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Estimating microbial growth and hydrogen consumption in hydrogen storage in porous media

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ABSTRACT

Subsurface storage of hydrogen, e.g. in depleted oil and gas fields (DOGF), is suggested as a means to overcome imbalances between supply and demand in the renewable energy sector. However, hydrogen is an electron donor for subsurface microbial processes, which may have important implications for hydrogen recovery, gas injectivity and corrosion. Here, we review the controls on the three major hydrogen consuming processes in the subsurface, methanogenesis, homoacetogenesis, and sulfate reduction, as a basis to estimate the risk for microbial growth in geological hydrogen storage. Evaluating our data on 42 DOGF showed that five of the fields may be considered sterile with respect to hydrogen-consuming microorganisms due to temperatures >122 °C. Only six DOGF can sustain all of the hydrogen consuming processes, due to either temperature, salinity or pressure constraints in the remaining fields. We calculated a potential microbial growth in the order of 1–17*10^7 cells ml^{-1} for DOGF with favorable conditions for microbial growth, reached after 0.1–19 days for growing cells and 0.2–6.6 years for resting cells. The associated hydrogen consumption is negligible to small (<0.01–3.2% of the stored hydrogen). Our results can help inform decisions about where hydrogen will be stored in the future.

1. Introduction

Zero-carbon energy generation from renewable sources can help mitigate carbon emissions and abate climate change [1–3]. One of the most significant challenges for renewable energy is the imbalance between supply and demand [3,4]. The generation of hydrogen (H_2) via electrolysis of water during periods of renewable energy oversupply and subsequent H_2 storage is one way of overcoming this imbalance, as H_2 can be recovered and used for electricity generation during periods of renewable energy shortage [1,5]. Subsurface storage of H_2 in salt caverns, depleted gas or oil fields or saline aquifers is being considered as an alternative to expensive purpose-built storage containers [6]. However, the artificial elevation of the H_2 concentration in the subsurface may stimulate the growth of H_2-oxidizing (hydrogenotrophic) bacteria and archaea, here collectively referred to as microorganisms, with possible adverse implications for gas injectivity and withdrawal via permeability reduction, H_2 volume loss and corrosion of metal infrastructure [4,7]. Understanding the controls on microbial H_2 metabolism is therefore highly important.

Much of the subsurface is characterized by combinations of elevated temperature [7], high salt concentrations and high pressure [3], reduced void space [8], limited nutrient availability [9] and typically highly reducing conditions [9–11]. The evidence for microbial life at depth is plentiful (e.g. Refs. [12–16]). Most microorganisms in nature grow in biofilms attached to surfaces (communities of aggregated microbial cells embedded in a secreted matrix of extracellular polymeric substances (EPS)) [17,18]. Even small amounts of biofilm can reduce pore throat sizes and increase the flow-path tortuosity, resulting in dramatic decreases in permeability [19].

Hydrogen plays a central role in the energy metabolism of subsurface life [9]. Yet, a quantitative assessment of the consumption of H_2 by deep microbial communities in the context of the global H_2 cycle is lacking [20]. In underground gas storage sites and oil reservoirs the most abundant H_2-oxidizers are hydrogenotrophic sulfate reducers, that couple H_2-oxidation to sulfate reduction to produce hydrogen sulfide

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Abbreviations and units

SSR	Sulfur species reduction
SSRM	Sulfur species reducing microorganisms
DOGF	Depleted oil and gas fields
EPS	Extracellular polymeric substances
M	Molarity (mol L^{-1})
MPa	Megapascal

(H_2S); hydrogenotrophic methanogens that reduce carbon dioxide (CO_2) to methane (CH_4) by oxidizing H_2; and homoacetogens that couple H_2 oxidation to carbon dioxide (CO_2) reduction to produce acetate [7,21–23]. These three groups of microorganisms are, amongst others, implicated in causing subsurface corrosion [7,22,24].

Several recent reviews discussed the potentially very important role of microbial activity in geological H_2 storage [6,7,23,25,26]. Gregory et al. [7] addressed the many possible abiotic and biotic H_2-producing and H_2-consuming processes in the subsurface. Dopffel et al. [23] characterized different microbial issues, giving key indicators for the processes, and advised in the monitoring and management of microbial activity in subsurface H_2 storage. Strobel et al. [26] summarized the concept and potential of underground methanation using experimental data from the Sun Storage project [27]. The authors highlighted controls on the growth of methanogens and changes in gas composition due to methanogenesis. All of the above efforts lacked a quantitative assessment of the processes of microbial growth and H_2 consumption relevant for H_2 storage. Indeed, many studies report changes in gas composition, biofilm growth and clogging near injection wells but hardly any provide quantitative figures on microbial growth or on permeability changes [28].

To date it remains unclear how subsurface microorganisms might react to elevated H_2 concentrations [7] and hence whether microbial growth is a concern for H_2 storage. Even in natural, non-engineered subsurface environments, there is little information on microbial H_2 turnover rates [29] and the behavior and population kinetics of microorganisms are not fully understood [26]. The majority of the available data on microbial H_2 turnover rates come from batch cultures at optimal growth conditions where the kinetics [29], the pace of life [30,31], the physiological states and the prominent organisms may differ widely from the subsurface environment [7,30]. A further complication arises from the fact that many microorganisms in the deep subsurface are not culturable with modern enrichment techniques [12,32].

In this work, we review the state-of-the-art understanding of the controls of temperature, salinity, pH, pressure and nutrients on microbial growth on H_2 in the subsurface, with emphasis on the three major H_2-consuming processes methanogenesis, sulfate reduction and homoacetogenesis, to determine what reservoir conditions will be unfavorable to microbial activity and as such more suitable sites for long term gas storage operations of 30 years or longer, such as the UK Rough gas storage site.

Physicochemical data from 42 depleted or close to depleted oil and gas fields (DOGF) of the British and Norwegian North Sea and the Irish Sea as well as five H_2 storage test sites provide the base for an evaluation of the number of sites where microbial growth of methanogens, sulfate reducers and homoacetogens can be expected. Using average nutrient contents of the microbial cells and site-specific dissolved ion concentrations, we calculate significant growth and a small H_2 consumption for growth-permitting DOGF.

2. State of the art understanding

2.1. Likely microbial hydrogen oxidation in hydrogen storage systems

Hydrogen oxidizing processes may be ranked according to the magnitude of their H_2 threshold and their standard free energy change ($\Delta G^{0'}$), two useful metrics to compare the likelihood of reactions to take place and the order at which they proceed (Table 1). The H_2 threshold defines the concentration of H_2 below which it is no longer consumed. Given all other factors are at optimum, the microbial population with the lowest H_2 threshold value is expected to be the most successful population in competing for H_2 [33].

The $\Delta G^{0'}$ marks the thermodynamic favorability of a reaction at ambient pressure and temperature, pH 7 and 1 M of all reactants. In oligotrophic (nutrient poor) high pressure and temperature environments, the order of the $\Delta G^{0'}$ may be used to determine which reaction is more energetically favorable. As can be seen from Table 1, more negative $\Delta G^{0'}$ values (more available free energy) are generally accompanied by lower H_2 thresholds. Not included in Table 1 are the kinetics which describe the rate of the electron transfer in the redox reaction. Abiotically, most of the H_2-oxidizing reactions are very slow but mediated by microbial enzymes the processes are catalyzed [35,39].

The three main microbial processes with implications for H_2 storage, hydrogenotrophic sulfate reduction, hydrogenotrophic methanogenesis (for simplicity from now on just referred to as sulfate reduction, and methanogenesis unless otherwise specified) and homoacetogenesis, require the highest threshold [H_2] and are among the processes with lowest $\Delta G^{0'}$ (Table 1). Nevertheless, e.g. sulfate reduction is instantaneous in most geologic settings [40] possibly due to fast kinetics [35] and/or a relatively high availability of sulfate.

Because sulfate reducers may use the same substrates as sulfur reducers (i.e. sulfide and thiosulfate [41,42]), they are here collectively referred to as sulfur species reducing microorganisms (SSRM) performing sulfur species reduction (SSR). Direct respiration of sulfur is limited by its low solubility ($1.6*10^{-7}$ M) and hence requires cell attachment to the sulfur particle [43]. However, sulfur readily reacts with sulfide formed during the reduction of sulfate to form easily metabolizable polysulphides [43,44].

