_4 and CO_2 production. These results are particularly important when considering CH_4 emission models and future predictions related to climate change. The current CH_4 emission estimations from paddy soils are between 31 and 112 Tg $year^{-1}$. The broad range of this estimation comes from lack of data regarding total irrigation area and differences in emissions with different agricultural practices (Van Amstel, 2012). It has also been reported that environmental parameters such as organic matter content, pH and redox potential affect CH_4 emissions from paddy soils and affect the precision of such predictions (Yang and Chang, 1998). Since long-term paddy use affects these parameters, considering paddy soil age in models is necessary to get more accurate predictions both for today's climate and for future climatic conditions. Since determining paddy soil age is currently difficult (in the absence of a record like the one existing for the Cixi chronosequence), we suggest that in the meantime, models should try to include the potential increase in CH_4 production not only because of increasing temperature, but also as a consequence of paddy soil aging itself. In the case of CO_2 production, our results suggest that older paddy soils with higher C stocks could be more sensitive to release stored C under future higher temperatures, having negative implications for paddy soils acting as C sinks.

3.3. Temperature effect on As mobility

Higher temperatures generally mobilized more As from all soils (Fig. 3a,b). The aqueous As concentrations were significantly higher ($p < 0.05$) at 32 °C and 35 °C compared to 30 °C, particularly in the early

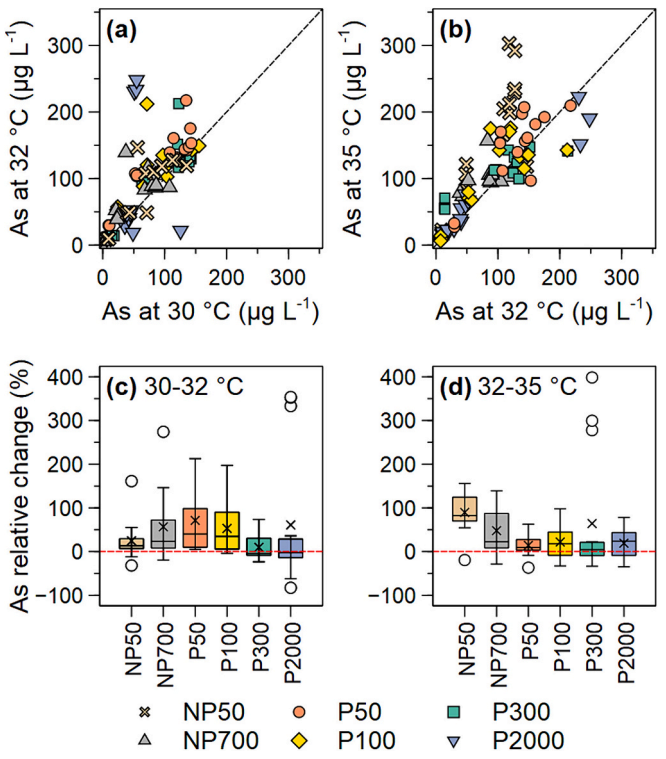


Fig. 3. Changes in aqueous phase As with incubation temperature across the chronosequence. Comparisons are done between 30–32 °C (a) and between 32–35 °C (b). Relative change in As concentration, integrated over all incubation times, based on both temperature comparisons (c, d). For a and b, data is displayed as individual results of experimental triplicates from all 5 incubation times ($n = 15$), color-coded per soil. The black dotted line represents a 1:1 line. For c and d, each box summarizes the results of triplicates through the incubation time for each soil (n = 15), with "x" showing the mean value and white circles showing outliers (1.5 IQR).

stages of the incubation (between days 1 and 5) (Fig. SI10). The relative changes in As mobility when comparing 30–32 °C (Fig. 4c) were particularly high in non-paddies and in young paddies (P50 and P100). When comparing 32–35 °C, the relative change on As mobility was increased further in non-paddies, while paddies showed lower relative changes and no age-related effect (Fig. 4d). The lower As mobility with increasing soil age is related to the high share of amorphous Fe^{III}-phases that form due to SOC accumulation. These phases act as sorption sites, lowering As mobility even under anoxic conditions. Non-paddies and young paddies, with less proportion of amorphous Fe^{III}-phases have less sorption sites, so As is easily mobilized when exposed at higher temperatures under flooded conditions.

