COMMUNICATION

Sedimentary Siloxanes: A Geochronological Study

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Selected samples of sediments from cores taken in the Ala Wai Canal (south-east Oahu, Hawaii) have been analyzed for organosilicon (silicone) content. Observed levels of silicone range from just above the detection limit (~0.01 ppm) to over 1 ppm, and vertical distribution in the sediment column generally increases upwards, with the highest silicone content in the most contemporary sediments (dated independently by ^{210}Pb and ^{137}Cs measurements). Further, there is clear evidence of spike events (i.e. high levels of silicone in older, buried sediments) which appear to be associated with major, documented storm events on the island of Oahu. Silicone assay was by solvent extraction, and quantitative spectrophotometric measurement at 7.95 μm. The Ala Wai Canal is an anthropogenic hydrographic feature on Oahu. © 1997 by John Wiley & Sons, Ltd.

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INTRODUCTION

Poly(organo)siloxanes (silicones) are a class of synthetic polymers useful for their unique physical properties and chemical stability under severe, and especially ambient, conditions. Silicones can be formulated to be water-like fluids, viscous liquids, gums or rubber-like solids. This property of easily tailor-made physical characteristics adds to the useful chemical properties of silicones. Thus, their unique mix of attributes has encouraged their use in a myriad of consumer products, often at the trace level. For example, fabric and leather water-proofing formulations, backings for self-adhesive labels and anti-foam additives for food processing all utilize silicone [most commonly poly(dimethyl) siloxane] as a trace constituent to attain a desired product performance. Such products, once used, can release silicone to the environment when discarded.

Previous work[1–4] has clearly established the utility of silicones as tracers for the movement of surficial sediments in a variety of aquatic systems. Indeed, silicones appear to collect preferentially on sedimentary particles, probably as a manifestation of their surface-active properties. Further research[5] had demonstrated the existence of a sedimentary siloxane horizon in a selected sediment column; sediments deposited prior to approximately 1945 showed no siloxane (Siloxanes have come into widespread use only since the early 1950s). However, the results reported in this latter work dealt with only a limited number of samples. The research presented here confirms and extends the initial limited observations concerning the presence of silicones in the sedimentary column.

The current research relied on sedimentary column samples gathered from the Ala Wai Canal on the south coast of Oahu, Hawaii (Fig. 1). The Canal was dug in the late 1920s to assist in the drainage of, and provide fill for, wetlands associated with Waikiki Beach. The hydrographic regime in the Ala Wai *Canal* itself is generally one of quiescence, even though the entire canal is subject to low-energy tidal flushing. Thus, sediments carried into the canal

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can collect anaerobically; sedimentary strata are well preserved (with little bioturbation) under such conditions. Occasional heavy storm activity (e.g. hurricanes) affecting Oahu can more fully mix and move the waters and upper sediments in the Ala Wai Canal. Note that the Ala Wai *estuary* (downstream from the Canal), in contrast, is routinely subject to more forceful tidal incursions and flushing (see Ref. 6 for a more thorough discussion). Overall, one could expect that the Canal sediments would preserve chemical signatures associated with the local sedimentation; the Canal has been dredged periodically (most recently in 1978), so one must be aware that sedimentary columns from some areas of the Canal may be only relatively intact from a historical perspective. However, selected Ala Wai Canal sediments are shown in this study to preserve such chemical information, at least in the case of the biologically inert silicones (Ref. 7 discusses other trace-chemical characteristics of the Ala Wai sedimentary regime).

METHODS

Sediment cores were collected from sites presumed not to have been impacted by major sedimentary disturbances such as dredging. Cores were acquired using 5 cm-diameter plastic core liners, driven manually into the sediments, capping the liner tube, and extracting the cores from the bottom. Later, the liners and cores were

