allowing for the van der Waals radii of the attached hydrogens, the 'free space' dimension of the channel in this direction (left to right in Fig. 2*A*) is close to 20 Å. The distance between a Cu(II) of one pair and the nearest Cu(II) of another pair across a channel is 15.64(2) Å.

We suggest that interpenetration of the sort observed for solvated Cu(tcp)$CuBF_4$ does not occur with solvated Cu(tpp)$CuBF_4$ because the required close approach of the Cu(I) centres from separate frameworks is precluded by the four bulky pyridyl units around each metal; by contrast it would be difficult to find four less sterically demanding donors than the nitrile ligands surrounding the Cu(I) in Cu(tcp)$CuBF_4$.

Paired metalloporphyrins have been studied as models for the 'special pair' of the photosynthetic system[22]; paired frameworks related to that described here with a range of metallo-tcp units in place of Cu(tcp) could perhaps be made, and may furnish interesting photophysical and photochemical behaviour.

With regard to future studies, porphyrins and phthalocyanins are particularly alluring as building blocks for networks with potential applications as microporous heterogeneous catalysts because (1) their relative rigidity and large size, in the correct circumstances, could be used to generate correspondingly large channels and cavities, (2) they show a high degree of thermal stability and could therefore be put to use at elevated temperatures, (3) they readily incorporate a wide range of metal centres and (4) as discrete molecular species, they are known to catalyse and promote diverse processes[23]. The porphyrin-containing networks described here are so delicate that they do not survive removal of nitrobenzene, so, at this early stage, materials of this general type fall far short of rivalling zeolites. We are presently exploring the possibility of putting to use the stability-enhancing chelate effect to provide more robust solids.

The exercise described here was conducted to demonstrate, in the simplest way we could visualize, what might be possible with porphyrin building blocks. The fact that the PtS network did assemble itself as intended is very encouraging with regard to future framework construction. On the basis of the results presented here, the deliberate construction of microporous heterogeneous catalysts (in which porphyrins and similar systems play the dual role of active site and framework component of sufficiently large size to produce large access channels) seems a realistic prospect. The basic approach is obviously amenable to wide variation; it seems feasible that appropriately designed building blocks may afford many nets other than PtS and diamond. With regard to the prospects for catalytic activity offered by framework solids in general, it is encouraging that a two-dimensional Cd(II)(4,4′-bipyridine)$_2$ sheet polymer containing corral-like square cavities surrounded by 4,4′-bipyridine 'fences'[1] has recently been shown to catalyse the cyanosilylation of aldehydes[24]. □

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Degradation of trifluoroacetate in oxic and anoxic sediments

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THE deleterious effect of chlorofluorocarbons on stratospheric ozone has led to international cooperation to end their use[1–3]. The search for acceptable alternatives has focused on hydrofluorocarbons (HFCs) or hydrochlorofluorocarbons (HCFCs) which are attractive because they have relatively short atmospheric residence times[4]. HFCs and HCFCs are attacked by tropospheric hydroxyl radicals, leading to the formation of trifluoroacetate (TFA)[5]. Most of the atmospheric TFA is deposited at the Earth's surface[6], where it is thought to be highly resistant to bacterial attack[5]. Therefore, use of HCFCs and HFCs may lead to accumulation of TFA in soils, where it could prove toxic or inhibitory to plants and soil microbial communities[5,7]. Although little is known about the toxicity of TFA, monofluoroacetate, which occurs at low levels in some plants[8] and which is susceptible to slow attack by aerobic soil microbes[9], is known to be acutely toxic[10–13]. Here we report that TFA can be rapidly degraded microbially under anoxic and oxic conditions. These results imply that significant microbial sinks exist in nature for the elimination of TFA from the environment. We also show that oxic degradation of TFA leads to the formation of fluoroform, a potential ozone-depleting compound with a much longer atmospheric lifetime than the parent compounds.

We chose to work initially with anoxic sediments because of their ability to degrade CFCs[14] and other halogenated methyl compounds such as methyl bromide[15]. We incubated anoxic sediments from a San Francisco Bay saltmarsh[16] and from a freshwater lake[17,18] in the presence of 1.85 μM 2-^{14}C-TFA (Fig. 1). Production of CH_4 (Fig. 1*a*) and $^{14}CH_4$ (Fig. 1*b*) in saltmarsh sediments only occurred when sulphate reduction was inhibited with molybdate[19] or by elimination of sulphate from the slurry salts. No $^{14}CH_4$ was noted in the controls, which included autoclaved sediments containing molybdate (Fig. 1*b*), thereby reinforcing our conclusion that this was a microbial rather than chemical phenomenon. However, unmanipulated freshwater sediments ($SO_4^{2-} < 1$ mM) also readily produced $^{14}CH_4$ (Fig. 1*b*), thereby demonstrating that TFA degradation can occur in other types of sediments. The unlabelled carboxyl group of TFA was therefore cleaved to CO_2, as occurs in acetoclastic methanogenesis[20]. Addition of 2-bromoethanesulphonic acid, an inhibitor of methanogenic bacteria[19], blocked production of CH_4 and $^{14}CH_4$.

