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COMMUNICATION

Bioturbation recorded by a sedimentary siloxane horizon

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A Puget Sound (Washington State, USA) sediment core was quantitatively analyzed for organic silicon content, as derived from post-1945 release of poly(organo)siloxanes (silicones). The sedimentary silicone data record and preserve a smeared event horizon, dating the first appearance of silicones in the sediment column. This record of bioturbation preserved deep in the column appears somewhat in contrast to the record provided by ^{210}Pb geochronology. Aliquots of the same core segments had been dated previously using ^{210}Pb, and analyzed for silicone content, as reported in this study. Core samples older than 50 years showed no detectable silicone, as measured by a new procedure utilizing inductively coupled plasma emission spectroscopy, after solvent extraction to collect the silicone from gram-sized sediment core samples.

Keywords: Poly(organo)siloxanes (silicones), environment, analysis, sediment, core samples, event horizon

INTRODUCTION

Poly(organo)siloxanes (silicones) are totally synthetic polymers useful for their unique physical properties, and chemical stability under environmental conditions. Previous work[1] had demonstrated the existence of a 'silicone event horizon' in a Puget Sound (Washington State, USA) core. This event horizon is the appearance, in the sedimentary record, of silicones in sediments approximately 15 years old. Older sediments did not exhibit detectable silicone, a fact ascribed to the increasingly widespread use of silicones only since World War II. However, the earlier report examined a limited number of samples for silicone content, and could not define exactly vertical location or extent of the silicone event horizon. Reported in this paper is the detailed examination of another ^{210}Pb-age geochronologically dated Puget Sound core, separate aliquots of which were analyzed for ^{210}Pb age and silicone content. The quantitative measurements of silicone in this case provide a clearer definition of the silicone event horizon.

EXPERIMENTAL

Sampling

The sediment core used in this study was obtained with standard metal Kasten coring equipment and was subsampled, and stored frozen soon after collection. There is no reported evidence that the deeper (i.e. buried) sedimentary record in the region of the core collection site (see Fig. 1) has been grossly disturbed (i.e. slumping, dredging). This sedimentary stability implies that a chemical event (e.g. first appearance of silicones in the sediment column) should be well preserved. However, the actual integrity of the buried sediments may need to be reconsidered, as will be discussed later. The core samples were dated by using ^{210}Pb (byproduct of ^{222}Rn decay) geochronology, as discussed in Refs 2 and 3; other aliquots of the same core were analyzed for silicone content. Sediment data is given in Table 1.

Sample processing for silicone content

Freeze-dried samples of the core sediment (average weight 3 g) were weighed out into new, chloroform (Fisher HPLC grade)-rinsed scintillation vials (borosilicate glass, Kimble, 20 cm^3) and covered with

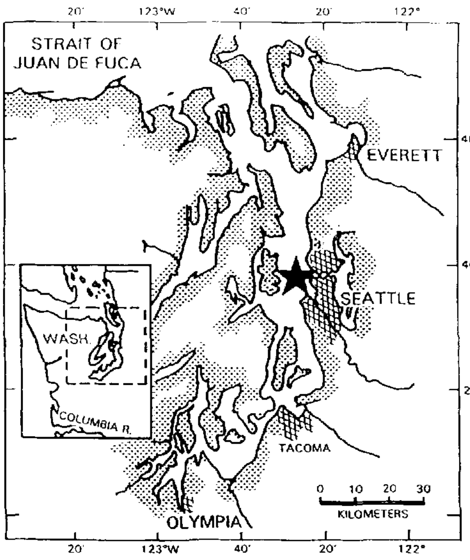

Figure 1 Study area in Washington State, USA.