Iron (III) reduction relies on the availability of iron oxides and iron-bearing minerals such as smectite and chlorite [45,46], as well as the availability of organic carbon, since dissimilatory iron reducing bacteria (DIRB) are strict heterotrophs, i.e. synthesize cell carbon from organic compounds [47]. Iron oxides are abundant in many sediments and aquifers [45] but are typically not available in the carbon-rich oil fields because they have been reduced over millions of years and are not replenished [21]. Meanwhile, bacteria capable of reducing iron are frequently isolated from hydrocarbon-contaminated or oil-associated sites (reviewed in Ref. [48]). However, the mere observation of iron reduction by bacteria, which are given a DIRB enrichment medium in the laboratory, does not imply that these bacteria will reduce iron in nature. In addition, cell counts are often low to intermediate (10–100 cells ml^{-1}) and may include non-hydrogenotrophs (e.g. Refs. [49,50]). In non-engineered environments rich in Fe oxides and organic carbon, DIRB may have a great advantage over SSRM, methanogens and homoacetogens, due to a very high affinity for H_2 [45]. We evaluate this process as of intermediate relevance for H_2 storage in DOGF.

Many DIRB and a few SSRM can also couple H_2 oxidation to reduction of a variety of other trace metal oxides, e.g. MnO_4^{2-}/MnO_2, CrO_4^{2-}, Co, SeO_4^{2-}, UO_2^{2}, TcO_4^{-}, AsO^{3-}, and VO_4^{-} [41,51,52]. After Fe, the most abundant metal in sedimentary environments is Mn (~10% of Fe abundance) [45,51]. Due to the trace content of these compounds in the environment, their reduction has low relevance for H_2 storage.

Oxygen and nitrate are scarce in the subsurface [11,21,53,54] and aerobic hydrogen oxidation, denitrification and ammonification hence only become significant when contamination of the aquifer occurs, e.g. by drilling fluid [55–57].

Halogenated compounds are common in aquifers, and may arise from contamination or via natural processes in sediment [58,59]. However, the concentrations of these compounds are extremely low: In aquifers of 170–1000 m depth, chloroflourocarbons reach maximum concentrations of $\leq$1.1 μg L^{-1} [59] and for pristine aquifers

Table 1
Biotic H_2-consuming processes ranked according to their free energy yield ($\Delta G^{0'}$) and measured H_2 threshold. Not included are Vanadium, Cobalt, Techneticum, Uranium and Selenium reduction, due their limited relevance for H_2 storage. NA = not available.

H_2- oxidizing process	Reaction	H_2 threshold (nM)	$\Delta G^{0'}$ (KJ mol H_2^{-1})	Typical ambient [H_2] (nmol L^{-1})	Relevance for H_2 storage
Chromate reduction	$\frac{1}{2}H_2 + \frac{1}{3}CrO_4^{2-} + \frac{5}{3}H^+ \rightarrow \frac{1}{3}Cr^{3+} + \frac{4}{3}H_2O$ (1)	<0.1 [34]	NA	NA	low
Aerobic hydrogen oxidation (Knallgas)	$H_2 + \frac{1}{2}O_2 \rightarrow H_2O$ (2)	0.051 [7]	−237 [7,34]	NA	low
Denitrification	$H_2 + \frac{2}{5}H^+ + \frac{2}{5}NO_3^- \rightarrow \frac{1}{5}N_2 + \frac{6}{5}H_2O$ (3)	<0.05–0.5 [7]	−240.1 [7,34] −224 [4,35]	<0.05 [4,33,34]	low
Halorespiration	$H_2 + halogenated\ \ compounds \rightarrow dehalogentated\ \ compounds + HCl$ (4)	0.05–0.27 [34] <0.3 [36] 0.27–2 [7]	−230 to −187 [7]	NA	low
Iron (III) reduction	$H_2 + ferric(oxy)hydroxides \rightarrow ferrous\ \ iron + H_2O$ (5)	<0.11–0.8 [34,36]	−228.3 [7,36] −182.5 [34] −114 [4]	0.2 [4,33] 0.2–1 [34]	intermediate
Manganese (IV) reduction	$2H_2 + MnO_2 \rightarrow Mn(OH)_2 + 2H_2O$ (6)	<0.05 [33]	−163 [4,33]	<0.05 [4,33]	low
Arsenate reduction	$H_2 + HAsO_4^{2-} + 2H^+ \rightarrow H_3AsO_3 + H_2O$ (7)	0.03–0.09 [34]	−162.4 [34]	0.4–0.7 [34]	low
Ammonification	$4H_2 + 2H^+ + NO_3^- \rightarrow NH_4^+ + 3H_2O$ (8)	0.015–0.025 [36,37]	−150 [4,36]	<0.05 [4,33]	low
Fumarate reduction	$H_2 + fumarate \rightarrow succinate$ (9)	0.015 [36,37]	−86.2 [36]	NA	low
Hydrogenotrophic sulfate reduction	$4H_2 + SO_4^{2-} + H^+ \rightarrow HS^- + 4H_2O$ (10)	1-15 [36,37]	−38 [7,36] −48 [34] −57 [4]	1-2 [4,33]	high
Hydrogenotrophic methanogenesis	$4H_2 + CO_2 \rightarrow CH_4 + 2H_2O$ (11)	0.4–95 [36–38]	−34 [4,36] −43.9 [34]	5-10 [4,33] 7-13 [34]	high
Sulfur reduction	$H_2 + S \rightarrow HS^- + H^+$ (12)	2500 [7]	−33.1 [7]	NA	intermediate
Homoacetogenesis	$4H_2 + 2CO_2 \rightarrow CH_3COOH + 2H_2$ (13)	328-3640 [36,37]	−26 [4,36] −36.1 [34]	100< [4], 117–150 [34]	high

0.003–0.007 μg L^{-1} of chlorinated hydrocarbons were measured [58]. We evaluate the relevance of this process to H_2 storage as negligible.

Literature on the importance of anaerobic fumarate respiration using H_2 is scarce. Fumarate may be used as an alternative electron acceptor by SSRM [41,60] and homoacetogens [61–64]. In the non-engineered subsurface, readily metabolizable organic matter, like fumarate, is rare [65]. Oil fields being rich in organic C compounds may contain more fumarate. Payler et al. [12] confirmed the presence of fumarate reductase, the key enzyme in fumarate reduction, in three out of five metagenomes from subsurface brines within sandstone. However, the metagenomes belonged primarily to non-H_2 utilizing bacteria (*Halorubrum*) and fumarate concentrations were not reported. Acknowledging the lack of data in this field, we evaluate this process as being of low relevance for H_2 storage.

2.2. Environmental controls on microbial growth

Microbial growth and H_2 consumption rates vary with nutrient availability and environmental variables (e.g. Refs. [17,66].) Each strain is adapted to an optimum set of nutrients and environmental conditions where potentially the greatest growth rates occur. Beyond the optimum conditions, organisms may grow but at reduced rate or they become dormant. In this section, we discuss the requirements for nutrients, and the overall impact of temperature, salinity, pH and pressure on the growth of the major microbial H_2–oxidizers in DOGF, in the ranges relevant to H_2 storage. The specific activity of microbial strains grown at optimum conditions varies as well (reviewed in Ref. [67]) but the elucidation of differences between strains is beyond the scope of this review.

2.2.1. Nutrients

The nutrient requirements of H_2-oxidizing microorganisms are poorly elucidated. Often, only a limited number of single strains within each diverse metabolic group have been investigated, which are unlikely to be representative of all strains. Below we summarize the few knowns.

Apart from water of sufficient thermodynamic activity (see section 2.2.4), hydrogenotrophs require H_2 as a source of electrons (energy), an electron acceptor and a carbon source for cell division, as well as a set of macro and trace elements and various organic nutrients [68]. Microorganisms can only access $H_{2(aq)}$ and hence the solubility of $H_{2(g)}$ is of direct relevance for all H_2-consuming reactions. Given a gas phase of ~100% H_2 in an H_2 storage system, the equilibrium solubility of H_2 exceeds the highest threshold value of an H_2-consuming microorganism of 3.6 μM (Table 1) by ~3 orders of magnitude at ambient pressure and temperature and under static conditions (Fig. A1a), with further increase at higher pressures (Fig. A1b and c). While under non-static conditions hydrogenotrophs will consume part of the H_2, these figures suggest no limitation by the H_2 solubility on microbial growth under H_2 storage conditions.

Elemental requirements include the macro elements C, N, H, P, Ca, Mg, S and Fe (>95% of the microbial cell dry weight), and the trace elements Co, Mn, Ni, Mo, Cu, Zn, W as well as Se for some metabolic groups [69,70]. For optimum growth, many microorganisms additionally require different vitamins (e.g. lipoic acid, biotin, riboflavin, folic acid, thiamine, etc.), yeast extract, coenzyme M, aromatic acids and phospholipids or a combination of these (e.g. Refs. [8,63,71–73]).