An interesting observation is how much more As is mobilized from NP50 at 35 °C compared to 30 °C and 32 °C (Figs. 3a,b, SI10). Sequential extractions (Fig. SI11) showed that NP50 had the highest contributions of easily mobilizable As (F2, Table SI1), and around 5.0 % of the total solid phase As was classified as weakly bound (theoretically defined as ΣF1 - F3), compared to 3.4 % of NP700. This higher proportion of easily mobilizable As is likely related to its early stages of soil development, since long-term paddy use causes wash out of different elements, including As (Kölbl et al., 2014). The wash out of As likely takes longer in non-paddies compared to paddies, since they are not exposed to the high volumes of water used in paddy management.

A second interesting observation is on P2000, which showed a 4.4-fold and 3.5-fold increased As concentration at day 3 when incubated at 32 °C and 35 °C, respectively, compared to the incubations at 30 °C (Fig. SI10). This high mobilization corresponds to the period of high Fe reductive dissolution. The fast rate of dissolution of a high proportion of amorphous Fe^{III}-SOC phases likely releases bound As into the aqueous phase. Supporting this observation, the sequential extraction (Fig. SI11) showed that P2000 had the highest contribution of weakly bound As (8.1 %) meaning that even though Fe^{III}-SOC associations are an effective sink for As, their fast reductive dissolution under increasing temperatures could act as an As source. However, the As concentrations then decrease strongly by day 5 (Fig. SI10), being even lower than those in the incubations at 30 °C. This drop corresponds to the start of DSR in P2000 (Fig. SI7), so the precipitation of secondary mineral phases such as Fe-S, As-Fe-S, and As-S could be responsible for the rapid removal of As from the aqueous phase (Xu et al., 2019; Burton et al., 2014; Burton et al., 2013). In contrast, non-paddies with lower S concentrations and less effective DSR had no effective sink for aqueous phase As over the time of our experiments. This is reflected in the constantly increasing concentrations of aqueous phase Fe (Fig. SI3a) and As (Fig. SI10a) in NP50.

In summary, we have previously shown that paddy soil development generally decreases As mobility due to effective sorption to amorphous Fe^{III}-SOC associations, together with reprecipitation as or sorption to secondary mineral phases. This is also effective in future warmer temperatures, with older paddies showing the least relative changes in As mobility. Younger paddies and soils that have never been used as paddies before were more sensitive to show an increased As mobility. According to our results, As mobility is highly dependent on temperature in freshly reclaimed non-paddies when first flooded, so there could be particular risks of high As mobilization when transforming upland soils or marshlands (like the chronosequence used in the present study) into paddies. Moreover, the specific risk that this mobilization will inflict on rice production is highly dependent on the As speciation.

3.4. Temperature effect on As speciation

Enhanced microbial activity with higher incubation temperature caused a significantly higher ($p < 0.05$) share of methylated As in the aqueous phase in all paddy soils compared to the incubations at 30 °C. This temperature effect on total As methylation was higher for the first +2 °C increase (Fig. 4a), compared to the additional +3 °C (Fig. 4b). This increase was particularly high for P100 (Fig. SI12), which at 30 °C was also the soil with the highest methylation potential among all the studied paddy soils (León Ninin et al., 2024). Since the changes in total As methylation were stronger with the initial +2 °C increase, when discussing the species subgroups (oxymethylarsenates and methylthioarsenates) we will focus on the changes between 30–32 °C. The data comparing 32–35 °C is presented in Fig. SI13. The contribution of oxymethylated As (MMA and DMA) showed a sharp increase when incubated at 32 °C (Fig. 4c). While the maximum contribution of oxymethylated species to As speciation were at around 30 % at 30 °C, their share almost doubled with higher temperatures. In some cases, there was a 4-fold increase in oxymethylated As at higher temperatures when compared to 30 °C, becoming the dominating species group over inorganic oxyarsenic (Fig. SI14a,b). Arsenic methylation was not only enhanced by higher temperatures but also started earlier in the incubation time (Fig. SI15). Furthermore, while in the incubations at 30 °C the concentration of methylated As constantly increased or eventually stabilized, at 32 °C and 35 °C their concentrations peaked at some point of the incubation before decreasing. The formation of methylthioarsenates (Fig. 4d, Fig SI13b) and inorganic thioarsenates (Fig. SI13c,d) was significantly hampered ($p < 0.05$) by higher temperatures.

