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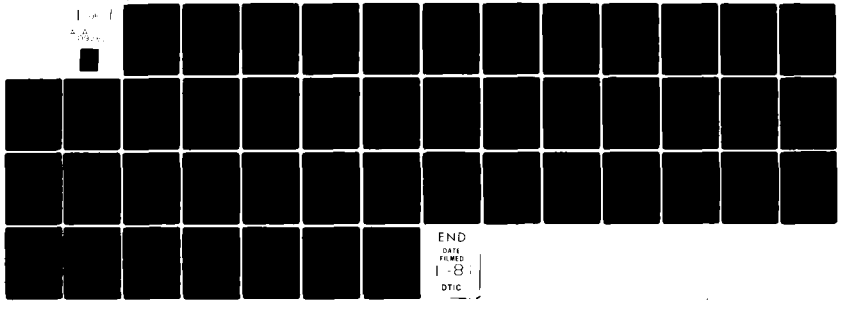

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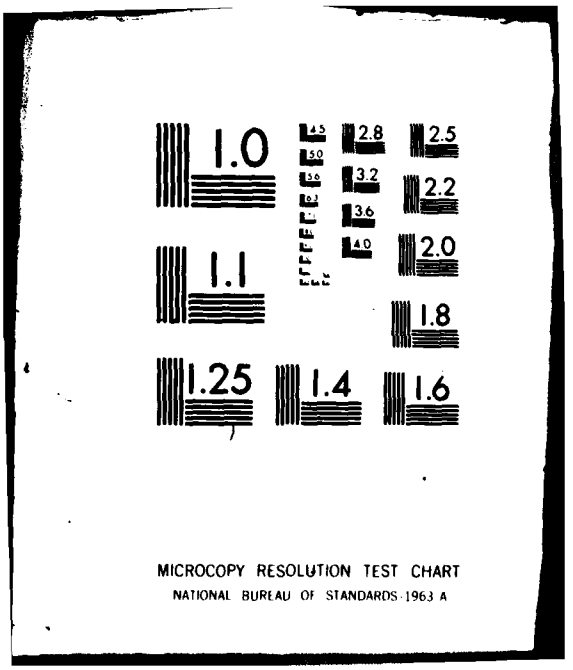
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ENVIRONMENTAL ORGANOTIN CHEMISTRY TODAY: EXPERIENCES IN THE FIELD AND LABORATORY

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SUMMARY

The relationship between organometal biogenesis, developments in the measurement of trace organotins, and applications of recent experimental results from the literature and the author's laboratory are reviewed (over 100 references) under the headings: abiotic chemistry of organotins in aqueous solutions; comparative reactivity and pathways of aquatic organotins, especially methyltins; recent progress in the speciation of environmental organotins; environmental organotin chemistry today: current problems and trends; occurrence and fate of methyltins.

INTRODUCTION

Perceptions of organometallic chemistry are being challenged by new and significant ideas relating to the environment and the flow of essential or toxic elements through it [1]. No better examples exist than the occurrence and fate of Group IVb elements, especially tin, in the biosphere because all of the major research obstacles and prospects of concern are embodied in their environmental chemistries.

Chemists have long recognized, and indeed originally differentiated, organic and inorganic disciplines in the basis of supposed biogenic and non-biological sources of carbon compounds. With the evolution of descriptive organometallic chemistry, this picture blurred. Thus, a carbon monoxide, originally regarded as an "inorganic" gas, is now known as a most important "organic" π-ligand on metals [2]. As organometallic chemists, we have sought to elucidate the intermediate, often unexpected, chemistry of carbon bonded to other elements, but primarily from a non-biological viewpoint. Successes in organometallic chemistry thus have led to escalating introduction of commercial organometallic materials into world technology [3]. We have not similarly fashioned a data base to aid in detecting or predicting the impact of such substances on environmental systems, nor are we very far advanced in interpreting the emerging facts concerning the biogeochemical transport of organometallic intermediates, including organotins, in the biosphere [4].

One may claim that the inapplicability of organometallic literature to environmental sciences stems from its narrow focus on non-aqueous reaction media. This is partly so, but other limiting factors must also be placed into perspective in order to adequately discuss environmental or aquatic organometallic chemistry as it stands today.

