Electronic Supplementary Material (ESI) for Environmental Science: Processes & Impacts.


***Microaerobic conditions in anaerobic sludge promote changes in bacterial composition favouring biodegradation of polymeric siloxanes***

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**Table 1.** Micronutrient solution developed by Labatut et al. based on Owen et al. 1979 and Angelidaki et al. 2009.

| Media Solution | mg/L in BMP unit |
|---|---|
| $NH_4Cl$ | 200 |
| KCl | 100 |
| $MgCl_2 *6H_2O$ | 600 |
| $KH_2PO_4$ | 138 |
| $K_2HPO_4$ | 176 |
| Vitamins | |
| Yeast extract | 100 |
| Trace elements | |
| $FeCl_3 *6H_2O$ | 200 |
| $MnCl_2 *4H_2O$ | 4 |
| $CoCl_2 *6H_2O$ | 10 |
| $NiCl_2 *6H_20$ | 10 |
| $ZnCl_2 *2H_2O$ | 0,5 |
| $Na_2SeO_3$ | 0,1 |
| $Na_2MoO_4 *2H_2O$ | 0,5 |
| $CaCl_2 *2H_2O$ | 100 |
| $CuCl_2 *2H_2O$ | 0,5 |
| KI | 10 |
| $H_3BO_3$ | 0,5 |
| Others | |
| Resazurin | 1 |
| $Na_2S *9H_2O$ | 100 |
| $NaHCO_3$ | 4200 |

**Supplementary materials and methods**

**MM1.** BMP assay oxygen addition

To oxygen addition per bottle, the total volume of the reaction unit was measured using a calibrated measuring cylinder. The total volume of each Schott bottle is 290mL; accordingly, the oxygen concentrations were calculated considering this total volume. For example, for 1% $^{v}/_{v}$ $O_2$, the proportional sets equation calculations result in a 2.9mL of pure oxygen (99.8% $^{v}/_{v}$) added to the corresponding BMP bottles. Pressure and temperature at the moment of the addition were the atmospheric ones (1atm, 293.15K), and pressure was equilibrated in a serum bottle that was purged with oxygen and then filled out with pure $O_2$ until slight (1 bar) positive pressure.

The $O_2$ addition volume was taken from the sealed serum bottle using a gastight glass syringe (30mL-Fisher Sci.) coupled with pressure valves to assure the precise oxygen dosage. Oxygen from the bottle was freely let flow to fill the syringe until the desired volume, so the gas is not under a differential pressure, then it was dosed on the BMP unit. For oxygen addition in the BMP bottle, each one was taken from the incubator and let out to equilibrate the temperature until 20°C (293.15K), then the volume amount will be added as oxygen was removed from the headspace to create a slight negative pressure. For example, in the 1% treatments, 2.9mL ± 0.2 internal gas was removed and then the same amount of oxygen was added, re-establishing the internal pressure of the BMP bottle. This procedure was employed every time that oxygen was added or replaced in all the BMP units.

**MM2.** Analytical determinations

Volumetric biogas production was measured using a gastight glass syringe (30mL-Fisher Sci.) connected to the exhaust valve of each BMP unit (**Fig. 1. MM2**) and let the biogas flow freely to fill the syringe, measuring the displacement volume. When volume was captured in the gas tight syringe, all of it was added to an impinger system (2 glass impingers) to volumetric measure methane in the system based on Standard Methods 2720B. Later, using a chromatographic glass syringe (500µL-Fisher Sci.), 100µL were removed from the BMP headspace and used for the biogas characterization in the GC-TCD equipment.

**Fig. MM1.** BMP experimental units

In order to prevent the ubiquitous VOSiCs contamination, the analyst involved in the sample measuring and extraction followed the recommendations given in Varaprath et al. ([76]) in terms of sample preparation, material pre-treatment and cleaning, and use of personal elements such as gloves, among others that could add VOSiCs to the measurement. As well, to control the background levels, several blanks were used to subtract the possible contaminations in the sampling or measuring process. GC-MS and GC-FID measurements with solvent blanks, column blanks with solvent, glass material (BMP bottles) with the only solvent, among others, were performed to account for the background VOSiC levels, finding that concentrations were minimal (<0.5ppm) and were considered for the analysis of the results in the experimental run. As well, detection and quantification limits were analysed according to Sánchez-Brutene et al. ([72]) methodology for D4 and D5 siloxanes. In brief, the lowest level of calibration curves was used as initial stock for serial dilutions to be measured in the GC-MS equipment, finding values for D4: LOD 8 $ng \cdot g^{-1}$, LOQ 20 $ng \cdot g^{-1}$ and for D5: LOD 2 $ng \cdot g^{-1}$, LOQ 9 $ng \cdot g^{-1}$. Finally, extraction recovery was evaluated by doping a known concentration of D4/D5 mixture in blank sludge

samples to perform later their solvent assisted extraction, finding a 95 to 97% VOSiC recovery using the proposed solvent mixture (Acetone:n Hexane – 1:1).