Nutrients may be assimilated from the solution or directly from minerals (e.g. Refs. [74–77]), the latter being of particular importance in oligotrophic environments [75]. Carbon, sulfur, phosphorous and iron are amongst the key elements released by mineral weathering [75]. The extent to which subsurface microbial communities depend on mineral weathering is unknown [75]. For soils, Huang et al. [78] analyzed that >50% of the 1100 microbial strains were capable of mineral weathering, as tested by their ability to mineralize biotite.

Microbial cell carbon may be assimilated from CO_2 alone (autotrophy) or from organic carbon compounds (heterotrophy) [79].

Table 2
Reservoir conditions for depleted, or soon to be depleted oil and gas fields. Except where otherwise indicated, the data are from Ref. [172]. ® = reference [171]. The salinity was calculated from the chloride concentration and the concentration of dissolved N_2 was estimated from the mol percentage in the gas phase, neglecting any effect of salinity. NA = not analyzed. See Table A4 for extended data.

Field name	Area (Km^2)	P (MPa)	Temp (°C)	Salinity (M)	pH	HCO_3^- (mM)	N_2 (mM)	SO_4^{2-} (mM)	K^+ (mM)	Ca^{+2} (mM)	Mg^{+2} (mM)	P (mM)	Na^+ (mM)	Cl^- (mM)	Fe^{+2} (mM)	Organic acids (mM)
Frigg	100	19.5	61	0.07–0.53	6.5–7.4	16.3	0.4	NA	26.3–31.2	0.4–2.0	1.9–7.1	NA	75.2–534.8	58.7–490.3	0.04–0.27	NA
Hamilton	15	9.6	30	1.59–4.18	5.8	4.8	2.1	0.6–7.4	8.4–29.7	72.8–720.0	19.5–37.6	0.012–0.028	1354.8–2210.9	1453.3–3700.7	4.03	NA
Barque	36	26.0	79	4.83	4.7	0.3	0.8	3.5	42.2	535.0	156.8	NA	2920.4	4405.4	2.15	NA
Hamilton North	8	10.5	30	2.93	7.9	11.0	2.3	23.1	18.8	13.6	13.6	NA	2640.9	2662.9	NA	NA
Miller	45	49.3	121	1.61	7.2	NA	0.6	0.0	41.6	30.0	NA	NA	1358.7	1471.9	0.02	NA
Beryl	49	36.0	101	1.88	6.1	5.6	0.4	0.0	20.8	90.0	NA	NA	1469.6	1717.9	0.05	1.9
Judy (Andrew 1)	NA	46.9	137	0.14–0.15	6.8	8.4	0.6	6.4	2.9	4.5	NA	0.002	117.4	131.7	0.11	NA
Amethyst	97	27.9	88	4.45	5.6	1.0	1.6	3.7	33.2	521.5	148.5	0.452	2673.9	4064.6	2.51	NA
Rhyl	NA	14.9	36	5.80	5.5	13.5	2.8	14.0	62.4	147.0	21.2	0.031	4777.0	5297.9	0.81	>1.2
Dalton	NA	28.8	91	0.26	5	0.9	1.0	1.8		15.6	5.5	NA	189.1	237.0	0.00	NA
Davy	6	28.2	88	3.87	6.8	6.5	NA	7.0	219.2	15.6	10.7	0.155	818.3	1142.7	0.66	NA
Veslefrikk®	NA	29.8–35.0	67–114	0.29–0.72	6.5	8.4–17.2	NA	0.1–0.15	NA	NA	NA	NA	298.0–666.0	281.0–745.0	NA	2.2–8.1
Average						7.9	1.1	5.2	44.7	166.8	42.2	0.113	1473.7	1857.4	0.97	3.3

Methanogens and homoacetogens can grow autotrophically or heterotrophically, and several can grow mixotrophically (e.g. Refs. [64,80,81]). SSRM typically grow heterotrophically but some grow autotrophically or mixotrophically [82,83]. Nitrogen may be assimilated from ammonia and nitrate or by nitrogen-fixation (diazotrophy). Diazotrophy is common amongst SSRM, methanogens and homoacetogens [84–87], though homoacetogens often inhabit ammonia-rich environments [86].

Little is known about the differences in the nutrient requirements on the level of functional groups and the variation in nutrient requirement within a functional group. SSRM have a higher requirement for iron ($1.8*10^{-6}$ M) than is usually observed for microorganisms [88] while methanogens have a higher requirement for sulfur with optimal levels ranging from 0.03 to 0.79 mM (reviewed in Ref. [89]).

Literature on when nutrients become limiting is also scarce. Sulfate reduction may occur down to 5–77 μM sulfate [90,91]. Specific data on the phosphorous requirement of the major H_2-oxidizing microbial groups are outdated/lacking but research on other extremophiles indicates that phosphorous concentrations as low as 1.7 μM may be sufficient for growth [92]. Methanogens of the order *Methanosarcinae* require 29.6 mM Mg for optimum growth and growth ceases at 16.5 mM (reviewed in Ref. [89]). When grown under optimum conditions, the growth rate of autotrophs may be limited by the rate of transfer of H_2 and CO_2 from gas to liquid, as was shown for the methanogen *Methanobacterium thermoautotrophicum* [93] and for the sulfate reducers within *Desulfotomaculum* sp. [94].

Carbon is unlikely to be limiting in the hydrocarbon-rich DOGF [54,95,96] but this is not a given in saline aquifers with no history of oil or gas. Sulfate is present in significant concentrations in most DOGF (Table 2) but H_2 injection can cause sulfate depletion due to accelerated growth of SSRM [97]. Nitrogen in the form of the preferred N-source, ammonium [98], may be limiting in DOGF [49,54,88] but nitrate levels of may be elevated [49], often due to contamination by drilling fluid [55–57].

2.2.2. Temperature

Temperatures of 22.5–80 °C or 20–100 °C have been suggested for H_2 storage based on a recommended depth range of 500–2000 m for H_2 storage in DOGF and saline aquifers [99–101]. Microorganisms are classified according to their preferred growth temperature: psychrophiles grow optimally below 20 °C, psychotrophs grow optimally at or above 20 °C and may tolerate temperatures below 5 °C, mesophiles grow between 20 and 45 °C, thermophiles grow above 45–50 °C, and