Since the biogeochemical cycles described in previous sections showed little differences between both non-paddies, only one of them (NP700) was selected for As speciation analyses. In NP700, As speciation was generally dominated by inorganic oxyarsenic species (Fig. SI16a) and contrary to what was observed in paddies, increasing temperature decreased the share of methylated species to total As (Fig. SI16b). Formation of thioarsenates showed a general decrease with increasing

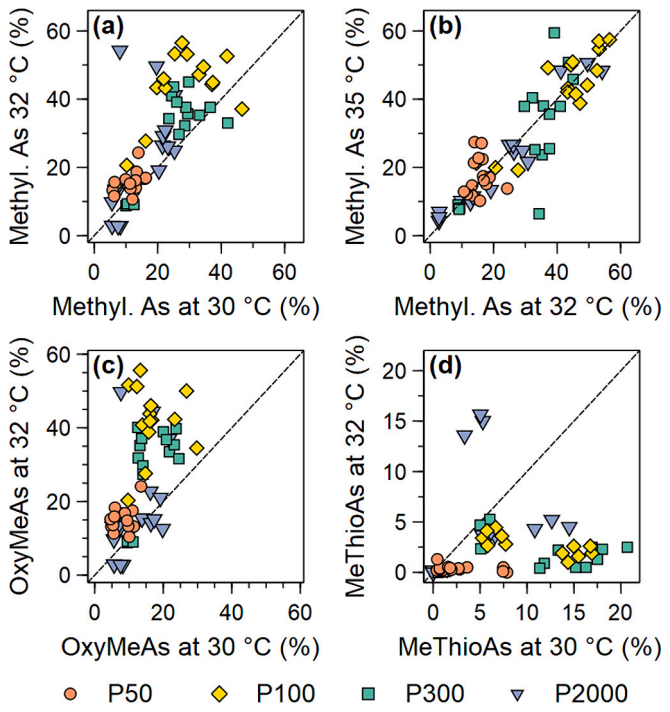


Fig. 4. Comparison of total As methylation between 30–32 °C (a), and between 32–35 °C (b) in the aqueous phase of the paddy soil chronosequence incubations. Comparison between both methylated As subgroups at 30 °C and 32 °C: oxymethylarsenates (c) and methylthioarsenates (d). Fig. SI1 shows how the individual As species have been grouped. The data is displayed as individual results of experimental triplicates from all 5 incubation times ($n = 15$), color-coded per paddy soil age. The black dotted line represents a 1:1 line.

incubation temperature, with some samples showing an increase at days 1 and 3 (Fig. SI16c,d). This period coincides with DSR in the non-paddies (Fig. SI7), suggesting a high availability of reduced S for thiolation.

Increased As methylation with higher temperature in paddy soils has been reported before and related to an increase in both bacterial activity (bacterial 16S rRNA) and abundance of the gene related to As methylation (arsenite S-adenosylmethionine methyltransferase, *arsM*) (Chen et al., 2021a; Müller et al., 2022). In non-paddies, like suggested above for methanogenesis, methylation could be limited by the low SOC and likely microbial communities not adapted to flooded conditions.