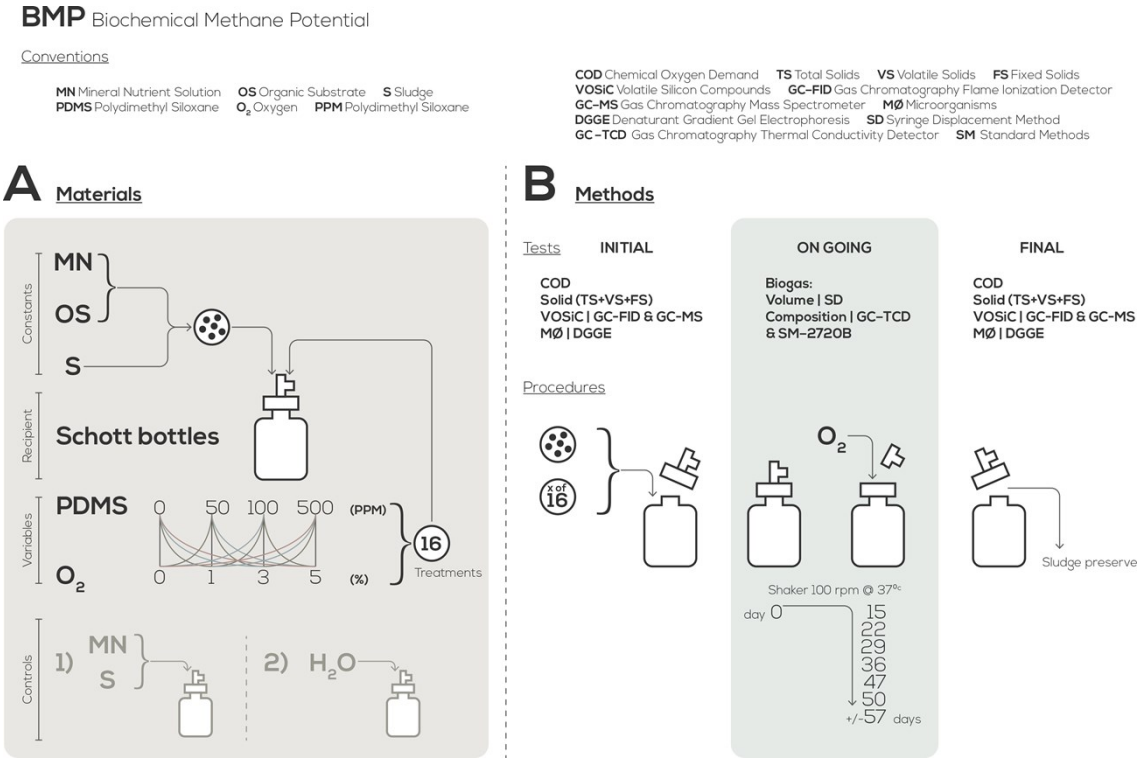


**Fig. S1.** Materials and methods of the BMP assay development.

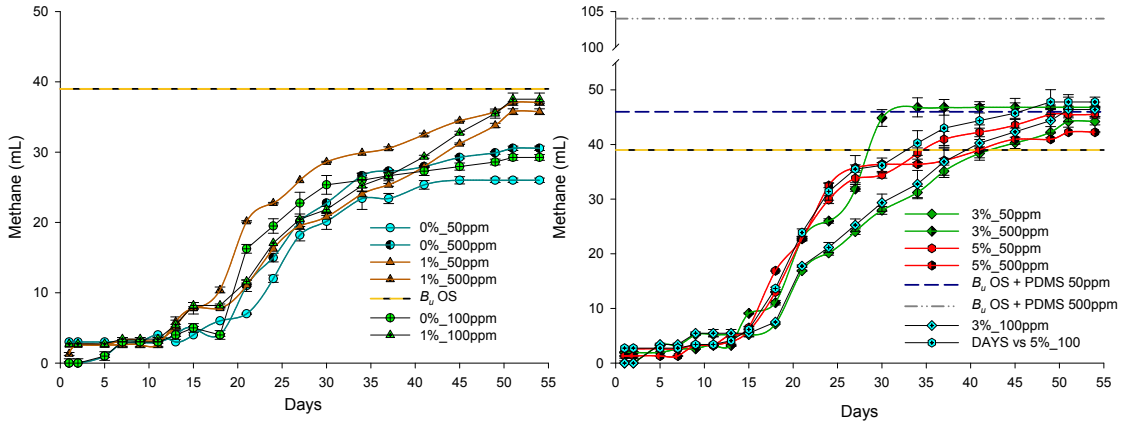


Fig. S2. Cumulative methane production of the organic substrate (OS) supplemented with increasing PDMS concentrations under anaerobic and microaerated conditions, including 100-ppm PDMS treatment not shown in Fig. 2.