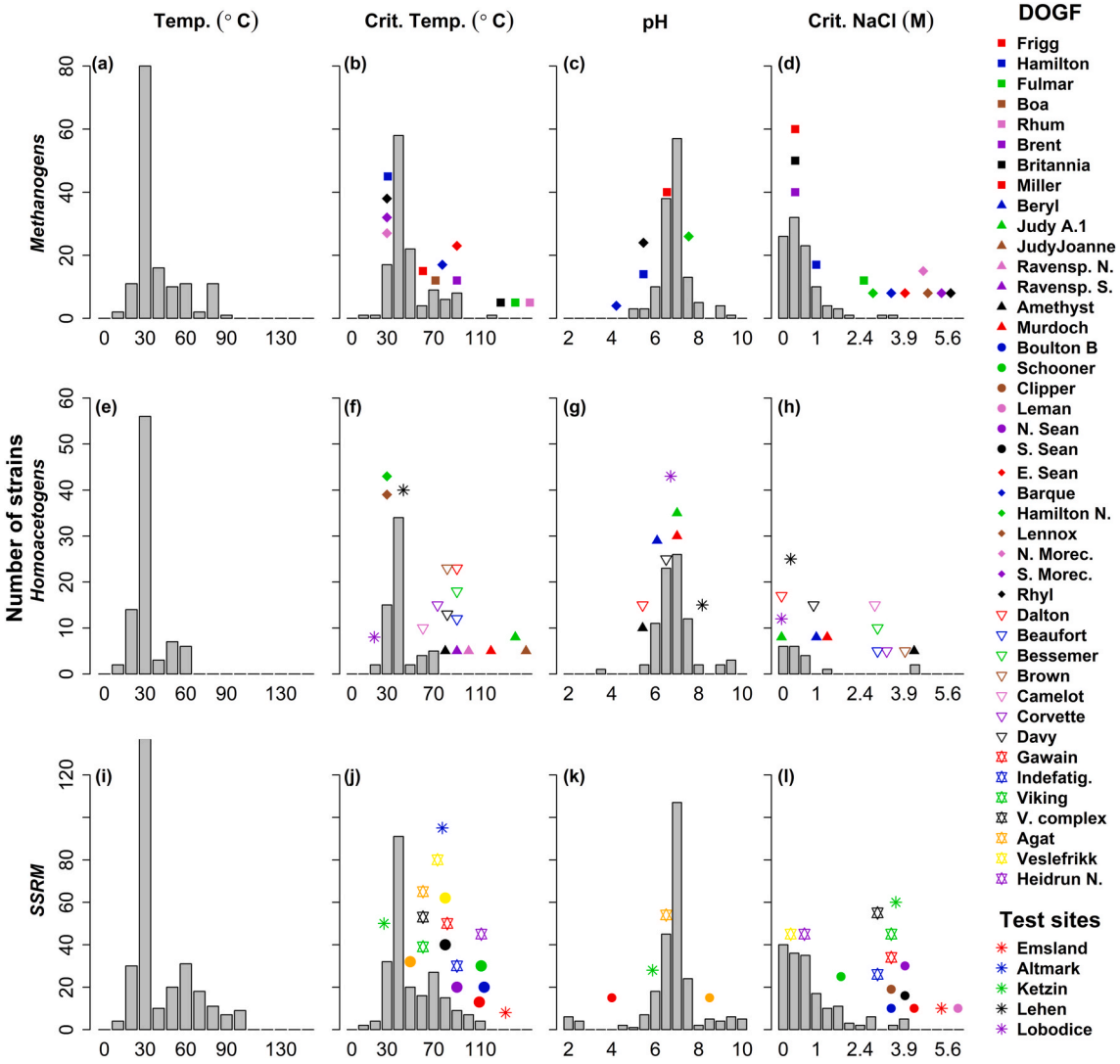

Fig. 1. Distribution of optimum growth temperature, critical growth temperature, optimum pH values and critical salinity for 101–143 methanogens (a–d), 19–88 homoacetogens (e–h) and 165–277 sulfur species reducing microorganisms (SSRM) (i–l). Distributed between the graphs for the different groups of H_2-oxidizers are the temperatures, pH values and salinities of 42 depleted oil and gas fields (DOGF) and five test sites for H_2 injection. Where ranges of a parameter were given (see Table A4), the lower end value was plotted.

hyperthermophiles show optimal growth at temperatures of 80 °C or above [102,103]. The upper limit for life is 121–122 °C [104,105].

High temperatures alter the energetic properties (e.g., vibrational modes) of biomolecules in their aqueous solvent, change the substrate solubility or viscosity and the ionization of the aqueous medium [106]. Adverse effects of high temperature include DNA denaturing or damage, decreased protein stability, hydrolysis of ATP and ADP, amongst others [104,106]. The metabolic strategies of thermophiles are highly diverse. For a discussion, the reader is referred to Ref. [107].

Thermophiles and hyperthermophiles are challenged by increased reaction rates at elevated temperature which can imply that abiotic reaction rates are so fast that there is no benefit to the microorganism if it catalyzes the reaction [39]. High-temperature-adapted microorganisms are therefore thought to produce enzymes with faster reaction rates [108].

Most cultivated hydrogenotrophic methanogens are mesophiles but known optimal growth temperatures for methanogens range from 15 to 98 °C (Fig. 1a). A considerable number of methanogens favor temperatures above 60 °C (Fig. 1a). The highest temperature that a methanogen was found to grow under is 122 °C (*Methanopyrus kandleri*) (Fig. 1b) [105].

Cultivated SSRM typically have optimum growth temperatures of 20–30 °C or 50–70 °C (Fig. 1i), where sulfur reducing archaea have higher optimum growth temperatures than sulfur and sulfate reducing bacteria. The full range for optimum growth of SSRM spans 10–106 °C (Fig. 1i). The critical temperature for growth of cultivated SSRM is 113 °C (*Pyrolobus fumarii*) [109].

Homoacetogens typically have optimum growth temperatures between 20 and 30 °C (85% of the here gathered cultivated strains; Fig. 1e). Thermophilic growth at temperatures ≥60 °C has been reported for eight strains, only (e.g. *Moorella mulderi*, *Thermoanaerobacter kivui*, *Acetogenium kivui*) [110–112]. Corresponding upper limits for growth are 70–72 °C (Fig. 1f) [110–112].

2.2.3. Salinity

The relevant salt concentration range for H_2 storage is 0–5 M NaCl [100], at which highly diverse prokaryote communities can be found [113]. Microorganisms are classified according to their salt tolerance: Non-halophilic microorganisms grow up to 0.2 M NaCl, slight halophile grow at 0.2–0.5 M NaCl, moderate halophile between 0.5 and 2.5 M NaCl, and extreme halophile that grow best in hypersaline media containing 2.5–5.2 M NaCl [113].

High salt concentrations exert osmotic stress [114], requiring any microorganism living at high salt concentrations to maintain its intracellular environment at least isosmotic with the environment [113]. Two main strategies to achieve osmotic balance exist: the salt-in strategy, and at the exclusion of salt and biosynthesis/accumulation of organic 'compatible' solutes [115]. For a discussion of these strategies in relation to different metabolic pathways, the reader is referred to Ref. [115]. Commonly, salt tolerance/requirement is enhanced at increased temperatures [113] but there are many examples of mesophilic halophiles.

Most cultivated hydrogenotrophic methanogens favor salt concentrations up to 0.77 M NaCl (the approximate salinity for seawater) but 16 known strains survive under more halophilic conditions. Two extremely halophilic mesophilic hydrogenotrophic methanogens, will tolerate salt concentrations of ~3.3–3.4 M, *Methanocalculus halotolerans FR1T* [116] and *Methanocalculus natronophilus* [117] (Fig. 1d).

The large majority of cultivated SSRM grow optimally at low salinities between 0 and 0.4 M NaCl. However, thirtyfour SSRM (all mesophiles) have upper salinity limits for growth of ≥1.7 M NaCl (Fig. 1l). The *Desulfovibrio oxyclinae*, *Desulfohalobium utahense* and *Desulfohalobium retbaense,* have some of the highest upper salinity limits for growth of 4.0–4.2 M NaCl [118–120] (Fig. 1h).

The salt tolerance of homoacetogens is poorly investigated. The majority of cultivated homoacetogens have low optimum salinities of 0–0.4 M NaCl. However, a few strains, i.e. *Natroniella acetigena* and *Acetohalobium arabaticum*, grow optimally around 2.5 M NaCl and will tolerate salinities up to 4.3–4.4 M (Fig. 1h) [121,122]. The upper growth temperatures for these strains are 42 and 47 °C, respectively [121,122].

A clear upper salinity limit to microbial activity has not been established [23,115]. It appears to be the brine composition, rather than the salinity alone, that puts a hard limit on microbial growth [12], see section 2.2.4. Salt tolerances based on activity measurements from natural microbial communities match results from laboratory studies on cultivated microorganisms for most metabolic pathways [115]. For sulfate reduction, however, activity measurements of natural microbial communities (using any available electron donor) indicate an upper salinity limit of 4.7–8.1 M NaCl [123–125].

2.2.4. Brine complexity

Natural brines contain dissolved ions whose interaction is extremely complex and may cause physicochemical stressors to brine habitability such as low water activity (a_w), high ionic strength, chaotropy (ability to disrupt the network of H_2-bonds between water molecules) or a combination of these [12]. Most bacteria grow well at a a_w around 0.98 (the approx. a_w for sea water) but relatively few species can grow at a a_w of 0.96 or lower [126]. Halophilic microorganisms, including halophilic methanogens are one exception; several can grow at a a_w as low as 0.75 [127] in Refs. [126,128]. Steinle et al. [129] challenged these limits by detecting SSR in a nearly $MgCl_2$ saturated brine with a a_w of ~0.4.

There are indications of a more important role of chaotropy over a_w in limiting microbial life [128]. Chaotropic agents include $MgCl_2$, $CaCl_2$, $FeCl_3$, KI, LiBr, LiCl while examples of kosmotropic agents are NaCl, KCl, Na_2SO_4, $MgSO_4$, K_2SO_4, $FeSO_4$ [130]. As such one may speculate that most subsurface brines due to their dominance of NaCl and richness in sulfate are kosmotropic and albeit also stress-inducing, more permissive of microbial growth [12,128]. Yet, the interactions between chao- or kosmotropic agents, a_w and other physicochemical properties of brines may be very complex and are hitherto not understood [12]. The further elucidation of this topic is subject to more research and beyond the scope of this paper.

2.2.5. pH

The brine pH may affect the growth of microorganisms via 1) a direct effect on the growth metabolism, and 2) an effect on the redox reaction. With respect to the former, most methanogens, homoacetogens and SSRM are adopted to a pH of 6.5–7.5 (Fig. 1c, g, k). Most methanogens and SSRM cannot grow outside the pH range 4–9.5 [26,131,132] (Fig. 1c, k). Seven known methanogens can endure a critical pH-value of 10 (e.g. the *Methanocalculus natronophilus* and *alkaliphilus* [133]). At the other end of the spectrum, nine known methanogens can endure acidic conditions of pH <5, e.g. the *Methanoregula boonei*, the *Methanothermococcus okinawensis*, the *Methanosarcina spelaei* and the *Methanocaldococcus bathoardescens* [134–137].