The temporal changes in the contribution of methylated As species observed at any time point is the net effect of methylation and de-methylation reactions. A net decrease in methylated As at a certain time point in the incubations at higher temperatures indicates a change in the rates of these reactions, yielding more active de-methylation. Methylotrophic methanogens have previously been suggested as playing an active role on As de-methylation (Chen et al., 2019; Chen et al., 2022; Chen et al., 2023) and considering the important increase on methanogenesis observed at higher temperatures, it is likely that they are contributing to As de-methylation.

Considering As uptake and accumulation by rice plants, and the high toxicity that inorganic As has on humans, an overall increasing share of methylated As species in paddies with future higher temperatures could be regarded as a meliorating effect. Methylated As species are, however, highly phytotoxic and reported to lead to plant sterility where no grains are produced (straight-head disease) (Zheng et al., 2013; Yan et al., 2005). Thus, when extrapolating the observations of our incubations to a soil-plant system, grain yield could decrease in paddies with already established microbial communities and a SOC pool that sustains them, but particularly in soils like P100, with high methylation potential. Most of the soils currently under paddy management are younger than 100 years old (Klein Goldewijk et al., 2017). Continued use of these paddies might increase the risk of high As methylation (as observed in P100) in a higher share of soils until the end of the century. Extent and kinetics of this shift will also depend on other factors such as individual agricultural practices or specific environmental factors.

If reduced S is available in the system, oxymethylated As species can readily go through abiotic thiolation to form methylthioarsenates (León Ninin et al., 2024; Wang et al., 2020). Considering the general increase in oxymethylated As and no major changes in pH when incubating the soils at different temperatures (Fig. SI17), the limiting factor for such a decrease in the formation of inorganic and methyl-thioarsenates can only be the lower availability of reduced S. While S reduction was observed in the aqueous phase (Fig. SI7), we suggest that the higher amount of reduced Fe with increasing temperatures scavenged the reduced S from the aqueous phase. Supporting this, no free sulfide was detected in any incubation. We have also suggested this Fe-related limitation on reduced S before, with paddies of increasing age showing a decrease in As thiolation (León Ninin et al., 2024). Interestingly, by the end of our 32 °C and 35 °C incubations, P2000 showed an increase of methylthioarsenates compared to the incubations at 30 °C. We have previously suggested that the high amount of Fe^{III} (oxy)hydroxides present in P2000 could support an active cryptic-S cycle, in which sulfide re-oxidation to S^0 is coupled to the reduction of Fe^{III} (oxy) hydroxides (Wang et al., 2020; Wind and Conrad, 1997), supplying small amounts of reduced S to the system. This supply of reduced S could support As thiolation in later stages of the incubations, even though no active DSR is taking place (León Ninin et al., 2024; Saalfield and Bostick, 2009). In non-paddies, the formation of methylthioarsenates was additionally limited by the decrease in oxymethylated arsenates as substrate.

In summary, non-paddies show a high share of inorganic oxyarsenic species, in contrast to paddies with a higher share of methylated As. While higher temperatures showed small effects in As speciation in non-paddies, +2 °C increased As methylation and decreased thiolation in all paddies. An additional +3 °C had little effect on As speciation. In the context of rice production, newly reclaimed soils and young paddies are at a major risk of showing increased As mobility when exposed to higher temperatures. These paddy soils in early stages of development also show a higher contribution of carcinogenic inorganic As to their speciation. Higher temperatures during the ripening stage and full maturation of rice plants have been correlated with higher As in rice grains (Arao et al., 2018; Dhar et al., 2023; Dhar et al., 2020; Farhat et al., 2023). The consumption of rice produced in these fields could present a risk for high inorganic As ingestion. Thus, it is key to understand how elevated temperatures will alter the dynamics of As mobility in the field (and eventual uptake by rice plants) depending on soil properties that are affected by paddy soil age. On the other hand, while older soils are less affected by increased As mobility, their higher SOC pool and microbial activity increased As methylation to an important extent. While considered to be less toxic to humans, methylated As can be phytotoxic and decrease grain yield, being a possible risk for securing sufficient yield.