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TABLE 1 Degradation of 2-^{14}C-TFA in sediment slurries

Electron acceptor	TFA (μM)	Incubation on time (d)	$^{14}CHF_3$ (μCi l^{-1})	$^{14}CO_2$ (μCi l^{-1})	$^{14}CH_4$ (μCi l^{-1})	TFA conversion (%)
O_2	0.925	27	0 (0)	0	0	0 (0)
	0.463	27	0.60 (0.10)	0	0	2.4 (0.3)
	0.463	15	0.50 (0.35)	0	0	1.9 (1.5)
	0.185	15	2.55 (2.35)	0	0	25.5 (23.7)
NO_3	0.925	15	0	0	0	0
	0.463	15	0	0	0	0
SO_4^{2}	1.850	12	0	0	0	0
	0.925	18	0	0 05 (0.1)	0	0 1 (0.2)
	0.463	18	0	3.05 (0.95)	0	12.2 (3.9)
None	1.850	8	0	0	72.95 (3.25)	73.0 (3.3)
	0.925	15	0	0	34.95 (0.80)	69.9 (1.6)
	0.463	15	0	0	21.45 (0.70)	86.9 (2.8)

Experiments were carried out with 20 ml of slurry in 57-ml serum bottles (except oxic incubations, which were performed in 160-ml serum bottles). Oxic samples were pre-incubated by shaking with exposure to the atmosphere for 20 h in order to remove all potential reducing agents. Mean of three replicate slurries are given (figures in parenthesis indicate standard deviation). Autoclaved slurries, incubated anoxically with sulphate or under oxic conditions, did not produce any ^{14}C-labelled gases, ruling out chemical processes.

Under these conditions, we did not observe the production of ^{14}C-trifluoromethane, ^{14}C-difluoromethane, ^{14}C-methylfluoride or $^{14}CO_2$ in the headspaces of any of the slurries (not shown). We interpret these observations to mean that TFA is readily degraded under methanogenic conditions, but we were surprised that conditions that favoured sulphate-reduction did not result in formation of $^{14}CO_2$, which we would predict to occur for acetate[21]. We pursued the question of TFA mineralization by sulphate reduction in a subsequent experiment (see below). Because in our first experiment, the only end product was $^{14}CH_4$, it implied that TFA underwent a complete defluorination to the level of acetate before methanogenesis. To test this hypothesis, we examined the liquid phase, as well as the gas phase, of a larger volume of saltmarsh slurry incubated without sulphate. Results clearly demonstrated that a sequential order of defluorination occurred in these sediments (Fig. 2). Thus, the disappearance of 2-^{14}C-TFA was respectively followed by the transient appearances of ^{14}C-difluoroacetate (2-^{14}C-DFA), ^{14}C-monofluoroacetate (2-^{14}C-MFA), 2-^{14}C-acetate, and eventually the production of $^{14}CH_4$. By the time $^{14}CH_4$ production had ceased, after 7 days incubation, there no longer were detectable counts in the liquid phase. Mean conversion efficiencies of 2-^{14}C-TFA to $^{14}CH_4$ was 80% for this experiment, and 66–77% in the previous experiments (see below). We attribute the slightly lower efficiencies to binding of acetate to sediment surfaces, a process which makes a portion of it unavailable to microbial degradation[22], as the cause for the less than 100% recovery of 2-^{14}C-TFA as $^{14}CH_4$. We did not detect any alteration of the 2-^{14}C-TFA in autoclaved controls after prolonged (6 weeks) incubation (data not shown). Additionally, sediments inhibited by 2-bromoethanesulphonic acid had only a slight loss of TFA (15–20%) after 27 days incubation (data not shown). We conclude that this rapid defluorination is carried out by microorganisms, and the results with 2-bromoethanesulphonic acid suggest direct involvement of methanogens in the reductive defluorination of the TFA. The anaerobic microbial reductive dehalogenation of aromatic and aliphatic compounds has been well studied, but mostly centres on dechlorination and debromination reactions[23]. Defluorination of fluoroaromatics occurs in methanogenic enrichments, but fluorine is removed before ring cleavage and acetate formation[24]. This work is the first report of multiple reductive defluorinations of the methyl group of acetate.