In this paper we shall deal with the environmental chemistry of tin, and this theme will require that we combine both conventional (for the organometallic chemist) laboratory and field experience. To some extent, these considerations involve interactions of tin with other metals or metalloids, since such processes may be importart in the environmental matrix. Three central areas are covered and, although these obviously overlap, some clarity in their respective contributions and status today is gained by their enumeration: (1) non-biological transformations of organotins in environmental media; (2) <u>speciation</u> or molecular characterization of trace organotins in the environment; and (3) biogenesis or biodegradation of organotins.

In many ways the flow of metals and metalloids through the environment is best stated in terms of their possible aggrayate relationships. Of special interest to organometallic chemists is one newly emerging version of the Periodic Table which considers biomethylation of major crustal elements and known or postulated biomethylation of minor elements [1,4-6]. Figure 1 summarizes current information available from the literature.

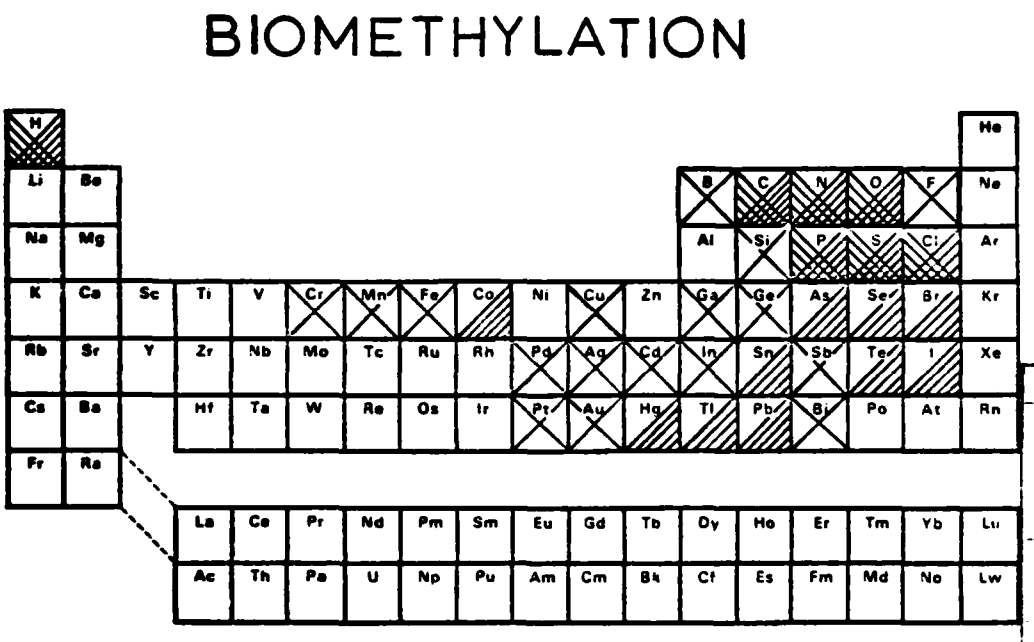


Figure 1. Known biomethylation of major (XXX) essential elements and trace essential or toxic elements (////) is compared with that postulated for other elements yielding stable or transitory aqueous methyl species (X).

Detailed or quantitative relationships cannot be inferred from the presently sketchy data, but it is clear that the extent of biomethylation of so-called non-essential or toxic metals and metalloids is probably partly limited to current capabilities for their detection. Thus far,

those methylelements known to occur in natural media form either relatively stable ions in saline solutions or volatile hydrophobic permethyl species that can rapidly degas from water.

In sum, consideration of Figure 1 suggests the following: (a) all the major elements essential to life can involve, but of course are not limited to, methylation in their environmental cycles; (b) both essential (Co, Se, I, Sn [5,7,8]) and toxic (Hg, Pb, As, Te [5,6]) elements are involved in, possibly limited to, biomethylation at trace levels; and (c) on the basis of documented water-stable σ-bonded methyl derivatives of other Main Group [1,9] and Transition metals [1,10], it appears likely that additional biogenic methylmetal(loid)s will be reported in the future as detection methods and associated aqueous chemistries become available. The Periodic Table illustrated denotes current information on methylated species only. Sparce and unconvincing evidence is available for biogenesis of other organometals such as aryl or higher alkyl homologs [11]. Figure 1, however, does not relate a substantial body of evidence for other important biological transformations of the metals and metalloids involving redox, hydride formation, oxide or sulfide production, and complex ligation, most of which is beyond the scope of this paper. Many excellent recent reviews provide comprehensive introductions to these aspects of the field [1,4-6,8].