Eighteen known SSRM are adapted to highly alkaline environments above pH 10, e.g. the *Desulfonatronovibrio hydrogenovorans,* the *Desulfurispira natronophila* and the *Desulfovibrio vietnamensis* [138–140]. Twentysix known SSRM grow down to a pH <5. Nine known SSRM, all of them sulfur reducers, grow down to a pH of 1, e.g. the *Thiobacillus caldus,* the *Sulfolobus acidocaldarius*, the *Acidianus infernus* and *brierleyi*, and the *Stygiolobus azoricus* [141–144].

Six known homoacetogenic strains have high critical pH values of 10.0–10.7, i.e. *Clostridium ultunense*, *Natroniella acetigena, Fuchsiella alkaliacetigena and ferrireducens, Peptostreptococcus productus B-52* and *Moorella* sp *HUC22-1* [145–149]. The *Clostridium drakai, ljungdahlii*, *scatologenes*, *coccoides* and *thermoautrophicum* are the most acidophilic known strains; they can tolerate pH values as low as 3.6–4.5 [150–154].

2.2.6. Pressure

Pressure ranges for H_2 storage of 5–20 MPa [99] or 1–50 MPa [100] have been reported. Life at high pressure requires homeostatic changes

[103]. The high pressures encountered in pore spaces in the crust are generally less inhibitory to microbial cellular activity than the high temperatures, partly because of the relatively high osmotic pressure of cytoplasm [102], in particular in thermophiles and hyperthermophiles [39]. Membrane fluidity, and DNA and protein synthesis are among the most pressure-sensitive cellular components and processes [103,155,156]. Different adaptive mechanisms and strategies are used by microorganisms to survive in high-pressure environments, including efficient expression and activity of proteins used in protein folding complexes (prefoldins), membrane fluidity maintaining, robust biocatalysts [156], and EPS [18] or spore formation [103].

An upper pressure limit to microbial life has not been established [23]. At 30–50 MPa, the growth of various mesophilic, atmospheric-pressure-adapted microorganisms is inhibited [155] whereas pressure effects are generally favorable for the growth of hyperthermophiles; above 100 °C, elevated pressures are required to maintain a liquid environment [104]. Microorganisms that grow optimally at 10 MPa or above are obligate and facultative piezophiles, where the former do not tolerate ambient pressure and the latter do [103]. A recent publication listed all identified piezophiles and grouped them according to their growth temperature optimum [103]. The list of species is rather short (and as we find incomplete despite being published in 2020), possibly due to the fact that, to date, it has not been possible to isolate genes associated with piezophily, so the effects of pressure on any particular organism can only be determined empirically [103,156]. Empirical efforts however, do not commonly include pressure tolerance in the description of the environmental growth constraints of a microorganism. In addition, most mesophiles and thermophiles from habitats with pressures of <50 MPa will grow in enrichment cultures incubated at atmospheric pressure [32]. The large majority of identified cultivated piezophiles are psychrophiles (27 strains) [103], the relevance of which is low to our study. Only four mesophilic strains were reported, three of them hydrogenotrophic sulfate reducers (the *Desulfovibro profundus*, *piezophilus,* and *hydrothermalis*), growing optimally at 10–40 MPa [103]. Eight thermophiles were identified, including one hydrogenotrophic methanogen, *Methanococcus thermolithrophicus*, growing optimally at 50 MPa. The hyperthermophilic group hosts the hydrogenotrophic *Methanopyrus kandleri* and *Methanocaldococcus jannaschii* growing optimally at 20–75 MPa, respectively. Examples of hydrogenotrophic piezophiles that are not included in Ref. [103] are the mesophilic SSRM *Paracoccus pantrotrophus* and *Pseudodesulfovibrio indicus* which growth optimally at 30 and 10 MPa, respectively [157,158], and the thermophilic SSRM *Piezobacter thermophilus* and *Archaeoglobus fulgidus TF2* which grow optimally at 30 and 42 MPa, respectively [73,159].

A temperature dependence of the pressure response was reported for the SSRM *Desulfovibrio indonesiensis* which has similar growth rates at high and ambient pressure 45 °C but reduces its growth rate at 20 °C and 30 MPa relative to at 0.1 MPa [160]. Elevated pressure may increase the maximum growth temperature by 2–12 °C relative to lower pressure (0.1–3 MPa) [104,105,161].

2.2.7. Inhibitors

Exposure to hydrogen sulfide, H_2S, and its bisulfide ion, HS^-, causes damage to microbial proteins and coenzymes [89,162]. It remains unclear whether H_2S or HS^- is responsible for the toxicity effect but there is general consensus that H_2S can penetrate the microbial cell membrane more easily than HS^- [162]. Hydrogen sulfide dissociates with a pK_1 of 6.99 at 10 MPa and 25 °C to form >99% HS^- at pH 8.5 [163].

Growth of SSRM and methanogens is adversely affected at concentrations of H_2S > 3.8–4.0 mM [164–166]. At 5.0–6.3 mM H_2S growth is completely inhibited for SSRM [164,166], without however stopping all metabolic activity [164]. For methanogens and homoacetogens 3.8–7.5 mM H_2S and total sulfide concentrations of 3.3 mM, respectively, stop the growth [162,166]. In systems with circumneutral pH and ferric ion concentrations above 1 mM, the concentrations of H_2S are predicted to be kept below toxic levels due to its precipitation in makinawite [44].

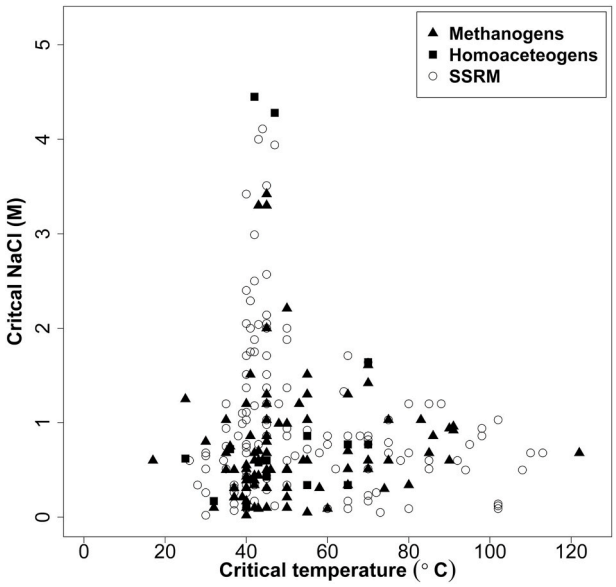

Fig. 2. Critical temperature (without salinity stress) versus critical salinity (without temperature stress) for methanogens, homoacetogens and SSRM.

Carbon dioxide pressure above 1 bar can be toxic for microorganisms as shown for the SSRM *Desulfotomaculum geothermicum* and the methanogen *Methanothermococcus thermolithotrophicus* [167]. For many anaerobes like methanogens and homoacetogens, oxygen is toxic too [62,102].

Nitrate inhibits homoacetogenesis [168], and ammonium [169] and sulfate inhibit methanogenesis (reviewed in Ref. [170]), with minimum inhibitory concentrations varying depending on the environment [166,169]. For instance, sulfate concentrations as low as $2*10^{-4}$ M were shown to inhibit methanogenesis for 10 h in lake sediments, possibly by competition with SSRM for available H_2 and C-substrate [165] (see section 2.3). Under H_2 storage conditions however, sulfate is likely not to affect methanogenesis, because sulfate inhibition was shown to be reversed by addition of H_2 [165]. For a discussion of an inhibitory effect of H_2, see section 2.5.

2.2.8. Summary of environmental growth constraints

Acknowledging the lack of data for the pressure sensitivity of many microorganisms [103], and considering a general abundance of nutrients in DOGF (Table 2), we evaluate temperature and salinity as the most crucial environmental factors constraining the growth of homoacetogens, methanogens and SSRM in DOGF. Pressures encountered in the crust are documented to have less effect than temperature on microbial cellular activity, particularly in thermophiles and hyperthermophiles [39,102]. The pH does not pose a similar constraint to the growth of homoacetogens, methanogens and SSRM because the pH ranges for growth typically span two to three pH units (not shown) and for most species they include typical aquifer pH values of 6–7 [171] (Table A4). Brine complexity and inhibitors were not included in this analysis due a lack of information on the brine composition of DOGF beyond a limited set of dissolved ions.

Fig. 2 shows the critical temperature versus critical salinity for 287 cultivated strains and reveals that salt tolerances up to 1–1.7 M are widely distributed over the entire temperature range while salt tolerances >1.7 M are only found at a critical temperature tolerances of 40–50 °C. Hence, from the point of view of minimizing microbial impacts on H_2 storage, sites with temperatures >55 °C and salinities >1.7 M are preferred.