4. Conclusions

The results obtained by our incubation experiments show that long-term paddy use leads to different biogeochemical responses related to increased temperature, both in terms of kinetics (accelerating processes or overruling delays) and magnitude of effect. While we focused here on two major issues related to paddy use, namely CH_4 production and As mobility and speciation, the dynamics of these processes are closely linked to the biogeochemistry of other major elements in paddy soils and their aqueous phase, mainly as a consequence of SOC accumulation with long-term paddy use. While it has been previously shown that organic C is an important parameter determining the response of soils to changes in temperature (Wei et al., 2019), this is, to the best of our knowledge, the first report considering a systematic accumulation of SOC related to long-term paddy use, rather than exogenous addition of labile C

substrates. Furthermore, another advantage of our study is that we studied the endogenous As concentrations in the soil, instead of amending them with higher As concentrations which could lead to changes in the partition of its natural binding environment. Additionally, by comparing the distinctive responses between paddies and non-paddy soils we were able to confirm that long-term paddy management modifies the response of CH_4 production to changes in temperature, As mobility and changes in As speciation. We focused here on the highly dynamic first 10 days of incubation to better elucidate changes in C, S, Fe and As redox chemistry. Next steps should include studies focusing on such changes in the field and on a temporal scale related to the cropping season, as well as considering daily temperature variations.

The last IPCC projections show that the previously established worst-case scenario is not likely and that the effects of climate change by the end of the century lay between +1.4 °C (SSP1–1.9) and + 2.7 °C (SSP2–4.5) increases in air temperature (Lee et al., 2023). It must be noted that in the context rice cultivation, the overlying water over the paddies would act as a temperature buffer, dampening the effect of air temperature on the soils. However, our results showed that the difference between current temperatures and + 2 °C is higher than between +2 and + 5 °C, so even small changes in temperature have an important effect mainly on As mobility and speciation, but also on CH_4 production. Thus, our results support previous claims of the important feedback between rice cultivation in a future climate and increased CH_4 emissions, as well as the additional constraints that altered biogeochemical dynamics could pose on food security (Muehe et al., 2019; Liu et al., 2020; Dijkstra et al., 2012).

CRediT authorship contribution statement

José M. León Ninin: Writing – review & editing, Writing – original draft, Visualization, Validation, Software, Methodology, Investigation, Formal analysis, Data curation, Conceptualization. **Alejandra Higa Mori:** Writing – review & editing, Validation, Methodology, Investigation, Formal analysis, Data curation, Conceptualization. **Johanna Pausch:** Writing – review & editing, Resources. **Britta Planer-Friedrich:** Writing – review & editing, Writing – original draft, Supervision, Resources, Project administration, Funding acquisition, Conceptualization.

Declaration of competing interest

The authors declare the following financial interests/personal relationships which may be considered as potential competing interests:

Britta Planer-Friedrich reports financial support was provided by the Federal Ministry of Education and Research Bonn Office. Jose M. Leon Ninin reports financial support was provided by German National Merit Foundation. If there are other authors, they declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Data availability

The data generated and analyzed for the current study are also available from the corresponding author on reasonable request.

Acknowledgements

We thank the German Academic Scholarship Foundation for the doctoral funding support for J.M.L.N and funding within the Federal Ministry of Education and Research project BMBF #031B0840 to B.P.-F. We thank Livia Urbanski and Angelika Kölbl for providing the chronosequence soils, Asel Traut for her help with the early lab work, Dr. Ben Gilfedder for providing access to CH_4 and CO_2 measurements, and Ilse Thaufelder for her assistance with the DOC analyses. The graphical abstract was created using Biorender.

Appendix A. Supplementary data

Supplementary methods with a detailed protocol for the Sequential Extraction Procedure (SEP) and example chromatogram indicating As species grouping. Supplementary data and figures showing biogeochemical data supporting the above-described observations and discussion. Supplementary files with additional statistical information from the one- and two-way-ANOVAs. Supplementary data to this article can be found online at https://doi.org/10.1016/j.scitotenv.2024.173793.

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