Biological waste gas purification of industrial methyl chloride emissions to protect the stratospheric ozone layer

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ABSTRACT**.** The feasibility of treatment of industrial methylchloride waste gas emissions using biotechnology has been studied. Microbiological aspects have been evaluated in relation to the low concentrations required after treatment. Important physiological parameters like affinity and toxicity for methylchloride have been researched to obtain optimal process conditions. Microbial aspects**,** as well as operational costs**,** showed that the biological waste gas treatment of methylchloride should be feasible. In a pilot-scale bioreactor, treating industrial methylchloride containing waste gas and inoculated with a mixed consortium of methylchloride degrading microorganisms, the required outlet concentrations can be reached.

1 INTRODUCTION

Methylchloride emissions are of concern, because it is estimated that it is responsible for 13% of the destruction of the stratospheric ozone layer (Montzka *et al.,* 1996; Butler, 2000). The destruction of the protective, ultraviolet radiation-absorbing ozone layer is associated with negative effects like skin cancer and eye problems. Among all volatile halogenated compounds, it is believed that methylchloride is the most abundant responsible for stratospheric ozone depletion (Harper and Hamilton, 2003; Harper *et al.* 2003).

Although the major sources of methylchloride are thought to be processes that occur in nature, methylchloride is emitted in large quantities by human related activities as it is widely used in the chemical industry as a methylating agent. Besides the production of silicones it is also used in the production of agricultural chemicals, methyl cellulose, quaternary amines, butyl rubber and for miscellaneous uses including tetramethyl lead (US-EPA, 2005).

To treat methylchloride waste gas emissions, conventional techniques like absorption (scrubbing), adsorption (active carbon) or oxidation (incineration) have different drawbacks. The most important is the significant high operational costs: the fuel for incineration, the replacement or regeneration of active carbon and the chemicals required for scrubbing.

Biotechnology for waste gas treatment has developed rapidly over the last ten years, since it has shown to offer one of the most economical and environmentally friendly

methods for air pollution control in many situations (Kennes and Veiga, 2001; Shareefdeen and Singh, 2005). The biological treatment of methylchloride emissions has not been demonstrated up till now. This paper shows the many aspects related to its development**,** among them economical feasibility and proven reliability.

2 BIODEGRADATION OF METHYLCHLORIDE

Methylchloride can be degraded under aerobic conditions. Several microbial strains are described that are capable to use chloromethane as the sole carbon and energy source. They have been enriched from different terrestrial and marine environments and are classified as *Hyphomicrobium* sp., *Methylobacterium* sp. and *Aminobacter* sp. (Hartmans *et al*., 1986; Doronina *et al.*, 1996**;** Vannelli *et al.,* 1998*;* Schaefer and Oremland, 1999; McAnulla *et al.,* 2001; Studer *et al.,* 2001; Schaefer *et al.,* 2002). Methylchloride is converted to HCl and formaldehyde. Formaldehyde is subsequently oxidized via formate to CO_2. This degradation pathway is most likely initiated by dehalogenation via a methyl transfer reaction, followed by a series of dehydrogenase based steps. In some of these bacteria an unique gene that codes for the enzyme responsible for the important first step has been identified (Vannelli *et al.,* 1998; McDonald *et al.,* 2004).

3 METHODS AND MATERIALS

The feasibility of applying biological air treatment of methylchloride emissions is studied by means of the following stepwise approach:

Phase 1a: Economical feasibility study

Microbiological studies are evaluated to see if microbes degrading methylchloride had the potential to be applied for industrial biological gas treatment. Affinity and possible toxicity for methylchloride**,** as well as important physiological parameters**,** are evaluated to obtain optimal process condition in order to treat methylchloride waste gas emissions. Operational costs of a full-scale biological waste gas treatment are calculated based on the process parameters that are expected to be required. For the process parameters of which the optimal conditions still has to be determined, a range for the expected optimal condition was estimated based on experiences of other full-scale biological waste gas treatment systems. Calculations are based on airflow of 40000 m^3/h with a methylchloride concentration fluctuating between 100-200 mg/m^3, a temperature ranging from 10-15 °C and a relative humidity of 60%.