For either those organotins introduced into the environment by increased technological reliance on their tailored properties as biocides or plastics stabilizers [3,12], or for biotransformations involving organotins, several additional basic points are to be noted. No evidence has been presented that suggests concerted mechanisms for multiple formation or removal of carbofunctional ligands on tin(IV) in environmental media. That is, present data generally supports the view that stepwise σ-carbon-tin bonding events are predominant in aquatic reactions, viz.,

$$R_4Sn \xrightarrow{k_1} R_3Sn \xrightarrow{k_2} R_2Sn \xrightarrow{k_3} RSn \xrightarrow{k_4} Sn(IV) \quad ,$$

or the reverse pathway. The rate-determining step in such a sequence is dependent upon minimum k. Most laboratory experience for organotins suggests $k_1 \leq k_2 >> k_3 > k_4$ for dealkylation, although specific solvolytic effects and differences in R groups can greatly influence such progressions, as we shall see. The situation becomes more uncertain for those intermediates, partially alkylated metal species which are subject to competitive unimolecular decomposition reactions, usually via reductive demethylation. Representative cases are found with $MeTl^{2+}_{aq}$ or $MePb^{3+}_{aq}$, which rapidly decompose to yield MeCl in saline solutions. Nonetheless, since either of these metals is demonstrated [13] to be biomethylated with formation of Me_2Tl^+ and Me_4Pb, respectively, we must assume that intermediate transient species are either more rapidly biomethylated than subject to unimolecular decomposition, or the last process is somehow inhibited by complexation during the enzymic methylation steps. Tin represents a simpler case since its intermediate aquated ions, $R_nSn^{(4-n)+}$ (n = 1-3), are stable in saline solutions over pH 6-8 simulating most environmental fluids.

The few reports based upon field experience with degradation of organotins are consistent with the picture of stepwise deorganylation. Crosby et al. and others [14] have shown that where R = cyclo-hexyl or phenyl, such degradation occurs in agricultural applications; Jewett and Brinckman found Bu_2Sn^{2+} with Bu_3Sn^+ in aqueous leachates from shipyard grits used to remove weathered Bu_3Sn-containing marine antifouling paints from ship hulls [15]. It is not certain that biological deorganylation is primarily involved, but photodecomposition is thought to play an important role [14,16]. One recent report concludes [17] that the pseudo-first order half-live of Bu_3Sn^+ species in pond water is considerably greater than that of Bu_2Sn^{2+}, though Bu_2Sn and Et_2Sn species decompose at nearly the same rates and both more rapidly under simulated summer irradiation.

DISCUSSION

Abiotic chemistry of organotins in aqueous solutions

Since the number and kind of organic groups bound to tin(IV) dictate the biological activity of organotins in the environment [3,12,18], we must deal with the question of how homologs of such series form or disappear in aquatic media, and at what rates. Under most environmental conditions, displacement of tin from carbofunctional ligands is not expected to occur by strong inorganic electrophiles familiar in the laboratory, such as mineral acids and halogens. These agents, nonetheless, model a very large group of homogeneous bimolecular displacement reactions of the type,

$$R_nSn^{(4-n)+}_{aq} + XY \longrightarrow R_{n-1}Sn^{(5-n)+}_{aq} + RX + Y^- \quad ,$$

which include other metallic electrophiles of environmental importance, considered in detail below.

Not to be excluded, however, are a number of possible metal-carbon bond formation and cleavage reactions in water which involve other pathways depending upon common environmental phenomena. Among these, sunlight may play a role, as has been shown with Hg^{II} [19,20] and suggested with Tl^{I} [20], both of which undergo photolysis in the presence of a common bacterial metabolite, acetate,

$$Hg^{2+} + OAc^- \xrightarrow{h\nu} MeHg^+ + CO_2\uparrow, \text{ and}$$

$$MeHg^+ + OAc^- \xrightarrow{h\nu} Me_2Hg + CO_2\uparrow, \text{ and}$$

$$Me_2Hg \xrightarrow{h\nu} Hg^\circ\uparrow + C_2H_6\uparrow \text{ , or}$$

$$Tl^+ + OAc^- \xrightarrow{h\nu} [MeTl] + CO_2\uparrow,$$

$$[MeTl] + D_2O \longrightarrow Tl^+ + OD^- + CH_3O\uparrow.$$

The analogous unimolecular reactions for Sn(IV) and Pb(IV) have not been demonstrated, but ESR evidence for photodecarboxylation of their acetates to form intermediate methyl radicals, probably via shortlived acetoxy free radicals, was reported [21].