Growth of cultivated strains in all of the investigated microbial groups may occur up to 72 °C (Fig. 1). Above 72 °C, cultivated homoacetogens will not grow, and at 80–94 °C sulfate reducers cease to grow.

Thirty-six cultivated SSRM and eleven methanogens have optimum growth temperature of ≥80 °C (Fig. 1a and i) and will still grow, albeit at reduced rate, beyond their optimum temperatures. The maximum growth temperature for known methanogens and sulfur reducers is 122 °C and 113 °C, respectively. The upper limits for salinity and pH that allow growth of cultivated strains from all of the major groups of H_2-oxidizing microorganisms are 3 M NaCl and pH 10.2, respectively. The upper pressure limit for most mesophiles is 30–50 MPa.

2.3. Growth regulation by competition and syntrophy

Homoacetogenic bacteria are ubiquitous in anaerobic sediments [63,173] and often co-exist with SSRM and methanogens [15,174], as revealed by a combination of molecular (16S RNA gene sequences) and culturing (e.g. metabolites, radiotracer) techniques. Few habitats have been identified in which homoacetogens compete with other H_2-consumers (culturing studies) [173,175]. Exceptions include a low-temperature and low-salinity petroleum reservoir where homoacetogens dominated over methanogens and SSRM (molecular study) [60], a granite groundwater at 400 m depth where cell numbers of methanogens and homoacetogens were balanced (molecular study) [81], and subsurface marine sediments where mixotrophic homoacetogenesis outperformed methanogenesis (culturing study) [80].

Kinetic advantages of SSRM and methanogens (i.e. a higher affinity for H_2, expressed as a low Michaelis-Menten constant, K_M, or Monod half saturation constant, K_S (H_2 concentration at which growth rate reaches half maximum growth rate), and a higher maximum growth/reaction rate, V_{max} or μ_{max} for Michaelis-Menten kinetics and Monod kinetics, respectively) were proposed as the underlying cause for the few examples of the poor competitiveness of homoacetogens [176]. Very limited information on the H_2 consumption kinetics of homoacetogenic bacteria is available in literature [177]. The available data show that μ_{max} differs by one order of magnitude between strains (0.02–0.5 h^{-1}) [4,177]. This may or may not be lower than the μ_{max} for SSRM 0.057–5.5 h^{-1} [4,38,178] and methanogens 0.032–1.4 h^{-1} [38,178]. Krumholz et al. [176] showed that homoacetogens were not able to compete effectively for H_2 in the presence of SSRM in a subsurface sandstone ecosystem at 30 °C regardless of pH_2, and despite significant homoacetogenesis at excess H_2. Findings by Berta et al. [4] for a groundwater sediment held under excess pH_2 and 20 °C contrasts this as homoacetogenesis rates were up to 21 times higher than SSR.

Environmental conditions may be a crucial determinant for the competitiveness of homoacetogens, as low temperatures (~15 °C) [179,180] and low pH values [62,181] favor their growth over methanogens. Under excess pH_2, homoacetogenic strains with high μ_{max} such as *Acetobacterium bakii* will outcompete methanogens [180]. The outstanding metabolic flexibility of homoacetogens for utilizing a vast variety of substrates may additionally explain why homoacetogens can compete with more specialized microorganisms like SSRM or methanogens [63,180,182].

As for the competitiveness of methanogens and SSRM, the H_2 thresholds of methanogens may be comparable (1–15 nM) or higher (>15–95) than for sulfate reducers and significantly lower than for sulfur reducers (≪2500 nM; Table 1), indicating an advantage of sulfate reducers over methanogens and sulfur reducers in most non-engineered, low pH_2 environments. In line with this, Lackner [183] recently reviewed that sulfate reducers outcompete methanogens for H_2 in most studies. However, at excess H_2, methanogens and sulfate reducers would be expected to process equal shares of the in situ H_2 pool [178]. Also, since concentrations of sulfate are much lower than bicarbonate in non-marine natural environments [38] (Table 2), the growth of sulfate reducers at excess H_2 will be limited by the availability of their electron acceptor, making it possible for methanogens to compete [38]. As a general rule pH values below 7 favor the growth of methanogens over sulfate reducers [132]. Above pH 7.5, sulfate reducers grow faster than methanogens and would be expected to outcompete them [132].

Syntrophic relationships between different functional groups have been documented frequently (whereby the metabolic products of one group serve as substrates for the other). For example, SSRM and homoacetogens were shown to participate cooperatively in microbial induced corrosion of steel where SSRM grew on acetate produced by homoacetogenesis [68]. Substrate provision by the co-cultured *Desulfovibrio vulgaris* enhanced growth of the dehalogen *Dehalococcoides ethenogenes* 195 by 24% and caused three times higher dechlorination rates [184]. Syntrophy may also explain the detection of a combination of the SSRMs *Desulfovibrio* and the homoacetogens *Acetobacterium* in petroleum and subsurface CO_2 reservoirs [60,185], and the presence of H_2-producing heterotrophs along with methanogens in petroleum reservoirs where the latter rely on H_2-transfer by the former [186].

2.4. Microbial ecology in natural gas and petroleum reservoirs

Recent years have seen a considerable effort in describing deep subsurface microbial communities, including those from gas and petroleum reservoirs. Isolated hydrogenotrophic microbes from these habitats are from the SSRM families *Hydrogenothermaceae*, *Sulfurospirillaceae*, *Rhodobacteraceae*, *Ectothiorhodospiraceae, Desulfomicrobiaceae*, *Peptococcaceae, Archaeoglobaceae, Desulforobacteraceae, Desulfobulbaceae, Desulfovibrionaceae, Syntrophobacteraceae* where the latter seven families are known with certainty to be capable of thiosulfate reduction [22,54,96,97,187–194], the *Eubacteriaceae* and *Sporomusaceae* families which host homoacetogenic strains [96,190,195], and the methanogen families *Methanosarcinaceae*, *Methanobacteriaceae*, *Methanomicrobiaceae*, *Methanopyraceae*, *Methanococcaceae*, *Methanocalculaceae* and *Methanosaetaceae* [97,116,190] in addition to uncultured microbial taxa [54,188,189,194,196]. Our collection of hydrogenotrophs (Fig. 1) lists many strains from the above microbial families, including the strain that holds the highest critical temperature for a methanogen, *Methanopyrus kandleri*. Sulfur reducing families that define the upper temperature limits for SSRM like *Thermoproteaceae* and *Pyrodictiaceae* were not reported. The cause for their absence may be a predominance of mesophilic and thermophilic sites but may also reflect a generally stronger growth of sulfate reducers over sulfur reducers in oil and gas reservoirs. Ranchou-Peyrouse et al. [97] showed that the microbial community in 35 out of 36 subsurface wells from seven natural gas storage sites was dominated by sulfate reducers.

2.5. Effect of high hydrogen concentrations on microbial metabolism and community structure

A range of studies investigated the metabolism of methanogens at excess H_2 and ambient pressure, with unambiguous results. Conrad et al. [197] demonstrated that excess H_2 stimulated methanogenesis and growth rates in a paddy soil (species not specified). Opposed to this, results by Topcuoglu et al. [186] and Stewart et al. [198] suggest an inhibitory effect of high partial pressures of H_2, pH_2, expressed as a ~10-fold drop in the growth yield (cells per mole CH_4) of *Methanocaldococcus jannaschii* and a slight drop of ~0.1–0.7 h^{-1} in the growth rate. Similar observations were made for *Methanothermobacter thermoautotrophicus* [199]. However, within the excess H_2 experiment, higher H_2 concentrations stimulated growth [186], suggesting a complex influence of pH_2. Methanogens seem to express a pH_2-dependent change in their ecological strategy, i.e. maximum growth rate vs. maximum growth yield, as a means to cope with different environmental conditions [186]. Indeed, *M. jannaschii* is capable of sensing subtle changes in dissolved H_2 concentration and restraining the energy-intensive growth of flagella to H_2-limiting conditions whereas at excess H_2 cells are mostly flagella devoid [200].

Only few studies investigated microbial H_2 turnover at high pH_2 of up to 1.5–24.8 MPa [4,201,202]. The growth of methanogens (*M. jannaschii*) was strongly inhibited at high pH_2 [201]. However, the authors added CO_2 at a pressure of at least 0.2 MPa to the hydrogen gas

mixture where a pCO_2 of 0.1 MPa can already be toxic some methanogens [167]. Hence it is not clear whether H_2 or CO_2 performed the toxic action. For homoacetogens and SSRM, the H_2 consumption was shown not to change in response to different pH_2 of 0.1–3.5 MPa [4,202], indicating neither stimulation nor toxicity at different levels of excess H_2. The comparison to limiting H_2 conditions was not made.

