ON THE ORIGIN OF METHYLATED GERMANIUM COMPOUNDS IN NATURAL WATERS

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Introduction

Discovery of picomolar levels \((10^{-12} \text{ M})\) of dissolved monomethylgermanium (MMGe) and dimethylgermanium (DMGe) in seawater and riverine sediments has led to suspicions that these organogermain compounds are biomethylated from dissolved inorganic Ge: germanic acid – Ge(OH)\(_4\) - a trace congenor of dissolved silica - silicic acid – Si(OH\(_4\)). This research focussed on finding Ge-biomethylation processes in natural environments to target discovery of potential silicon biomethylation agents. Ge-methylation might proceed by processes similar to those for other methylated metalloids (e.g., Hg, As, Se, Sb). Attempts to find methylated-Ge (MexGe) in extracts from natural marine and freshwater plankton or sediments were unsuccessful. Attempts to methylate inorganic-Ge (IV) in aerobic cultures/media with marine and freshwater organisms, their extracts, or methyl donors, using known methylating targets, were also unsuccessful. However, over the past decade several investigators have detected high concentrations (nM) of MMGe, DMGe & trimethylgermanium (TMGe) in terrestrial aquatic environments exhibiting both anaerobic diagenesis and anthropogenic metalloid enrichment - anaerobic digesters of wastewater treatment plants (WWTP) and methanogenic sediments of rivers downstream of WWTP’s. We thus investigated possible anaerobic Ge-methylation processes.

Experimental

With support and collaboration from Dow Corning & Genencor, we tested if methanogens could biomethylate Ge. Cultures obtained from anaerobic digesters of two WWTPs producing MexGe were fed dextrin & peptone. These cultures were analyzed every few weeks for gases (CH\(_4\) & CO\(_2\)), pE, pH and Ge-speciation. Despite well-developed methanogenic activity, methane production and low pE, no Ge-methylation was detected. Methanogenic cultures were subsequently initiated from other anaerobic digesters and from a methane-producing Chattahoochee River sediment with high concentrations of inorganic and MexGe, including TMGe, which is not found in the ocean and only rarely in rivers immediately downstream of WWTPs. Presence of TMGe was thus interpreted as a sentinel for proximal Ge-methylation. These cultures were manipulated by (1) feeding activated sewage sludge; (2) amending with Ge and methyl-acceptors (As, Se); (3) feeding dextrin & peptone; (4) feeding H\(_2\):CO\(_2\) (to lower pE); and (5) adding methyl donors (Methyl-B12, Se-methionine). Parallel LD-50 experiments with elevated Ge and MexGe demonstrated that anaerobic microbes are unaffected up to [Ge] concentration levels exceeding 1 µM and do not destroy MexGe.

Results and Discussion

None of these experiments showed evidence of sustainable MexGe production. Thus mixed methanogene cultures maintained under a variety of feeding conditions, even at high [Ge], do not produce MexGe. During this research we inadvertently discovered that MexGe, including TMGe, is created in a Dow Corning production plant during inorganic (industrial) methylation of silicon (the "Direct Process" or Rochow-Muller method). This Process methylates pure intrinsic silicon to produce the building blocks of the silicone polymer industry (MM-chlorosilane, DM-chlorosilane & TM-chlorosilane) which are subsequently polymerized into polysiloxanes. Apparently, traces of Ge in the silicon feedstock are inadvertently methylated during the Direct Process to MM-chlorogermane, DM-chlorogermane and TM-chlorogermane. These trace methylgermane compounds are then co-distilled with their methylsilananes and co-polymerized into silicones. Release of silicones to terrestrial aquatic environments with subsequent anaerobic breakdown to methylsilanols probably releases the methylgermanols (MMGe, DMGe, TMGe) to natural waters. If intrinsic silicon contains about the crustal Ge/Si ratio (~10\(^{-6}\) atom/atom), and if the methyl conversion efficiency for Ge is about the same as for Si in the Direct Process, then we predict that silicones contain Ge at the ppm level (Ge/Si ~ 10\(^{-6}\)) and their breakdown results in the same methylgermanol to methylsilanol ratio. MexGe in freshwaters may thus be a tracer of difficult-to-detect methylsilanols.

Conclusions

The sources of MexGe in the marine environment remain enigmatic. However, this research suggests that MexGe occurrences in WWTPs and terrestrial freshwaters may be the result of anaerobic breakdown of man-made silicones containing trace amounts of methylated-Ge.