Another environmental pathway for creating or cleaving tin-carbon bonds in non-biological events, involves heterogeneous reactions with inorganic or organic solid particulates that typically abound in natural aquatic systems. This field is largely unexplored for organotins, but several recent reports highlight the utility of additional studies. For example, saline aqueous effluents containing 100 ppm of trace alkyllead species are detoxified (to less than two ppm) by dealkylation in a direct treatment with bulk electropositive element, zinc [22],

$$R_nPb^{(4-n)+}{}_{aq} + Zn^{o}{}_{s} \longrightarrow [R_6Pb_2]$$

$$[R_6Pb_2] \longrightarrow RH\uparrow + Pb^{o}\downarrow + Zn^{2+}{}_{aq} + \text{other products.}$$

$$(R = Me, Et;\ n = 2, 3)$$

Subsequently, we shall see that a number of related homogeneous bimolecular reactions occur, involving free radical redox of the alkyl acceptor metals, which can demethylate tin. Kochi has summarized many of these reactions [23]. Such deorganylation reactions may represent an important group of natural processes for removal of those metal-carbon moieties which impart volatility and lipophilicity leading to bioaccumulation and toxicity of metals.

On the other hand, in another example, we may consider the possibility of forming metal-carbon bonds on otherwise inert solid substrates typified by mineral or anthropogenic solids. Such metathetical solubilization of heavy metal(loid)-containing particulates, possibly by methylation, is suggested in a preliminary report by Thayer [24]. The oxides of As^{V},

Au^{III}, Bi^{V}, In^{III}, Pb^{IV}, Sb^{V}, and highly insoluble SnO_2 were observed to demethylate methylcob(III)alamin and to dissolve by second-order or pseudo first-order rates (depending upon excess of oxide) between $\sim 10^{-0.35}$ to $10^{-5.8}$ $\underline{M}^{-1}s^{-1}$, tin oxide being the slowest. As we shall see, these are reactions which proceed at rates comparable to those observed for homogeneous transmethylation between aquated metal ions, including tin [20,25]. Since Thayer was unable to characterize the soluble trace products forming from the oxide particulates, we can only speculate here as to their possible environmental fate. Methods available for speciation of such metal-containing solutes at low concentrations ($<10^{-5}\underline{M}$), within time frames suitable for kinetic interpretation, clearly limit such investigations; prospects for improvements will be discussed later. In related work, Akagi *et al.* showed [26] that photolysis of $Hg(OAc)_2$ in the presence of HgS resulted in the latter's solubilization *via* photosensitization of sulfur atoms produced during the production of methylmercury species. Studies extending this heterogeneous photomethylation in the presence of potential sensitizers to other refractory metal salts or minerals merit increased attention.

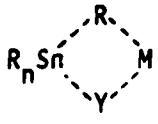
Finally, another pathway for formation of organotins from common environmental substances is suggested by two reports describing oxidative alkylation of Sn(II). Dizikes *et al.* described [27] oxidative addition to $SnCl_2$ by methylcob(III)alamin in anaerobic saline solutions to give $MeSnCl_n^{(3-n)+}$ and the reduced Co(II) complex. The rate was rapid at $10^{0.15n}$ $\underline{M}^{-1}s^{-1}$, and unaffected by additions of Sr(IV). Those authors suggested this reaction as a model for our previously reported [28] findings on the microbial methylation of Sn(IV) by a marine *Pseudomonas* species isolated from the Chesapeake Bay. From another standpoint, oxidative organylation of Sn(II) by reactions reported in non-protic media is also noteworthy. In a preliminary report, Lappert and his associates [29] found that both bis-(trimethylsilylmethyl)- or (-amido)-tin(II), both sterically crowded d^8 substrates, rapidly react with a large variety of RX (R = alkyl or phenyl) to give R'_2RSnX [16]. As will be discussed below, portions of

the environmental system of interest to organometallic chemists include non-aqueous phases as well, composed of organic liquids, e.g., hydrocarbons, esters. To exclude possibilities for transformations of such tin or other metal species in aprotic microenvironments would be short-sighted.

