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Sedimentary siloxanes: A depositional history

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A Puget Sound sediment core has been quantitatively analyzed for organic silicon content, as derived from post-1945 release of poly(organo)siloxanes (silicones). The sedimentary silicone data record and preserve at depth, a smeared event horizon, or first appearance of silicone in the sediment column. Core samples older than 50 years showed no detectable silicone as measured by a new procedure utilizing inductively coupled plasma (ICP) emission spectroscopy after solvent extraction to collect the silicone from gram-sized sediment core samples.

Keywords: Siloxanes (silicones), lead-210, inductively coupled plasma spectrophotometer, environment, sediment deposition

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 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 research qualitatively examined a limited number of sediment samples for silicone content, and could not exactly define vertical location or extent of the silicone event horizon.

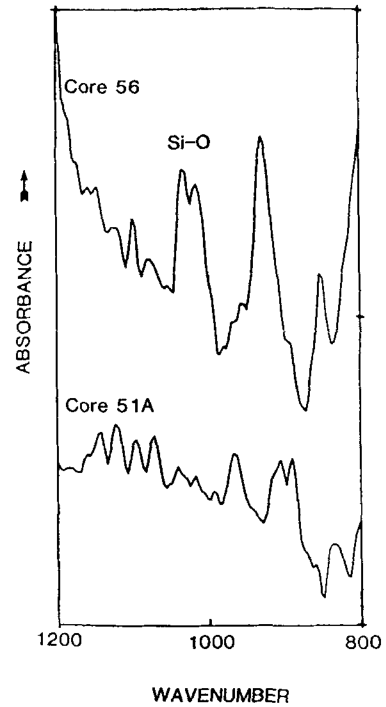

Figure 1 Example of FTIR silicone data.[5]

Figure 1 shows the type of data obtainable using the Fourier transform infrared (FTIR) spectroscopy technique reported earlier. While a spectroscopy-based technique offers several advantages, such as rapid sample throughput and preservation of the sample for further analyses, such an approach is, unfortunately, largely qualitative in nature.

Reported in this paper is the detailed examination of lead (^{210}Pb) age-dated Puget Sound core. The quantitative measurements of silicone in this case provide a clearer definition of the silicone event horizon. Indeed, it may be useful to combine the two techniques, using FTIR to characterize the extracted organosilicon species (e.g. methyl, phenyl, mixed silicone) and then the new procedure to quantify the extracted organosilicon material.

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EXPERIMENTAL

Sampling

The sediment core used in this study was obtained with metal Kasten coring equipment, and was extruded, 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. 2) has been grossly disturbed. Thus a chemical event (i.e. first appearance of silicones in sediment column) should be well preserved. The core samples were dated by using ^{210}Pb (a by-product of ^{222}Rn decay) geochronology, as discussed previously.[2,3]

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) and covered with 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 chloroform-rinsed 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.

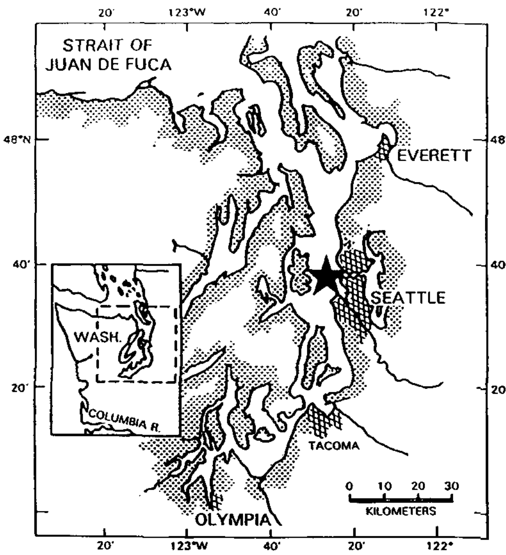

Figure 2 Study area in Washington State, USA.[1]

Table 1 Inductively coupled plasma operations — parameters

RF power	1500 W
Plasma gas flow	$17\ \mathrm{dm^3\ min^{-1}}$
Auxiliary gas flow	$1.5\ \mathrm{dm^3\ min^{-1}}$
Nebulizer gas flow	$0.5\ \mathrm{dm^3\ min^{-1}}$
Monochrometer	1800 line $\mathrm{mm^{-1}}$ holographic grating
Si analytical wavelength	251.618 nm

Procedural notes Large-diameter injector tube used in torch to eliminate carbon deposition. Chloroform softens both standard and solvent-flexible peristaltic pump tubing; silicone rubber tubing gives large Si blank. Therefore, concentric nebulizer is used for $CHCl_3$-based samples, as the concentric nebulizer does not require peristaltic pump for sample delivery.