Phase 1b: Obtaining biocatalyst (micro-organisms)

A laboratory study is conducted to select micro-organisms degrading methylchloride. The study is conducted with a mixed consortium of micro-organisms, which was taken from different sources. Different pure cultures are selected and are cultivated using methylchloride as substrate. A soil sample from a site contaminated with chlorinated solvents is suspended in mineral medium and shaken. A sample of an aerobic domestic sewage treatment plant and samples collected from a rubber producing plant emitting methylchloride are used as well. This mixed culture is researched for growth in a mineral media with methylchloride as substrate for energy and growth. After obtaining micro-organisms degrading methylchloride, experiments are performed to verify the degradation rate of methylchloride and the influence of some important process parameters on the activity of the micro-organisms. These activity experiments are performed with the microbial consortium pre-grown on methylchloride and tested for methanol oxidation using a Biological Oxygen Monitor.

Phase 2: Onsite bioreactor pilot-scale study
A pilot-scale bioreactor is built and installed on site at a rubber producing plant emitting methylchloride. The bioreactor has a diameter of approximately 1 meter and has a height of approximately 5 meter. The waste gas (250-1000 m^3/h) is led from the bottom of the bioreactor through two layers of differently structured synthetic media to obtain optimal contact between the gas-phase and the biocatalyst. Water is discontinuously re-circulated over each layer from a water reservoir at the bottom of the bioreactor. The temperature of the inlet airstream can be increased by the injection of steam in the inlet ductwork. The pH of the recirculation water can be controlled by the automatic addition of caustic. A constant salt concentration of the recirculation water can be controlled by the automatic draining of recirculation water at certain salt content. The water level in the water reservoir is automatically kept at a constant level to compensate for water losses due to evaporation or automatic draining. The enriched microbial consortium, as well as nutrients, is added to the bioreactor at the start**.**
Twice a day methylchloride concentrations are determined of the inlet air stream, the air in between the layers and outlet air stream using a gas chromatograph. Weekly the airflow, the pressure drop (Testo 445), the biomass concentration and the nutrient concentration of the recirculation liquid are measured. The outlet temperature (GF signet 2350), pH (Meurs) and salt content (Meurs) of the recirculation liquid**,** as well as water recirculation flow (GF 2536), caustic dosing amount (pulse counter of the dosing pump (Milton Roy) are measured online and stored at a PC with a SCADA operator interface.

4 RESULTS AND DISCUSSION

4.1 Phase 1a: Economical feasibility study
4.1.1 Microbiological aspects
A high affinity of a micro-organism for methylchloride as carbon and energy substrate is crucial in order to use the microorganism in waste gas purification to obtain the required low concentration. The affinity is expressed by the substrate affinity constant (K_s) as is used in the Monod-equation. The Monod-equation describes the relation between specific growth rate of a micro-organism and the concentration of the substrate in the liquid-phase. The substrate affinity constant, or Monod-constant, represents the substrate concentration at which the growth rate is half of the maximum growth rate.
Normally waste gas emissions need to be reduced below a certain maximum concentration as determined by the authorities. This maximum emission concentration is the goal for a waste gas treatment. The maximum emissions concentration in the gas-phase can be transformed to a maximum liquid-phase concentration using the gas/liquid partition coefficient.
The feasibility of biological waste gas purification can be determined by comparing this maximum liquid-phase concentration with the affinity of micro-organisms for the compound to be treated (Table 1). For an optimal microbial degradation rate the substrate affinity constant of a micro-organism should be lower or in the same order of magnitude than the above mentioned maximum liquid-phase concentration. The liquid phase concentration should also not be below the minimum substrate concentration for growth. This minimum substrate concentration is the substrate concentration at which the substrate consumption is the same as required for maintenance of the micro-organism itself. So a biological waste gas treatment process can only be developed

when the substrate affinity constant of a micro-organism combined with partition coefficient are low enough.

Table 1. The comparison for different chlorinated compounds of the affinity of halogenated compound degrading micro-organisms with the requirement for waste gas treatment.