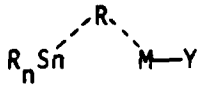
Comparative reactivity and pathways of organotins in aquatic media, especially trimethyltin species

In dealing with the fate of organotin molecules in aquatic media, possibly formed or degraded to some extent by the processes outlined above, we recognize that rates and mechanisms will conform to laboratory experience with surrogate electrolytes. Therefore, we must regard ionic strengths, dielectric constants, specific ion interactions, ion-pairing, pH, pCl, and the like, as necessary yardsticks for quantitatively characterizing the aquatic organometallic chemistry of tin, and projecting these results to environmental questions in natural fluids.

Many metal ions displace Sn(IV) from saturated carbon in aqueous solutions. These bimolecular processes are thought to involve S_E2 transition states in either symmetric closed (I) or asymmetric open (II) complexes:



I S_E2 (closed)



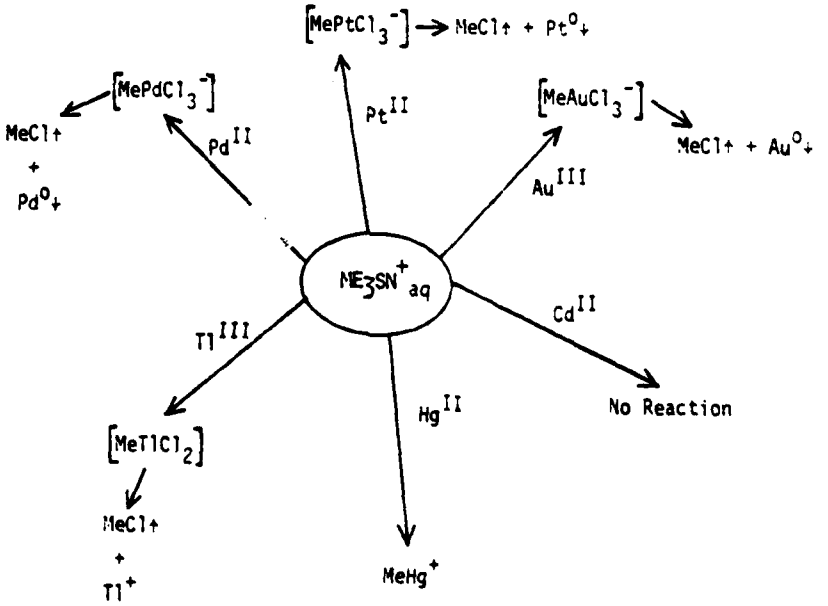
II S_E2 (open)

Compelling stereochemical evidence for the S_E2 (open) route was shown for the reaction in methanol,

$$R_3SnR' + Br_2 \longrightarrow R_3SnBr + R'Br \quad ,$$

where inversion of configuration accompanied scission of the optically active R' group (R = neo-pentyl; R' = sec-butyl*) [30]. The S_E2 (closed)

four-center transition state I can only yield retention of configuration. Such configurational tests, unfortunately, are not yet possible with metal electrophiles in place of Br_2 because the reactions are extremely slow, or where smaller R' groups are used (with greatly increased reaction rates) these are sterically inactive. Consequently, workers have relied upon evaluation of kinetic salt effects [31] or solvent polarities [31,32] to aid in establishing mechanisms of α-carbon cleavage from R_4Sn by metals. Generally, the S_E2 (open) pathway is regarded as predominant, and the steric (cleavage) sequence Me > Et > n-Pr > n-Bu > neo-C_5H_{11} > i-Pr is proposed [33] as diagnostic of the S_E2 (open) mechanism in protic solvents with retention of configuration. Presently, nothing is known about the stereoselective manner by which aquated $R_nSn^{(4-n)+}$ (n = 1-3) ions interact with metallic electrophiles, but probably more important for environmental considerations, no data are reported on the steric course of their reactions with enzymic models, e.g., organometallic ion cleavage while bound to sulfhydryl sites.



SCHEME 1

We studied [20,25,34,35] the chemistry of Me_3Sn^+ in dilute ($\sim 10^{-2}$ M) aqueous saline solutions and found this to be a powerful methylator of a number of metal ions (SCHEME 1), though not as extensive or as rapid as analogous $Me_3Pb^+_{aq}$ [35]. Not surprisingly [33], the rates of dealkylation by Hg^{2+} of the higher R_3Sn^+ homologs appear very slow, but no quantitative kinetic data are yet available.

Co-product Me_2Sn^{2+} does not react further with any of the metal electrophiles indicated. All the reactions are bimolecular, first order in trimethyltin and in the electrophile through > 90 percent transmethylation for the fast reactions. Table I summarizes the relative rates for the reactions depicted in SCHEME 1 along with several others.