Instrumental

For analysis, the sample extracts were examined with a Perkin–Elmer Model Plasma II inductively coupled plasma (ICP) spectrophotometer. Instrumental parameters are given in Table 1. The instrument was calibrated with octaphenylcyclotetrasiloxane (OPCTS, Kodak) in chloroform, using solutions of low ppm organosilicon content as standards. Figure 3 shows the analytical flow scheme used in this study.

RESULTS AND DISCUSSION

Results are presented in Table 2 and Fig. 4. It should be noted that all core segments examined exhibited some silicone content, but with a 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[4] argue that increasing amounts of silicone would be available for release to the environment, to be seen in the

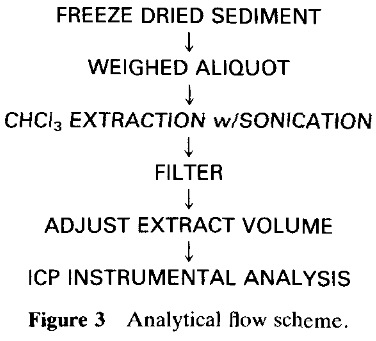

Figure 3 Analytical flow scheme.

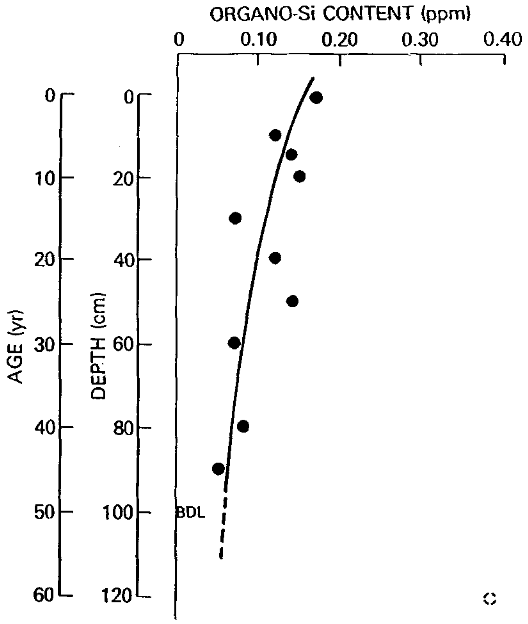

Figure 4 Organosilicon data for Puget Sound core.

upper (younger) segments of the core. Second, the data indicate that some 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, whereas at that depth there is a low level of silicone observed. In fact, 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.

Table 2 Data associated with Puget Sound core

Depth interval[a] (cm)	^{210}Pb age[a]	Organosilicon content (ppm)[b]
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 y^{-1}. See Ref. 3 for details.

[b] ICP detection limit is 0.01 ppm Si in chloroform; data are good to ± 0.02 ppm; BDL, below detection limit. Silicones are 39% silicon.

[c] This value appears to be an artifact of sample collection, handling, processing or analysis, and is not included in the text discussion.

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 some 1–40-cm thickness, depending on location in the Sound. Their estimates are made by measuring excess ^{210}Pb in the upper layer of the sediment column; this excess ^{210}Pb is carried into the uppermost sediment by biological activity (bioturbation), and is designated as ‘supported’ ^{210}Pb. However, both authors assign the bottom of the bioturbated layer to the appearance of unsupported ^{210}Pb in the sedimentary record. This unsupported ^{210}Pb then decays exponentially with depth (time, $\rho = 22.3$ y), allowing one to assign an age to a position 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 seems to preserve the effects of bioturbation to a degree not possible with a less stable chemical or radioactive tracer. Of course, the input-to-sediment rate function for silicone is not a constant as it is for ^{210}Pb. Further, bioturbation of sediments may affect silicone differently than ^{210}Pb. This difference would arise because silicone associates with the organic portion of the sediment, where ^{210}Pb is largely associated with the inorganic (mineral) fraction.

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 with which sediments can be analyzed for silicone content (solvent extraction combined with atomic absorption or 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.

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, and can be usefully combined with an earlier reported procedure to quantify (via ICP analysis) and characterize (via FTIR spectroscopy) organosilicon materials in sediments.

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