Compound	Strain	Affinity constant of strain (K_s)		Air/water partition coefficient	Requirement for waste gas treatment	
		(umol)	(mg/l)	(-)	Gas Phase (mg/m^3)	Liquid phase (mg/l)
Methylchloride	*Methylobacterium chloromethanicum* CM4	0,27 [1]	0,01	0,376	< 20	< 0,05
	Facultative methylotroph strain IMB-1	6,1 [2]	0,3	0,376	< 20	< 0,05
Dichloromethane	*Hyphomicrobium* DM2	1 [3]	0,08	0,125	< 20	< 0,16
1,2-Dichloroethane	*Ancylobacter a.* AD25	24 [4]	2,4	0,056	< 10	< 0,18
Vinylchloride	*Mycobacterium a.* L1	2 [5]	0,2	1,25	< 10	< 0,08

[1] K_m of the chloromethane dehalogenase as determined by Studer *et al.* (2001) and is here assumed the enzyme that is the rate limiting step for methylchloride consumption. [2] K_s of whole cells as determined by Schaefer and Oremland (2004). [3] K_s of whole cells as determined by Hartmans and Tramper (1991). [4] K_s of whole cells as determined by van den Wijngaard *et al*. (1993). [5] K_s of whole cells as determined by Hartmans *et al*. (1992).

It can be concluded that biological waste gas treatment of methylchloride should be feasible when using micro-organisms with a substrate affinity lower than 0,05. The micro-organisms degrading methylchloride that are mentioned in Table 1 are not both suitable, as the substrate affinity of the *Methylobacyerium chloromethanicum* is much better than the substrate affinity of the facultative methylothroph strain. From Table 1 it can also be concluded that biological waste gas treatment could be difficult for 1,2-dichloroethane and vinylchloride. Biological waste gas treatment of dichloromethane is feasible as has been demonstrated at labscale (Hartmans and Tramper, 1991; Diks, 1992).

4.1.2 Full-scale operational aspects

The feasibility of a new technology will be strongly influenced by the investment costs as well as operational costs. The operational costs of a full-scale biological air treatment installation treating methylchloride will be determined by the usage of caustic, fresh water, electricity, nutrients, costs for operating (man hours), costs for maintenance and steam for heating the inlet air stream. Caustic is required to neutralize the produced hydrochloric acid (HCl) in an installation as illustrated in the overall process reaction:

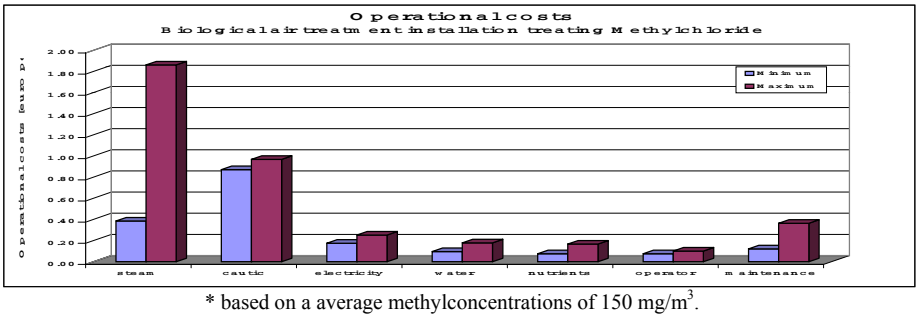
$$CH_3Cl + 1{,}5O_2 + NaCl \rightarrow NaCl + 2H_2O + CO_2$$

The input of fresh water is required to remove the produced sodium chloride (NaCl). The optimum sodium chloride concentration should be determined in practice, but is here estimated to be around 10 gram NaCl/l (range used for cost calculation: 7,5 till 12,5 gram NaCl/l). Electricity for an installation is used for a recirculation pump, a fan and a control panel. The required time for an operator to inspect and to operate an installation will be about 2,5 and 3 hours per week. Instrumentation on an installation

will probably not require much maintenance. A recirculation pump and a fan are probably of most important. It is estimated that the cost for maintenance for wear and tear parts is between € 5000,- and € 15000,- per year. The required temperature for an optimal operation is most likely between 15 and 25 °C, but should be determined more precisely in practice. In most cases the actual temperature of methylchloride waste gas emissions is most likely lower. Probably an increase of the temperature is required especially during the winter. For the determination of the operational costs, the following scenario's are used: worst case: inlet air 10°C, 60% relative humidity → bioreactor 25°C,100%; best case: inlet air 15°C, 60% relative humidity → bioreactor 15°C, 100%. Table 2 shows the utilities required and the unit price as used in the cost calculations. Figure 1 shows the total operational costs for a full-scale biological air treatment installation treating methylchloride emissions. It can be concluded that the operational cost is predominantly determined by two utilities: steam to increase the temperature of inlet waste gas and caustic to neutralize the produced hydrochloric acid.