Table I

RELATIVE RATES[a] FOR METHYLATION OF METAL ELECTROPHILES[b] BY Me_3Sn^+ IN WATER[c]

$HgCl_2$[d]	$TlCl_3$	$CdCl_2$	$InCl_3$	$AuCl_4^-$	$PdCl_4^{2-}$	$PtCl_4^{2-}$	$IrCl_6^{2-}$
100	97	<0.01	<0.01	~ 5	768	<0.08	~ 10

[a]Determined from ^1H NMR measurements [20,25,34]; [b]Indicated in form added; [c]Typically 0.025 M of each reactant with Me_3Sn^+ added as chloride, $\mu \sim 0.05$; [d]$k_2 = 10^{-2.03}$ $M^{-1}s^{-1}$ [20].

The reaction path shown in SCHEME 1 for $PtCl_4^{2-}$ reacting with Me_3Sn^+ is based on that observed with the analogous Me_3Pb^+ case [34] and the formation of faint Pt metal precipitates in NMR tubes standing overnight with the tin reactions. It may be noted in passing that the corresponding reaction between $Me_3Pb^+_{aq}$ and Hg^{2+} in water proceeds 180 times faster than the tin reaction at 5.5 °C [34], and similarly faster rates were noted for lead with the other methyl acceptors. The transient methylmetals (in brackets) in SCHEME 1 are based upon characterization of the final gaseous and metal products shown and, in the case of Pd(II) with Me_3Sn^+ or Pt(II)

with Me_3Pb^+, clearcut NMR evidence of such intermediate transmethylation species [34-36] which also lead to production of ethane.

The reaction rates are greatly affected by chloride ion concentration, especially for Hg(II) and Tl(III). Introduction of other competing gegenions, such as Br^- with Cl^- results in non-statistical production of mixed secondary product gases, viz., MeBr and MeCl, from the transition metal electrophiles. Additions of "soft" ligands like CN^- or SCN^- inhibit rates of transmethylation. It is important to note that methylation by Me_3Sn^+ involves low-energy pathways. Activation energies of 59.4 kJ mol^{-1} and 79.9 kJ mol^{-1} found for Hg(II) and Tl(III), respectively, [25] should be compared with those found for dealkylation of R_4Sn by $HgCl_2$ in solvents of lower dielectric constants, including methanol (~ 41-63 kJ mol^{-1}) [31]. These results require a mechanism of low coulombic repulsion, that is, involvement of the methyltin donor and metal electrophile in the transition state as species with reduced or dispersed charge, either as ion-pairs or inner sphere complexes.

Fortunately, for both trimethyltin and mercuric cations, sufficient data are available to estimate the relative concentrations of their chloro- and hydroxy-complexes from respective stability constants [9,25]. Employing such information along with experimental reaction parameters of total reactant concentrations, pH, and pCl, the nature and concentrations of both Me_3Sn- and Hg-species occurring as reactants for a series of kinetic runs at different total (Cl^-) and ionic strength, μ, were examined. Multiregression analyses of the various k_2(obs) at different chloride values permitted us to determine a specific reaction rate profile for all the six major (> 99.9 percent) reactant species present [25]; no hydroxy species were formed under these conditions. The observed second-order rates thus obtained were evaluated in the form of a series of summed concurrent reactions by the method previously used by Dodd and Johnson [37]. These are summarized as the individual reaction pairs along with the respective rate constants for the Me_3Sn-Hg transmethylation process in SCHEME 2.

SCHEME 2

$$Me_3Sn^+ + Hg^{2+} \xrightarrow[H_2O]{Cl^-} Me_2Sn^{2+} + MeHg^+$$

$$k_2(obs) = \sum_{\substack{n=0 \\ m=2}}^{\substack{n=1 \\ m=4}} \chi_n \cdot \chi_m \cdot k_{nm}$$

	k_{nm}, $l^3 M^{-1} s^{-1}$
$k_{02} = [Me_3Sn^+]\,[HgCl_2^0]$	17.4 ± 1.9
$k_{03} = [Me_3Sn^+]\,[HgCl_3^-]$	7.9 ± 0.6
$k_{04} = [Me_3Sn^+]\,[HgCl_4^{2-}]$	9.4 ± 1.3
$k_{12} = [Me_3SnCl^0]\,[HgCl_2^0]$	115.8 ± 9.3
$k_{13} = [Me_3SnCl^0]\,[HgCl_3^-]$	129.8 ± 17.3
$k_{14} = [Me_3SnCl^0]\,[HgCl_4^{2-}]$	<0.01