Apart from the microbial metabolism, the microbial community may also change in response to high pH_2. Given a pertubation by H_2 injection it can be anticipated that other types of microorganisms, e.g. the in hydrocarbon reservoirs common fermenters [21,95,97,187], will decrease in abundance while hydrogenotrophs will increase [7], in line with the Baas Becking principle [203]. An increase in hydrogenotrophs in response to H_2 addition was recently confirmed for soils, however H_2 consumption increased in only one of the investigated soils, suggesting a pronounced influence of the indigenous microbial community [204]. Bioreactor experiments support a decrease in microbial diversity in response to high pH_2 [205,206]. Puente-Sanchez et al. [207] were the first to report differences in the subsurface H_2-consuming community in response to varying pH_2 within the Iberian Pyrite Belt. Ranchou-Peyruse et al. [97] showed that town gas storage with more than 50% H_2 changed the microbial community from a predominantly sulfate reducing community to a dominance of methanogens, and this balance was active even decades after injection stopped, possibly via H_2 trapping in the microporous system [97]. It was suspected that all sulfate was initially used up by SSRM following increased growth of methanogens [97].

3. Evaluating the potential hydrogen consumption in DOGF

3.1. Calculation of the microbial growth

We screened 42 DOGF in the North Sea and the Irish Sea and five H_2 storage test sites for temperature, salinity, pH and pressure data (Fig. 1, Table A4). We discovered significant differences in the salinity of the DOGF as reported by different sources [172,208]. Because we relied on the solution compositions for the calculation of the potential microbial growth in the fields, which are available from Ref. [172], we chose to use the salinity data from the same source.

The environmental data from the DOGF and H_2 storage test sites were aligned with the constraints for growth of methanogens, homoacetogens and SSRM (Figs. 1–2) to select in which fields growth can be expected. For the few fields that fulfil the growth constraints of all investigated microorganisms, we calculated a first-order estimate of the microbial growth using the elemental cell composition as a proxy for the nutrient requirement [209,210] (Text A.1).

Our calculations assumed that the supply of N and C are covered by diazotrophic and autotrophic growth, respectively. Requirements for trace elements were neglected in the calculation due to a lack of information on the relevant trace element contents in the reservoirs. Where a nutrient for a specific field was not available we used the average value from the fields given in Table 2. Any effect of the pH_2 on microbial growth was neglected. We assumed that cells neither die nor are removed, and that nutrients are not replenished by inflow, remineralization from decaying biomass or mineral dissolution. Simultaneous growth by different microorganisms was not considered.

Percentages of nutrients in the cells (Text A.1) were converted to mass using a wet cell mass of $1.77*10^{-12}$ g for methanogens [211], 3.2–$6.2*10^{-13}$ g for homoacetogens and $7.81*10^{-13}$ g for SSRM. The cell wet weight of homoacetogens was calculated by dividing the cell volume of 1.62–3.14 μm^3 for the subsurface mixotrophic homoacetogen *Acetobacterium psammolithicum* [176] with an assumed bacterial density of $1*10^{-12}$ g μm^{-3} [212]. The cell wet weight of SSRMs was calculated using a cell dry weight of $3.125*10^{-13}$ g for *Desulfovibrio desulfuricans* [213] and dividing this with a general bacterial dry weight to wet weight ratio of 0.4 [214]. Subsequently, the concentrations of C, H, O, Ca, K, Na, S, Mg, P and Fe in the DOGF (Table 2) were divided by the mass of the respective cell nutrient per microbial cell calculated above. This resulted in the maximum cell count within each microbial group, *G*, that could potentially be created based on a single nutrient, where the lowest *G* indicated the limiting nutrient for cell growth. For an example of those calculations, see Text A.1.

3.2. Estimation of the cell-specific hydrogen consumption

Hydrogen may be consumed by growing and resting microbial cells at rates of 0.02–$5.0*10^5$ nM h^{-1} for homoacetogens, 0.02–$5.8*10^5$ nM h^{-1} for methanogens and 0.005–$130*10^5$ nM h^{-1} for SSRM (Tables A1-A3), the latter considering sulfate concentrations in the range of 0–$2.3*10^{-2}$ M in the DOGF (Table 2). In a few studies, the microbial H_2 consumption was related to growth (Tables A1-A.3), enabling the calculation of the H_2 consumption per synthesized cell and the time for when the microbial cell count *G* would be reached (Text A.2).

3.3. Calculation of the hydrogen consumption in a hydrogen storage system

We calculated the minimum H_2 consumption for the DOGF Frigg and Hamilton by dividing the H_2 consumption per synthesized cell with the microbial cell count. The calculation of the moles of H_2 the in aquifer anticipated equal volumes of H_2 and water and used the ideal gas law and the field size, temperature and pressure data in Table 2 and Table A3. The percentage of H_2 that was consumed as a function of growing and resting microbial cells was calculated by dividing the potential H_2 consumption with the H_2 concentration in the reservoir. Text A.3 shows our calculations for the Frigg reservoir and methanogens.

4. Results and discussion

4.1. Characterization of the likelihood for microbial growth in 42 DOGF

Using the environmental limits constraining microbial growth on H_2, we analyzed the physicochemical parameters for 42 DOGF in the British and Norwegian North Sea and the Irish Sea and five H_2 storage test sites (Fig. 1, Table A4). Of the 47 fields, five fields have a temperature of 122 °C or higher and may be considered sterile with respect to H_2-consuming microorganisms. Where long-term injection of cold sea water has been a practice, cooling of reservoirs is a likely scenario. Therefore, any H_2 storage operation in these fields will require a renewed measurement of the reservoir temperature. Thirty-two fields have a temperature >72 °C, implying that homoacetogenesis cannot take place. Fifteen DOGF have temperatures >90 °C and <122 °C and pressures of 18.2–44 MPa where (piezophile) hyperthermophilic methanogens and SSRM, principally sulfur reducers, will grow.

Of the fifteen sites with temperatures <72 °C where all investigated groups of microorganisms will grow, only nine fields (Frigg, Hamilton, Hamilton North, Camelot, the V gas field complex, Veslefrikk, Ketzin, Lehen and Lobodice) fulfill the remaining pressure and salinity requirements for growth. Five fields, Lennox, North Morecambe, South Morecambe, Leman and Rhyl, have salinities ≥4.4 M where no cultivated microbial H_2-oxidizing microorganisms can grow but not cultivable SSRM may still be active. This finding is supported by stable gas compositions at the similarly saline H_2-storage test sites of the H2STORE project, Emsland and Altmark (Fig. 1, Table A4), where low microbial populations of $\sim 10^2$ cells ml^{-1} were present [215]. Hamilton North, Camelot and The V gas field complex with salinities of 2.9–5.0 M may permit the growth of SSRM and homoacetogens. The Viking field has temperatures of 65–80 °C and a salinity of 3.8 M and so is likely to host only mesophilic SSRM, although pressures >30 MPa could become growth inhibiting [155]. The H_2-storage test site Ketzin has similar salinity to the Viking field but a lower pressure (4.0 M NaCl, 35 °C, 6 MPa). Here SSRM were suspected to cause a 2–4% decrease in H_2 and a reduction in the concentration of sulfate from 22 to $8*10^{-3}$ M [215].

4.2. Microbial growth estimates for two low-temperature and low-salinity DOGF

Our first order approach to calculating microbial growth, designed to give a first approximation to microbial numbers, only, yielded a maximum of $1*10^8$ methanogenic cells mL^{-1}, $1*10^8$ SSRM cells mL^{-1} or $2*10^8$ homoacetogenic cells mL^{-1} in the Frigg reservoir. The Hamilton reservoir [120] could host a maximum of $1*10^7$ methanogenic cells mL^{-1}, $2*10^7$ SRCM cells mL^{-1} or $6*10^7$ homoacetogenic cells mL^{-1}. These cell counts describe a maximum cell growth for each hydrogenotrophic group because simultaneous growth of hydrogenotrophs was not considered. The higher growth of homoacetogens over SSRM and methanogens results from a lower wet cell mass that causes a lower nutrient demand per cell (see Text A.1). Our calculations are in line with total cell concentrations of 10^5-10^{15} cells/mL^{-1} in oil reservoirs [216], and equal to or up to four order of magnitudes higher than cell counts from gas reservoirs (0.001–$1.2*10^7$ cells mL^{-1}) [49,96,189].

Acknowledging that trace elements were not accounted for in our calculation, N and P are the first limiting nutrients in the reservoirs Frigg andHamilton However, this does not imply that microbial growth is N and P limited, as many microorganisms may use of ammonium as N-source (not measured), and in the Hamilton reservoir the C:P ratio was between 59:1 and 158:1, whereas the limiting C:P ratio for microbial growth is in the range of 400:1 to 800:1 (reported for the SSRM *D. desulfuricans*) [217]. At moderately acidic pH values such as the pH of 5.8 in the Hamilton reservoir, P may further be continuously replenished by mineral buffering with apatite.