Table 2. Required utilities for full-scale biological waste gas treatment installation (40000 m^3/h containing a methylchloride concentration ranging from 100-200 mg/m^3).

	Required (per kg MCl removed)	Price per unit
Caustic* (mol NaOH)	23-26	0,35 euro per kg (33% NaOH, 11,2M)
Water* (m^3)	0,13-0,15	1 euro per m^3
Nutrients* (liter)	0,014-0,031	30 euro per kg
Electricity (kW)	4,9-5,6	0,04–0,05 euro/kW
Manpower (days)	0,028 – 0,034	320 euro/day
Steam (kg)	1,2 – 5,8	10 euro per kg



* based on a average methylconcentrations of 150 mg/m^3.

Figure 1. The total operational costs for a full-scale biological air treatment installation treating 40000 m^3/h with a methylchloride concentration ranging from 100-200 mg/m^3.

4.2 Phase 1b: Obtaining biocatalyst (micro-organisms)

A mixed microbial consortium capable of degrading methylchloride is obtained. Using a stable microbial consortium, a degradation rate of a maximum degradation rate of 3,7 nmol/min/mg protein is observed with a concentration of 150 mg/m^3 methylchloride in the head space. The robustness of the bacteria to a tenfold higher methylchloride concentration is also studied. A tenfold higher methylchloride concentration than the methylchloride concentration in the emitted waste gas showed no toxicity effect to the microbial consortium.

Low concentrations of n-hexane can be present in the waste gas containing methylchloride. The influence of n-hexane on the degradation of methylchloride is determined and showed not to have an effect. The effect of important parameters like pH, temperature and sodium chloride concentration are shown in Figure 2a-c.

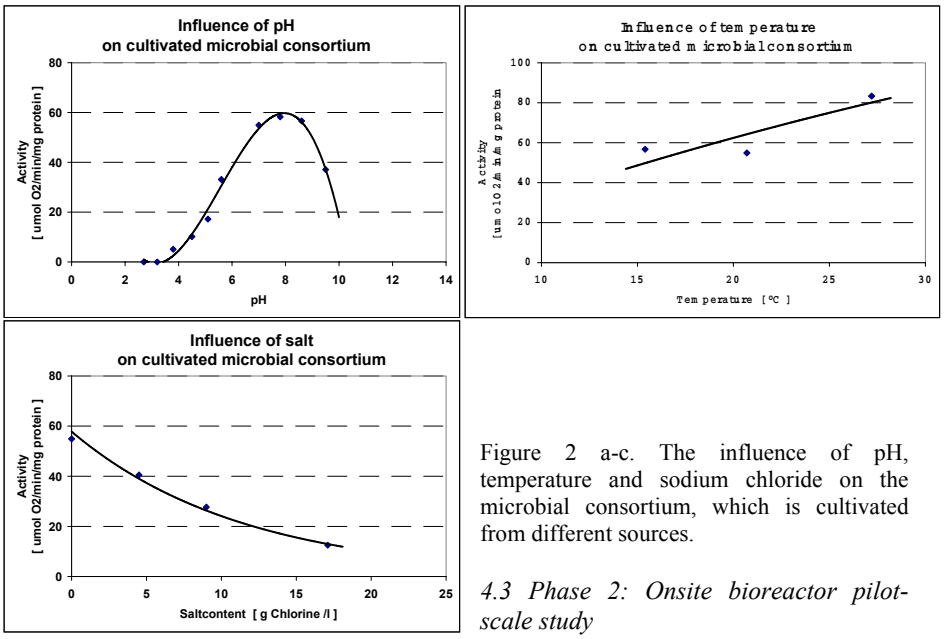


Figure 2 a-c. The influence of pH, temperature and sodium chloride on the microbial consortium, which is cultivated from different sources.

4.3 Phase 2: Onsite bioreactor pilot-scale study

Preliminary results of the pilot-scale reactor treating methylchloride emissions proved that the goal to reduce the concentration to the required level can be obtained (Figure 3). After the start-up period of 6 weeks the average outlet methylchloride concentration is 9,7 mg/m^3, which is lower than the required 20 mg/m^3.