Table 1 Data associated with Puget Sound core

Depth interval[a] (cm)	^{210}Pb age[a]	Sediment organosilicon content,[b] (ppm)
0–2	Contemporary	0.17
9–11	5	0.12
14–16	7.5	0.14
19–21	10	0.15
29–31	15	0.07
39–41	20	0.12
49–51	25	0.14
59–61	30	0.07
79–81	40	0.08
89–91	45	0.05
99–101	50	bdl
119–121	60	0.38[c]

[a] Core collected at 47° 42.31 N, 122° 26.4′ W. Sedimentation rate here is approximately 2 cm/year. See Ref 3 for details. [b] Detection limit is 0.01 μg g^{-1} Si in chloroform; sediment data are good to ±15%; bdl = below detection limit. Poly-dimethyl-silicones are 39% silicon. PDMS are the most widely used (released) silicones on a tonnage basis.[5] [c] This value appears to be an artefact of sample collection, handling, processing, or analysis, and is not included in the text discussion.

Table 2 Inductively coupled plasma (ICP) operations parameters

Instrument	Perkin-Elmer Plasma II ICP Spectrophotometer
RF power	1500 W
Plasma gas flow	17 dm^3 min^{-1}
Auxiliary gas flow	1.5 dm^3 min^{-1}
Nebulizer gas flow	0.5 dm^3 min^{-1}
Monochrometer	1800 line mm^{-1} holographic grating
Silicon analytical wavelength	251.618 nm

Procedural notes: A large-diameter injector tube was used in the torch to eliminate carbon deposition. Chloroform softens both standard and solvent-flexible peristaltic pump tubing; silicone rubber tubing gives a large silicon blank. Therefore, a concentric nebulizer is used for ICP analysis of chloroform-based samples, as the concentric nebulizer does not require a peristaltic pump and tubing for sample delivery. Please see Ref 6 for a more detailed consideration of the analyses of organic species in organic solvents by ICP.

chloroform. The samples were sonicated for half an hour, allowed to settle, and filtered through 0.22 μm pore-size filters (Millipore Type GS pre-rinsed with chloroform), held in a Pyrex Millipore filter apparatus. Filtrates were transferred to new, rinsed scintillation vials; all transfers were with separate, new chloroform-rinsed borosilicate glass Pasteur pipettes. Just prior to instrumental analysis, the samples were made up to 5.0 cm^3 with chloroform.

The technique reported here probably extracts in excess of the 35% extraction rate of the total silicone spiked into test samples reported in Ref 4, an earlier study which used diethyl ether solvent extraction to measure sedimentary silicones. The lipid solvent chloroform combined with the sonication used in the current work should at least match the results reported earlier.[4] There is also no evidence for silicone retention on walls of sample vials if the vial contents are kept moist with solvent. Ultimate sensitivity of the technique is related to sample size: samples with low silicone content may require larger sample (e.g. tens of grams) for processing. Please see Table 1 for instrumental sensitivity data.

Instrumental

For analysis, the samples were examined with a Perkin–Elmer Model Plasma II inductively coupled plasma spectrophotometer (ICP). Instrumental parameters are given in Table 2. The instrument was calibrated with octaphenylcyclotetrasiloxane (OPCTS:

Kodak) in chloroform, using solutions of low $\mu g\ g^{-1}$ (ppm) organosilicon content.

RESULTS AND DISCUSSION

Results are presented in Table 1 and Figure 2. Note that all core segments examined exhibited some silicone content, but with a generally decreasing amount of silicone as a function of depth in the core. This situation is plausible for two reasons. First, data relating to the steadily increasing manufacture of silicones[5] argues that increasing amounts of silicone would be available for release to the environment (especially through the discard of silicone-bearing consumer products, e.g. hand lotions), where they would be seen in the upper segments of the core. Second, the data indicate that bioturbation is occurring in the area of collection of the core examined. Specifically, one could expect that, if the core's surface layers were not bioturbated, the core at 89–91 cm depth (45 years old; ca. 1940) should exhibit no silicone at all whereas at that depth there is in fact a low level of silicone observed. Indeed, only at 99–100 cm (50 years old) is no silicone observed. Thus, the deep-sediment silicone event horizon appears somewhat smeared because of post-depositional bioturbation, which is preserved in the deeper-sediment record.