4.3. Hydrogen consumption in two low-temperature and low-salinity DOGF

The H_2 consumption in the Frigg reservoir by homoacetogens constitutes <0.01–3.2% of the H_2 in the aquifer, <0.01–1.3% for methanogens and <0.01–1.3% for SSRM. In the Hamilton reservoir, the rates are <0.01–2.0%, <0.01–2.3% and <0.01–0.5% for homoacetogens, methanogens and SSRM, respectively. For actively growing cells these consumption rates may be reached after only 0.1–19 days, which is the time it takes for the microorganisms to grow up to their maximum cell counts, based on the dissolved nutrient concentrations. Resting cells, i.e. cells that undergo no or only very little cell division, need 2.5–3.5 months (SSRM) or up to 3.6–6.6 years (methanogens) to reach the maximum cell count and consume the given percentage of H_2.

In a real aquifer system, nutrients are likely to at least partly be replenished by decaying cells, mineral weathering and inflowing brine, and cells will continue to consume H_2 beyond the time it takes to reach the maximum cell count (maintenance). As such our H_2 consumption estimates may be regarded as minima. On the other hand, considering that, with the exception of one study (Berta et al. [4]), our calculations employ laboratory H_2 consumption rates at optimal nutrient supply and optimal physicochemical conditions (Tables A1-A.3), the H_2 consumption in the oligotrophic subsurface is likely overpredicted. Comparing the employed laboratory H_2 consumption rates to H_2 consumption rates by SSR and methanogenesis in oil and natural gas reservoirs of ~0.4–330 nM h^{-1} and 0.02–1205 nM h^{-1}, respectively (SO_4^{2-}: $8.3–805*10^{-5}$ M; HCO_3^-: $3.5–246*10^{-4}$ M) [49,187], shows that the field H_2 consumption by SSR is 1.5 times to five orders of magnitude lower, and 1.4 times to 7 orders of magnitude lower for methanogenesis. Within the operation and injection wells of a natural gas reservoir, H_2 consumption rates by SSR and methanogenesis were 2393 and 4475 nM h^{-1}, respectively [49], which falls within the lower range of the values reported from laboratory studies. Acknowledging the unknown but presumably low pH_2 in above experiments, and that maintenance requirements were not included in our H_2-consumption calculations, we expect the actual H_2 consumption in a H_2 storage system to lie within the higher range of our calculated values.

Our upper end results are in agreement with H_2 losses of ~3% by methanogens and 2–4% by sulfate reducers at the H_2 storage test sites in Lehen, Austria [27] and Ketzin, Germany [215], respectively. Reports from H_2-rich town gas in Beynes, France, reports are contradictive ranging from no H_2 consumption during storage operations [218] to significant (unspecified) reductions of H_2 and CO_2 contents along with increases in CH_4 [219,220]. A H_2 consumption of 17% by methanogens at the Lobodice town gas storage site over a time span of seven months [218,221] seems exceptional in the light of our calculations and the reported SSR and methanogenesis rates from the field. With a very low salinity of 0.03 M, temperatures of 20–45 °C, a pH of 6.7 and 4 MPa pressure, Lobodice is among the few sites which has highly favorable conditions for microbial growth considering *all* of these parameters (Table A4). *The high H_2 consumption at Lobodice highlights the importance of environmental parameters for controlling microbial activity, as H_2 storage may face serious economic and technical problems if a site with growth-favoring conditions is selected.*

As mentioned, Berta et al. [4] measured high H_2 consumption rates under excess H_2 and oligotrophic conditions ($P < 9.7*10^{-7}$ M; $SO_4^{2-} \leq 9.5*10^{-4}$ M; DOC = $2.6*10^{-4}$ M), indicating that nutrient scarcity does not imply low H_2 consumption. A comparison to the nutrient concentrations in the DOGF reveals that many of them have a higher nutrient status (P = 0.002–$0.452*10^{-3}$ M; SO_4^{2-} = up to $23.1*10^{-3}$ M; organic acids = 1.2–$8.1*10^{-3}$ M, Table 2), implying that H_2 consumption in DOGF under excess H_2 conditions may be even higher than reported in Ref. [4]. The experiment by Berta et al. [4] is further highly relevant because cells were at steady state, i.e. at the predominant growth stage in nature, but still consumed vast amounts of H_2. Indeed the H_2 consumption of cells at steady state or resting may be just as high as or higher than for growing cells but growth is low or absent (Tables A1-A.3).

4.4. Knowledge gaps and future research

More work is needed to predict the magnitude of microbial growth, H_2 consumption rates, and (not least) the mutual interaction of microbial processes in DOGF. The list of unknowns and uncertainties is long. To begin with are the poorly elucidated nutrient requirements of microorganisms, especially in mixed cultures (e.g. Ref. [69]). Adding to this are the missing or incomplete datasets on the physical environment of certain reservoirs along with their gas phase and brine compositions, including chaotropy and kosmotropy characteristics. A better elucidation of the latter would allow a calculation of the dominating microbial processes via their free energies of the reaction. Combined with an analysis of the microbial community and metabolism this could give new insights into whether or not we can theoretically predict which microbial processes occur in DOGF and to which extend.

A further complication is the non-cultivability of many microorganisms in the deep subsurface, including DOGF [12,32,54,97,187]. Considering tiny culturabilities of ≤0.1 % of the total viable cell count in many subsurface environments [32], any attempts to assign sterile habitats or quantify microbial H_2 consumption via cultivated microorganisms, only, are characterized by a significant uncertainty. In gas reservoirs, the percentage of cultured bacteria may be higher, ranging between 86 and 95 % within each phylum [97]. Field-based metabolic activity measurements could circumvent any non-cultivability issues observed in laboratory experiments. Initially, however, DNA-based laboratory tests are recommended to obtain general cell numbers. The number of cultivable microbes may be maximized using a large array of modern cultivation techniques [222–227].

The lack of knowledge about the changes in microbial ecology as a response to increased H_2 concentrations beyond the level of functional groups is one of the major hurdles in our attempt to understand of the effect of high H_2 concentrations on the subsurface microbiology. Emerging evidence on the subject highlights species-specific responses to high pH_2 [97,205,207], and that H_2 injection may leave its fingerprint on the subsurface microbial community for decades [97]. Knowledge

about the initial effect of a drastic increase in pH_2 in the subsurface is lacking. Considering the pressure increase and the toxicity of high pH_2 on some methanogens [186,199,201], one possibility is that more EPS will be produced as a response to the perturbation with elevated H_2 pressures, as has been shown for other types of perturbation [18,217,228], with possible adverse effects on gas injectivity and withdrawal.

Future research should address the effect of high pH_2 on the metabolisms of different functional groups in different geological settings and under changing nutritional supply and physicochemical conditions. Mixed culture studies at low and high pH_2 can give insight into competitive and syntrophic relations under these conditions and reveal changes in the microbial community structure caused by the pertubation with elevated H_2. More base-line research includes determinations of the critical salinities and pressure tolerances that to date are missing for many cultivated strains, as well as the study of the brine compositional effects on the microbial community and metabolism. Future lab-based research should aim to employ chemostat studies that mimic the natural environment [17].

5. Conclusion

In this work we presented the growth conditions of 518 cultivated strains from the three major groups of H_2-oxidizing microorganisms and aligned those with physicochemical data from 42 DOGF in the British and Norwegian North Sea and the Irish Sea to predict where microbial growth can be expected in a future H_2 storage scenario. Our results can –with some certainty- exclude life in several high-temperature, i.e. deeper reservoirs. For low-salinity and low-temperature reservoirs our initial calculations indicate significant microbial growth and a small H_2 consumption, both of which may further increase during repeated storage cycles, giving replenishment of nutrients by mineral weathering, decaying microbial cells and inflowing water. Hence, from the point of view of minimizing H_2 loss, clogging and corrosion, sites with more extreme conditions may be chosen over low-temperature and low-salinity reservoirs where the majority of microorganisms can proliferate. Yet, any storage operation will have to consider increased operational difficulties and costs with increased depth. Experimental investigations of subsurface life on H_2 are needed to verify our calculations and manifest whether H_2 consumption in low-temperature aquifers is a threat to H_2 storage. All sites of interest to H_2 storage should be carefully investigated and tested for microbial growth beforehand.

Data availability

A dataset related to this article can be found at https://doi.org/10.17632/4dksb2x4zn.1, an open-source online data repository hosted at Mendeley Data.

Author contributions

The manuscript was written through contributions of all authors. All authors have given approval to the final version of the manuscript.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.rser.2021.111481.

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