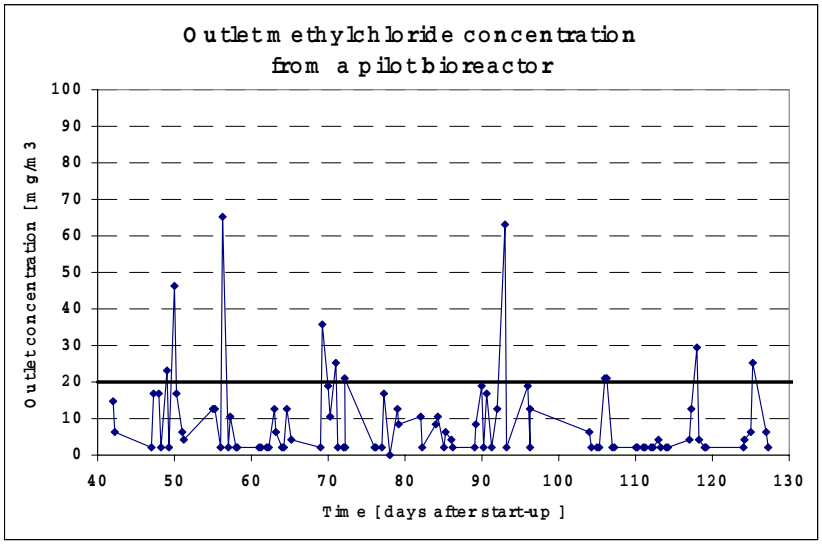


Figure 3. Outlet methylchloride concentrations from the pilot-scale bioreactor treating methylchloride emissions. The required concentration to be obtained after treatment is 20 mg/m^3.

Figure 4 shows the removal of methylchloride at different loadings. The maximum loading seems not to be obtained. The influence of temperature in the bioreactor on the removal efficiency is illustrated in Figure 5. The influence of temperature in the bioreactor proved to be of less influence than the influence of temperature on the activity of free cells (figure 2b). The decrease of temperature in the bioreactor will decrease activity of the bacteria in the bioreactor, but showed to be compensated by the increase of the mass-transfer. A lower temperature increases the solubility of methylchloride (a lower Henry-coefficient). A lower operational temperature showed to be important as can be seen in Figure 1 illustrating the costs required for steam to increase inlet air temperature can be relatively high.

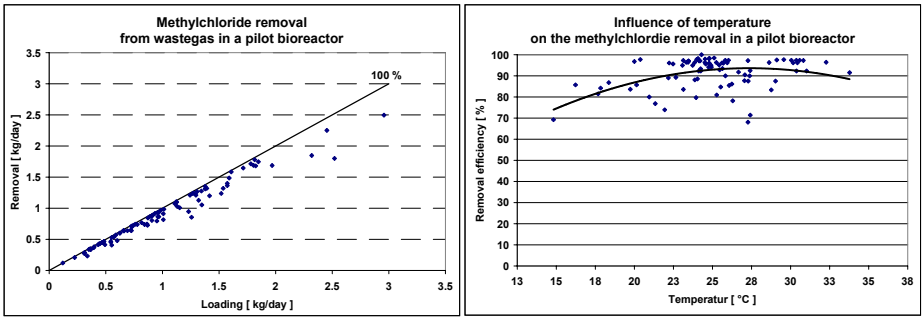


Figure 4. Loading of methylchloride versus removal of methylchloride in the pilot bioreactor.
Figure 5. The influence of temperature on the removal of methylchloride in the pilot bioreactor.

Although not all tests are performed to quantify robustness (Kraakman, 2003) of the bioreactor, some upsets are studied. The absence of carbon and energy source (methylchloride) for one week and the absence of recirculation water for about 1 day are tested and proved that full recovery took in both upsets at least one, but not more than a few days.

5 CONCLUSIONS

Microbial and operational aspects illustrated that the biological waste gas treatment of methylchloride should be feasible. The micro-organism with a high affinity for methylchloride is important. In a pilot-scale bioreactor, inoculated with a mixed consortium of methylchloride degrading micro-organisms, the required outlet concentrations can be reached. The influence of temperature in the bioreactor proved to be of less influence than the influence of temperature on the activity of free cells. This is of importance as the operational costs required to obtain optimal temperature can be significant.

6. REFERENCES

Butler, J.H. (2000) Better budgets for methyl halides? *Nature.* 403: 260-261.

Diks, R.M.M. (1992) Removal of dichloromethane from waste gases in a biological trickling filter. Dissertation Technical University of Eindhoven, The Netherlands.