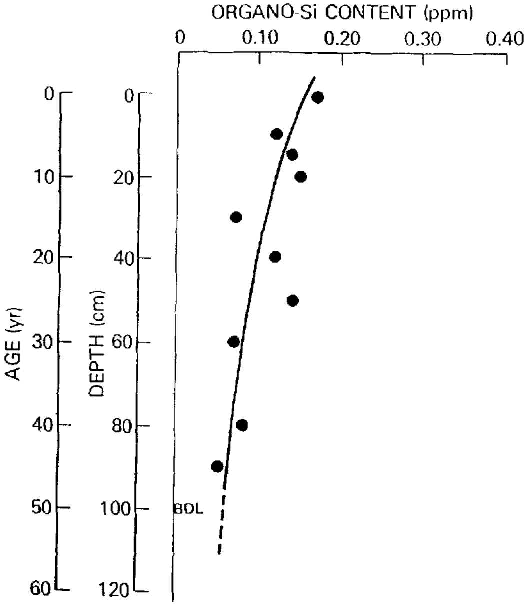

Figure 2 Organosilicon data for Puget Sound core.

Both Carpenter, *et al.*[2] and Lavelle, *et al.*[3] discuss measurement of the thickness of the upper bioturbated layer in the sediments of the generally well-oxygenated waters of Puget Sound. They report bioturbated layers of 1 to 40 cm thickness, depending on location in the Sound. These estimates were made by measuring excess (above natural) ^{210}Pb in the upper layer of the sediment column; this excess ^{210}Pb is carried into the uppermost sediment by biological activity (bioturbation). However, both authors assign the bottom of the bioturbated layer to the appearance of unsupported ^{210}Pb in the sedimentary record. If there were no biological activity in the sediment column, once a parcel of sediment were buried, its ^{210}Pb would decay exponentially. However, bioturbation can mix upper sediment ^{210}Pb into the buried sediment: this mixed-in ^{210}Pb is excess ^{210}Pb, or ^{210}Pb content supported by bioturbation. Only below the bioturbated layer is the ^{210}Pb unsupported, and this unsupported ^{210}Pb then decays exponentially with time, ($\tau_{1/2}$ = 22.3 yr), allowing one to assign an age to a position (depth = time) in the sediment column. The significant point, though, is that the thickness of the bioturbated layer may be less well defined by a tracer that changes with time (e.g. ^{210}Pb), especially if movement of the tracer into the upper sediment layer occurs over a significant portion of the half-life of the tracer. The historical record of sedimentary silicone preserves the effects of bioturbation to a degree not possible with a less stable chemical or radioactive tracer. Note, of course, that the input-to-sedimentation rate function for silicone is not a constant as it is for ^{210}Pb. That is, as silicone usage expands, there is an increasing amount of silicone in the materials input to the sediment, whereas, ^{210}Pb input via atmospheric radon decay is fairly constant year to year. However, the combination of biological and chemical inertness of silicones argues that silicones can well complement radioisotope measurements of sedimentary processes, and that silicones serve as especially effective tracers for anthropogenic influences in the sedimentary record. Furthermore, the relative ease and rapidity with which sediments can be analyzed for silicone content (solvent extraction combined with atomic absorption or inductively coupled plasma (ICP) atomic spectroscopy) makes silicones an attractive adjunct to radioactive tracers which require specialized and dedicated processing and counting equipment for assay.

CONCLUSIONS

This study extends an earlier, more qualitative, observation concerning the existence of a silicone event horizon in Puget Sound sediments. Sediments older than about 50 years contain very little, or no, detectable organosilicon (silicone) while more contemporary sediments exhibit increasing amounts of silicone as the sediments become younger. In spite of evidence of bioturbation preserved at depth in the sediment core, the silicone event horizon appears to occur some 40 to 45 years ago, an observation coinciding with the widespread use and release of silicones since about the late 1940s. Indeed, it is this occurrence which allows the appearance of chemically and biologically inert silicones as a definitive chemical event, and allows examination of the effects of bioturbation on sediment deposition. Silicones record these bioturbation effects more completely than do potential markers which can decay with time. In addition, the solvent extraction – ICP analytical procedure presented in this paper offers both speed for sample processing and the sensitivity to measure organosilicon species in gram-sized samples of sediment.

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