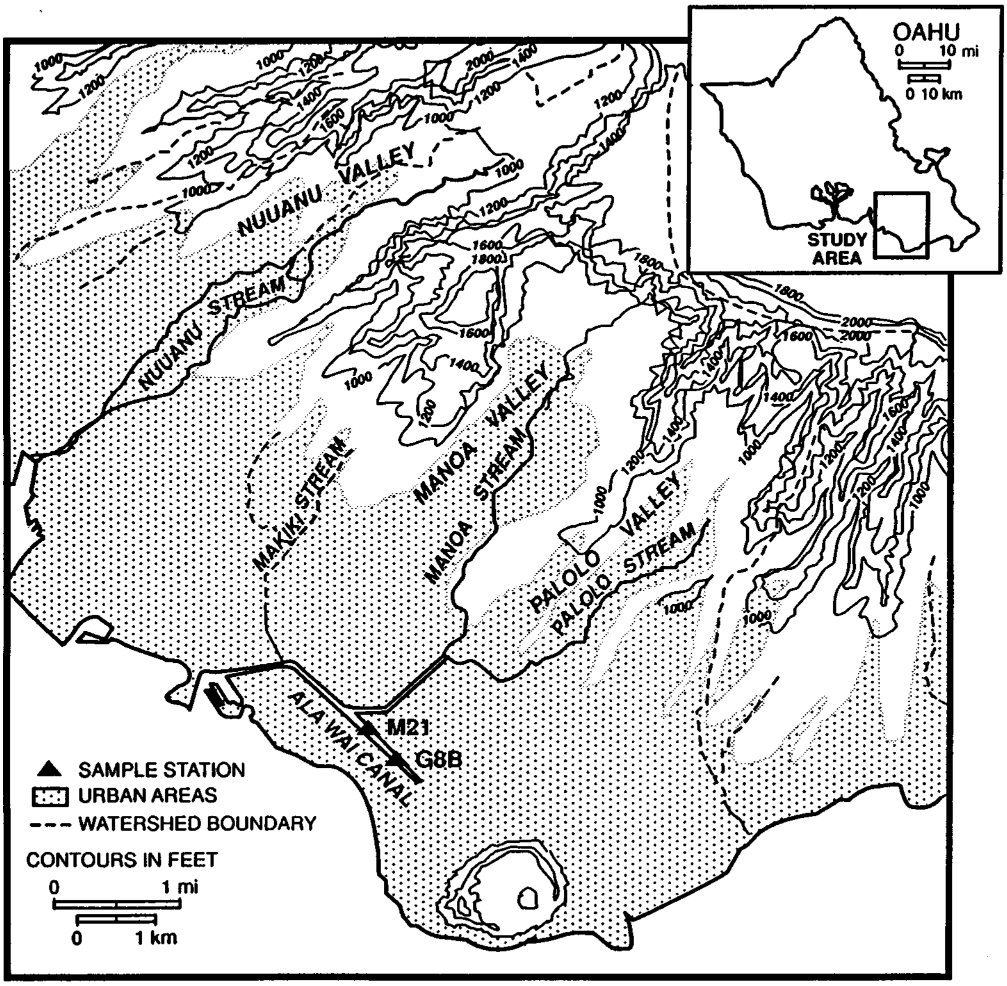

Figure 1 Study area on Oahu, Hawaii.

split, examined for stratigraphic sequences, and subsampled every 2–4 cm from the surface of the core. Special attention was paid to avoid collecting sedimentary material which had contacted the plastic core liner, or been disturbed by the saw blade used to split the liner. These subsamples were homogenized, sieved and freeze-dried prior to storage in glass containers.

Aliquots (0.5 g) of the core sections were selected for assay in this study. A sediment sample was combined with 3.0 mL of chloroform (Fisher) in chloroform-rinsed Pyrex scintillation vials, then sonicated for 5 min. The chloroform extracts were decanted with chloroform-rinsed Pyrex Pasteur pipettes, and gravity-filtered individually through chloroform-rinsed paper filters (Whatman), held in a Pyrex funnel, to remove sedimentary particles from the extracts. Extracts were then rotary-evaporated to a volume of a few drops, taken up in tetralin (1,2,3,4-tetrahydronaphthalene, Fisher), and made to 5.0 ml prior to storage in chloroform-rinsed scintillation vials. Transfers between glass containers were performed with chloroform-rinsed Pasteur pipettes.