Doronina, N.V., Sokolov, A.P. and Trotsenko, Y.A. (1996) Isolation and characterization of aerobic chloromethane-utilizing bacteria. *FEMS Microbiol. Lett.* 142(2-3): 179-183.

Harper, D.B. and Hamilton, J.T.G., (2003) The global cycles of naturally-occurring halomethanes, In (G.W. Gribble., eds.) The handbook of environmental chemistry. Springer-Verlag, Berlin, Germany. pp. 17-41.

Harper, D.B., Hamilton, J.T.G., Ducroq, V., Kennedy, J.T., Downey, A. and Kalin, R.M. (2003) The distinctive isotopic signature of plant-derived chloromethane: possible application in constraining the atmospheric chloromethane budget. *Chemosphere.* 52: 433-436.

Hartmans, S. and Tramper, J. (1991) Dichloromethane removal from waste gases with a trickling-bed bioreactor. *Bioprocess Eng.* 6: 83-92.

Hartmans, S., Kaptein, A., Tramper, J. and de Bont, J.A.M. (1992) Characterization of a *Mycobacterium* sp. and a *Xanthobacter* sp. for the removal of vinyl chloride and 1,2,-dichloroethane from waste gases. *Appl. Microbiol. Biotechnol.* 37: 796-801.

Hartmans, S., Schmuncle, A., Cook, A.M. and Leisinger, T. (1986) Methyl chloride: naturally occurring toxicant and C-1 growth substrate. *J. Gen. Microbiol*. 132: 1139-1142.

Kennes, C. and Veiga, M.C. eds. (2001) Bioreactors for waste gas treatment, Kluwer Acadamic Publicers, Dordrecht, The Netherlands.

Kraakman, N.J.R. (2003) Full-scale biological treatment of industrial CS_2-emissions at extreme conditions; The robustness of a biological system and its risks to the waste gas purification. *Environ. Eng.* 22(2): 79-86.

McAnulla, C., McDonald, I.R. and Murrell, J.C. (2001) Methyl chloride utilising bacteria are ubiquitous in the natural environment. *FEMS Microbiol. Lett.* 201: 151-155.

McDonald, I.R., Warner, K.L., McAnulla, C., Woodall, C.A., Oremland, R.S. and Murrell, J.C. (2004) A review of bacterial methyl halide degradation: biochemistry, genetics and molecular ecology. *Environ. Microbiol.* 4 (4): 193-203.

Montzka, S.A., Butler, J.H., Myers, R.C., Thompson, T.M., Swunson, T.H., Clarke, A.D. Lock, L.T. and Elkins, J.W. (1996) Decline in the tropospheric abandance of halogen from halocarbon: implications for stratospheric ozone depletion. *Science.* 272: 1318-1322.

Schaefer, J.K. and Oremland, R.S. (1999) Oxidation of methyl halides by the facultative *methylotroph* strain IMB-1. *Appl. Environ. Microbiol.* 65(11): 5035-5041.

Schaefer, J.K., Goodwin, K.D., McDonald, I.R., Murrell, J.C. and Oremland, R.S. (2002) *Leisingera methylohalidivorans* General nov., a marine methylotroph that grows on methylbromide. *Int. J. Syst. Evol. Microbiol.* 52: 895-900.

Shareefdeen, Z. and Singh, A. eds. (2005) Biotechnology for Odour and Air Pollution Control (2005) Springer-Verlag, Heidelberg, Germany.

Studer, A., Stupperich, E., Vuilleumier, S. and Leisinger, T. (2001) Chloromethane: tetrahydrofolate methyl transfer by two proteins from *Methylobacterium chloromethanicum* strain CM4. *Eur. J. Biochem.* 268: 2931-2938.

U.S. Environmental Protection Agency, Air toxic website www.epa.gov/ttn/atw/hlthef/methylch.html. (2005).

Van den Wijngaard, A.J., Wind, R.D. and Janssen, D.B. (1993) Kinitics of bacterial growth on chlorinated aliphatic compounds. *Appl. Environ. Microbiol.* 59: 2041-2048.

Vannelli, T., Studer, A., Kertesz, M. and Leisinger, T. (1998) Chloromethane metabolism by *Methylobacterium* sp. strain CM4. *Appl. Environ. Microbiol.* 64(5): 1933-1936.