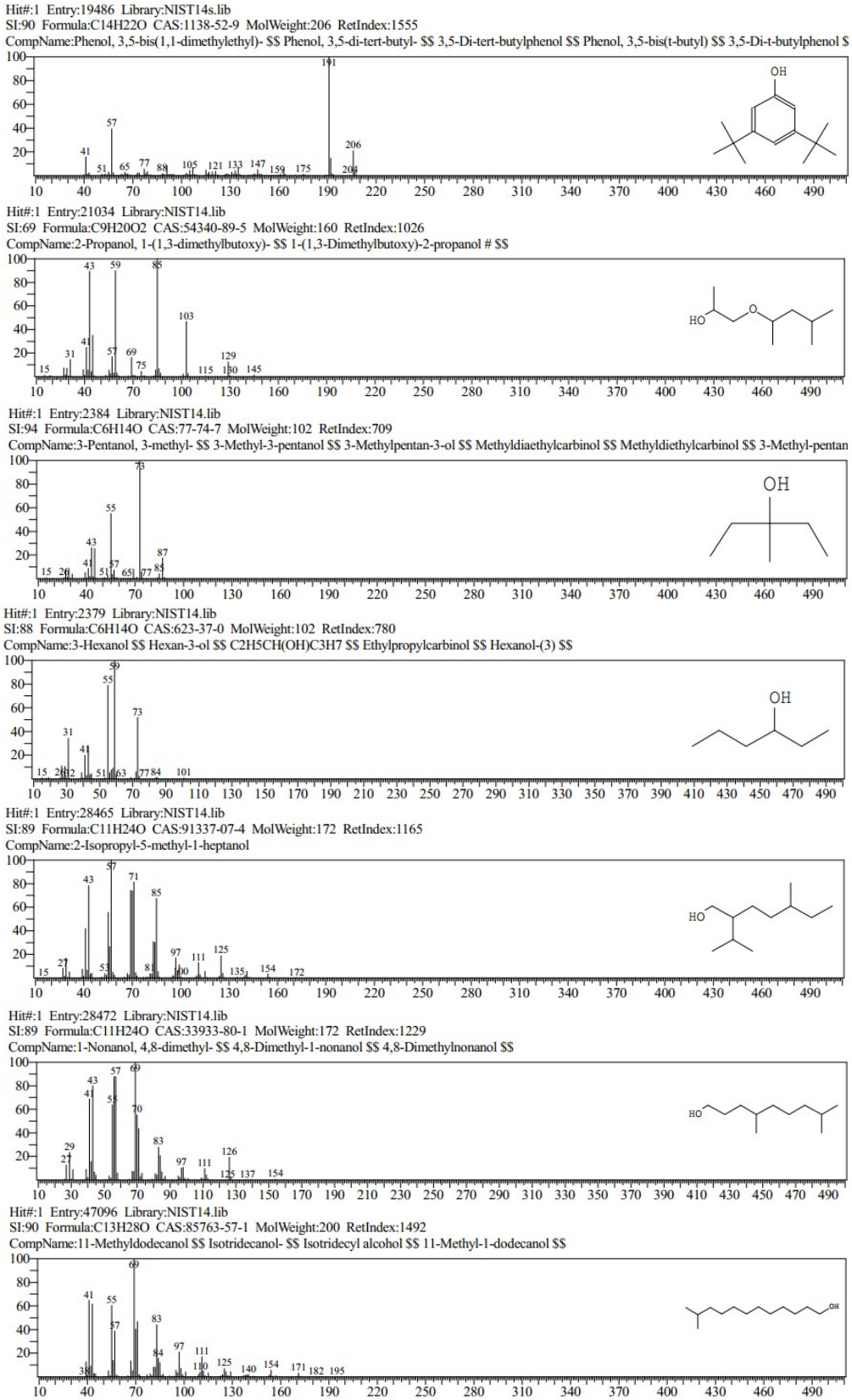


Fig. S3 Microbial inhibitory compounds (aliphatic alcohols and phenol) found in the liquid phase under microaerobic treatments $O_2$ 3% - 5% $^{v}/_{v}$, n-Hexane: Acetone extraction and GC-MS (QQQ) elucidation.