Fluorinated compounds have been employed as microbial metabolic inhibitors[13,18]. Monofluoroacetate, an intermediate of TFA degradation in our study, inhibited acetoclastic methanogenesis in lake sediments when applied at a concentration of ~20 μM (ref. 13). We observed an inhibitory effect of added unlabelled TFA on methanogenic activity at concentrations ⩾1 μM. After 10 days incubation of sulphate-free saltmarsh slurries, mean methane levels (μmoles per 20 ml slurry; ±1 stan-

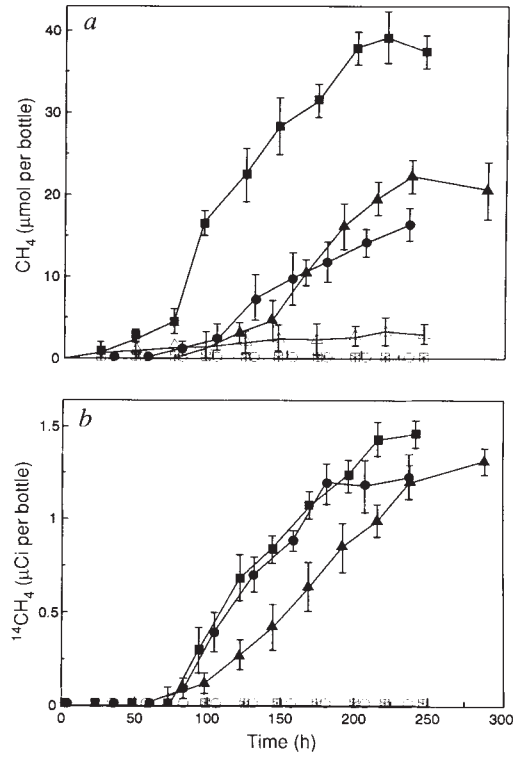

FIG. 1 Production of CH_4 (*a*) and $^{14}CH_4$ (*b*) in anoxic sediment slurries. Sediments were homogenized anaerobically with either artificial bay water (for saltmarsh sediments)[24] or with lake water (for fresh water)[17,18] to yield final ratios of 1:3, sediment:water. Slurries (20 ml) were contained in 57-ml serum bottles sealed under O_2-free N_2 with black butyl crimp-seal stoppers. Samples received 2 μCi of 2-^{14}C-TFA (Amersham Inc., Arlington Heights, Illinois); purity, 99.6%; specific activity, 54 mCi mmol^{-1}). Slurries were incubated in the dark at 23 °C with constant rotary shaking (200 r.p.m.). Gas phases were subsampled (250 μl) by syringe, and methane was analysed by flame-ionization gas chromatography[33], whereas $^{14}CH_4$ and $^{14}CO_2$ were analysed by gas chromatography in conjunction with proportional counting[34]. Retention times were (min): CH_4 (0.8), CH_3F (2.5) and CHF_3 (3.5). At the end of the incubations, samples were injected with 2 ml of 6 M HCl and shaken overnight before determination of $^{14}CO_2$. Symbols: saltmarsh sediments incubated with 20 mM sulphate (∗), without sulphate (■), with 20 mM sulphate plus 2.5 mM molybdate (●), without sulphate plus 5 mM bromoethanesulphonate (△), autoclaved with 20 mM sulphate and 2.5 mM molybdate (□), autoclaved with 20 mM sulphate (○); live freshwater sediments (▲). Symbols represent the mean of three individual slurries and error bars display ±1 standard deviation.

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dard deviation; $n=3$) were; without additions (90 ± 15); plus 0.1 μM TFA (73 ± 7), plus 1 μM TFA (4.0 ± 2.1), and plus 10 μM TFA (2.4 ± 0.5).

Therefore, we hypothesized that our initial observation of no $^{14}CO_2$ production under conditions favouring sulphate-reduction may have been caused by stronger inhibitory effects of TFA (or of MFA) on sulphate-reducers. This led us to perform a series of experiments in which lower concentrations of TFA (0.185–0.925 μM) were applied. The results from these incubations clearly show that sulphate-reducers can oxidize the methyl carbon of TFA to CO_2, provided that the TFA concentration was lower than 0.925 μM (Table 1). Conversion efficiencies were highest at the lowest concentration (0.463 μM) of added TFA. We did not detect any degradation of TFA (that is, loss of TFA or formation of products) under conditions favouring nitrate respiration (Table 1), despite the fact that these slurries actively formed as much as 60% more unlabelled CO_2 than any of the other electron-acceptors tested (data not shown). However, with O_2 as electron acceptor, we detected a peak with a slightly shorter retention time than that of $^{14}CO_2$. We then used a 4 times longer column (7.3-m Porapak Q) which separated $^{14}CHF_3$ (retention time, 5.8 min) from $^{14}CO_2$ (retention time, 9.0 min), thereby confirming that the observed product was only $^{14}CHF_3$. We only observed production of $^{14}CHF_3$ when the concentration of TFA was <0.463 μM, with the highest conversion ratio at the lowest TFA concentration tested (Table 1). Collectively, our results demonstrate that trace levels of TFA can be degraded by reductive defluorination under anoxic conditions, and by decarboxylation under oxic conditions. Assuming that our lake and saltmarsh sediments are representative of processes occurring elsewhere in the biosphere, these results suggest that the microbial flora present in most soils and sediments have the capacity to attack and degrade TFA.