The extracts were assayed using a Nicolet Magna IR 750 FTIR instrument, equipped with a Wilkes variable-volume sodium chloride window liquid cell. The characteristic Si–O–Si band at 7.95 μm was used for semi-quantitative measurement of extracted silicone.[8] The technique was calibrated using a serially diluted solution of hexamethylcyclotrisiloxane (Petrarch/Hüls) in tetralin as a standard. The path length for all measurements was identical, and could be easily reset using the calibrated dial on the Wilkes cell, after the cell was rinsed between samples. The assay consumed approximately 0.2 ml of the extract; the solutions in the low-volatility tetralin were stable to volume changes in storage, and thus are useful for other analytical work. The assay procedure is summarized in Fig. 2. Blanks were run and gave a zero result. Core *end* samples may have been contaminated by core *caps* placed on the core liners during sample collection. There was no evidence of contamination during sample assay.

Freeze-dried sample, finely divided
⇓
Weigh aliquot into glass vessel
⇓
Cover with solvent (chloroform)
⇓
Sonicate (5 min)
⇓
Allow sediment to settle
⇓
Supernatant through pre-washed **paper** filter
⇓
Rotary-evaporate to a few drops
⇓
Take up in tetralin to 5 mL
⇓
Final assay (e.g. spectrophotometry at 7.95 μm)

Figure 2 Flow chart for silicone assay.

RESULTS AND DISCUSSION

This study reports on results from two cores from the Ala Wai Canal. Core G8B is closest to the landward end of the Canal, while Core M21 is farther downstream, and in fact is in close proximity to the Manoa and Palolo Streams confluence with the Canal, the largest stream fresh water inputs to the Canal (Fig. 1). The hydrography associated with these differing locations assists in interpreting the results of this study.

Specifically, sedimentary silicone data as a function of depth (Table 1) are plotted in Figs 3 and 4. The data appear to be variable, but this situation is influenced by several factors. In both cores, the deepest sediments appear to be about 1 ppm in organosilicon. It is possible that these deepest sediments represent either silicone contamination of the samples during collection (core barrels were closed with rubber and plastic stoppers) or handling, or by inclusion of small amounts of silicone-bearing sediments from enriched, overlying strata as a function of local storm activity (possible), or bioturbation (less likely in the anoxia of the Canal). Thus, the observation of higher levels of silicone in the deepest sediments is difficult to explain, and lacking a clear explanation of the situation, the observed levels in these deepest sediments only will be excluded from the following discussion.

Now the uppermost sediments in both cores are generally higher in silicone content than are underlying sediments (except for the discounted deepest ones). This observation is in accord with those reported earlier[5] which discuss a general rise in sedimentary silicone with time: contemporary sediments reflect an increase in silicone as a function of generally increased use of silicone in discarded consumer products which can distribute silicone, in trace amounts, to the environment. In the specific case of the Ala Wai Canal, Canal sediments could receive silicone from the general commercial discards (litter) associated with upstream communities (Kaimuke, Manoa, Palolo) and Waikiki and carried into the Canal by surface freshwater storm runoff, and as material leached from marine applications of silicone (lubricants, paints) associated with the boating activities in the Ala Wai marina, and carried tidally into the Canal. Furthermore, save for the deepest sediments in the Canal, the reported data show a general increase in sedimentary silicone from some 0.1 ppm at 100 cm depth (100 cm in G-8B *ca* 1940; in M21 *ca* 1972) to the higher levels seen in more contemporary sediments.

It is believed that the non-zero silicone level in the Ala Wai Canal sedimentary column is related to storm rework of sediments in the Canal (data given have been corrected for process blanks, and appear to be truly non-zero). Evidence for such a rework in the Canal sediments is seen in the high levels of silicone seen at ~50 cm in Core G8B, and at ~60 cm in Core M21. These

Table 1. Organosilicon data* for Ala Wai Canal cores

	Core	
Depth interval (cm)	G8B	M21
0–4		0.90
1–3	0.90	
12–16		0.15
20–22	0.15	
20–24		0.40
32–34	0.06	
32–36		1.20
40–44		0.15
48–50	0.90	
56–60		0.90
61–63	0.15	
72–84	0.12	
86–88	0.15	
102–104	0.09	
104–108		0.09
123–125	0.90	
128–132		0.03
152–156		0.90
155–157	0.90	

[1] Data are in ppm organosilicon in the freeze-dried sediment; polydimethylsilicones are ~38% silicon; detection limit ~0.01 ppm polydimethylsilicone. Data are means of four measurements (±0.03) made on single samples. Blanks mean no sample available at that depth. Depth intervals (viz. *x*–*y* cm) means the tranche inclusive of those depths.