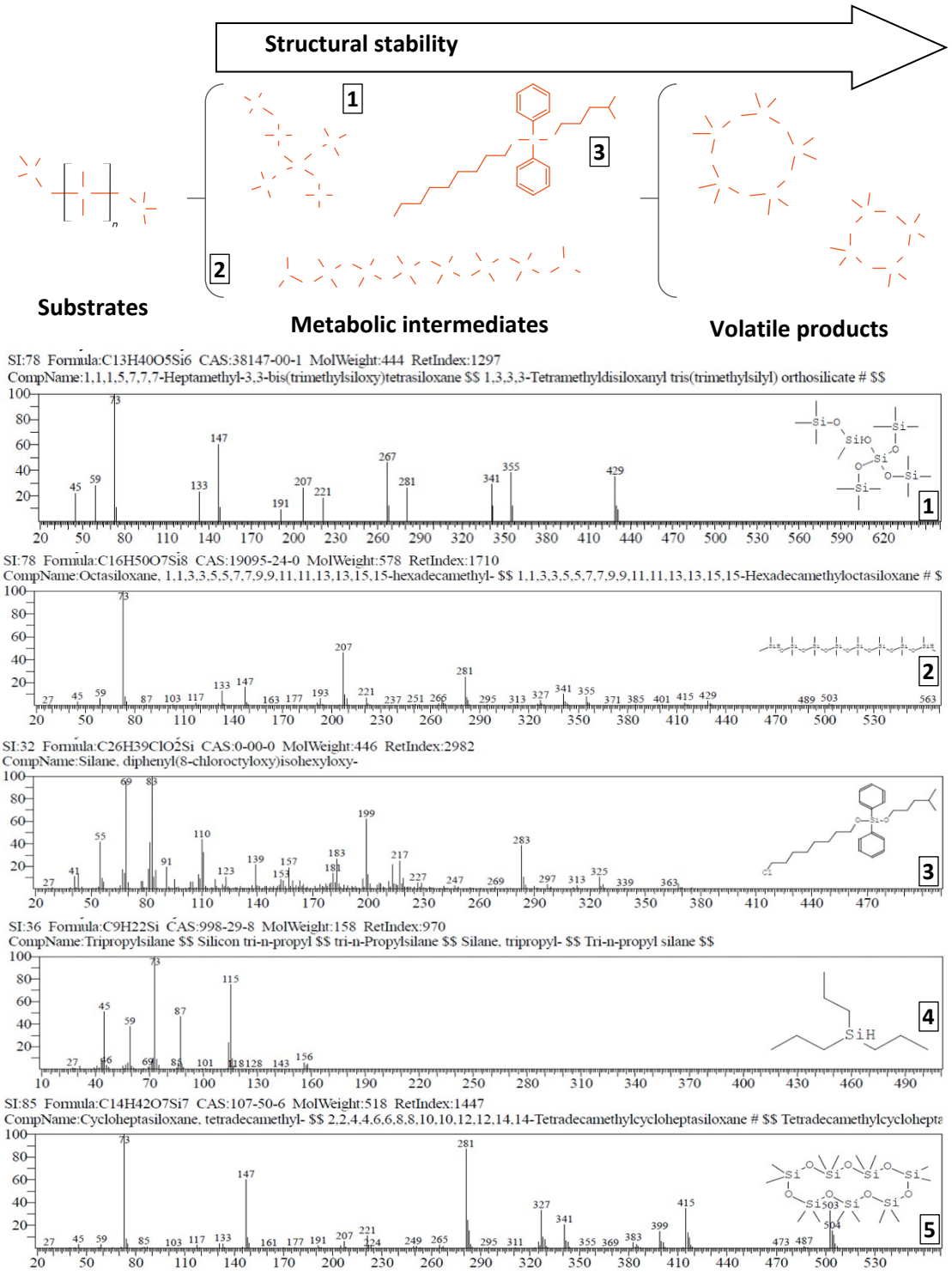


**Fig. S4.** Other products from PDMS cleavage and metabolism under microaerobic treatments $O_2$ 3% - 5% $^{v}/_{v}$, n-Hexane: Acetone extraction and GC-MS (QQQ) elucidation. Found compounds in the mass spectra correspond to **1.** Heptamethyl 3,3 bis (Trimethylsiloxy) Tetrasiloxane, **2.** Hexadecamethyl-Octasiloxane, **3.** Diphenyl (8 Choloroctyloxy) Iso-Silane, **4.** Tri-n-Propylsilane, **5.** Tetradecamethyl Cycloheptasiloxane.