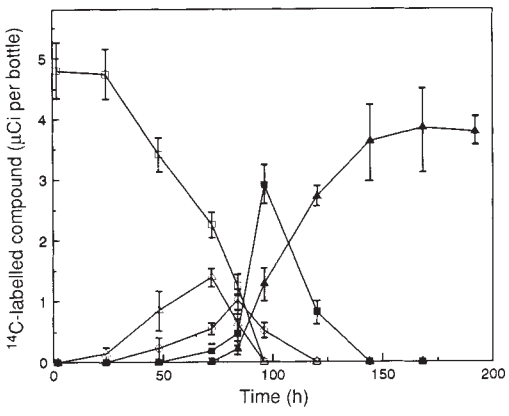

FIG. 2 Reductive defluorination of 2-^{14}C-TFA in saltmarsh sediment slurries incubated without sulphate. Preparation was the same as described for Fig. 1, except the volume was increased to 80 ml slurry in 158-ml serum bottles. Samples received 5 μCi of 2-^{14}C-TFA. Slurry subsamples (1 ml) were removed by syringe and centrifuged in a microcentrifuge (15,900*g* for 3 min). The supernatant was expressed through disposable 0.2 μm nylon filters and kept frozen until analysis (<3 weeks). Samples were analysed by high-performance liquid chromatography with an ultraviolet absorbance detector coupled with an in-line β-emission radiation detector[35]. Retention times determined with unlabelled standards were (min): TFA (4.5), difluoroacetate (6.0), monofluoroacetate (7.5) and acetate (9.5). There was a 1.2 min delay, determined by injection of 2-^{14}C-acetate and 2-^{14}C-TFA, between the mass detector and the radiation detector which allowed for identification and quantification with the use of a dual-pen chart recorder. Acetate concentration was <30 μM throughout the experiment (not shown). Symbols: 2-^{14}C-TFA (□), 2-^{14}C-difluoroacetate (△), 2-^{14}C-monofluoroacetate (○), 2-^{14}C-acetate (■) and $^{14}CH_4$ (▲). Symbols represent the mean of three individual slurries and bars indicate ±1 standard deviation.

Clearly, the concentration of TFA is a critical factor in this work. Our use of radiolabelled TFA enabled us to conduct experiments at concentrations that were at least four orders of magnitude lower than that employed previously by researchers using standard analytical chemical methods (F. G. Chumley, personal communication). The lowest concentration tested in our experiments was 0.185 μM, based on the specific activity of the 2-^{14}C-TFA which we added. Although this is still ~1–2 orders of magnitude higher than that predicted for rainwater[5,6], we feel that degradation of TFA, especially if it is a co-metabolic feature[25,26] is likely to occur unimpeded at even lower concentrations. Similarly, methanogenesis is inhibited by halogenated hydrocarbons[27,28] like CCl_4, although anaerobic degradation of CCl_4 occurs when the concentration $\leq$0.5 μM (refs 29, 30). Certainly our results with various electron acceptors indicated a trend of higher conversion efficiencies with decreasing TFA levels (Table 1). Although our present analytical techniques preclude conducting experiments at TFA concentrations <0.1 μM, we have no reason to question extrapolation of our results to anticipated natural concentrations. Still unanswered is the fate of TFA under conditions which favour other electron acceptors such as Fe^{3+}, NO_3^- and Mn^{4+}. However, our observation of TFA degradation under both oxic and anoxic conditions indicate that broadly-based microbial sinks exist for this compound in the terrestrial biosphere. Under anoxic conditions, TFA can be degraded to innocuous products like CH_4 and CO_2. The fact that aerobic decarboxylation of TFA yields CHF_3, a gas with a long atmospheric residence time, focuses attention on the fate of this product. That methane-oxidizing bacteria can degrade methylfluoride[31] as well as HFC-143 (1,1,2-trifluoroethane) (ref. 32) suggest the possibility of a soil biological sink. □

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