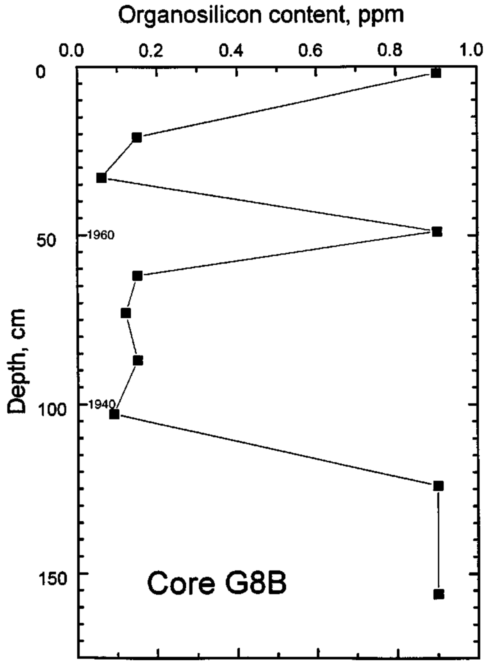

Figure 3 Sedimentary organosilicon content versus depth for core G8B.

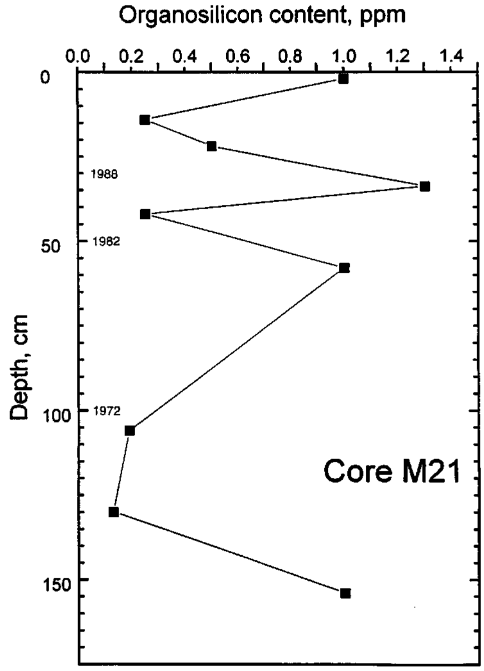

Figure 4 Sedimentary organosilicon content versus depth for core M21.

depths correspond to *ca* 1960 (G8B) and *ca* 1982 (M21). Although the former is not readily explained in terms of storm events, the latter may be associated with a major storm (Hurricane IWA, November 1982) that affected all the Hawaiian Islands, and Oahu in particular. Note, too, the silicone spike at ~30 cm in core M21 (*ca* 1988). The latter may represent a storm event, perhaps one which reflects only a freshwater input from streams and street runoff and which failed to disturb the sediments from core G8B, collected upstream of all stream inputs to the estuary. Indeed, a large rain event and associated flood occurred on 31 December 1987, and affected all the Hawaiian Islands. This storm, unlike hurricane events (e.g. IWA in 1982) would not have caused any large storm surges from the ocean into the upper reaches of the Canal.

In summary, the study of the Ala Wai sediments reported in this paper confirm and extend the observations reported earlier for a Puget Sound core. Specifically, the Ala Wai Canal sediments record a trend of increasing sedimentary silicone in younger sediments, higher levels in the late 1960s to mid 1970s as a reflection of increasing use of silicones in the Ala Wai watershed, and highest levels in contemporary sediments. Furthermore there is clear evidence of spike events in the Ala Wai sediments which appear to be associated with major storm events on the island of Oahu.

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