K. L. Jewett et al., 1978.

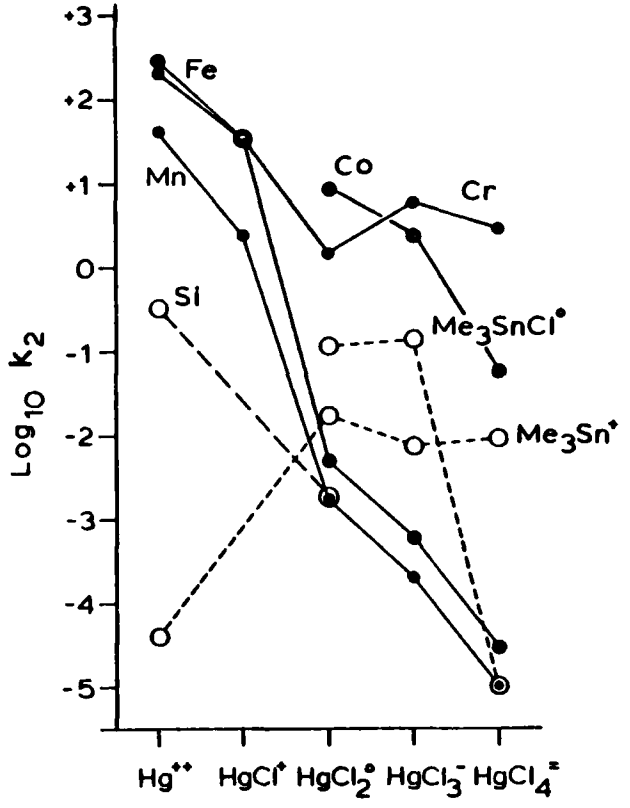


Fig. 2. Reaction rate profiles for a number of aqueous methylelement species known to methylate $HgCl_n^{(2-n)+}$ are compared with n. Ionic strengths ~ 0.3-0.6; pH < 5 (estimated). Symbols explained in the text.

With these results we can now compare a range of aqueous methyl transfer capabilities, in terms of specific Hg(II) electrophiles, for a number of Main Group IVb elements and Transition metals bearing active methyl or substituted methyl groups. Our data, along with other available to date, is summarized in Figure 2. Several major trends are noted. With the exception of $Me_3Sn^+_{aq}$ or Me_3SnCl^o, the remaining methylelements including 3-trimethylsilylpropionate-d_4 or TSP (Si) [38], show a substantial decrease in the rate of their demethylation as the effective electrophilicity [10,23] of the mercury acceptor is diminished by increased coordinate saturation by chloride. Thus, in the acceptor series $HgCl_n^{(2-n)+}$, from n = 0 to 4, iron (Fe) as the 3-pyridinium-derivative of $-CH_2Fe(CO)_2(\pi\text{-}C_5H_5)$ displays the largest diminution in methylation rate [9] of over 10^7-fold! Intermediate reductions in methylation rates with increasing salinity of aqueous solvent ($Hg^{2+} \rightarrow HgCl_4^{2-}$), range from manganese (Mn), also as the 3-PyH^+-derivative of $-CH_2Mn(CO)_5$ [37], at 10^6-fold to chromium, as the 3-PyH^+-derivative of $-CH_2Cr(H_2O)_5^{3+}$ [40], (Cr), or silicon (Si) and cobalt as the 4-PyH^+-$CH_2Co(CN)_5^{3-}$ derivative [41] which both show about a 10^2-fold reduction in demethylation rate.

In sharp contrast to the above methylelements, the two methyltin donors prevalent in saline aqueous media, show pronounced maxima in their rate profiles centering on the $HgCl_2^o$ and $HgCl_3^-$ electrophiles. These maxima represent 10^2 to 10^3 increases in methylation rate as a function of pCl, and suggest profound significance for estimation of transmethylation rates of various types of methylelement donors in natural waters. Interestingly enough, one finds that $HgCl_2^o$ and $HgCl_3^-$ are significant species in coastal and oceanic waters, exceeded only by $HgCl_4^{2-}$ [20,42,43]. Consequently, we would infer that, barring very substantial alterations of model laboratory transmethylation rates (Figure 2) by naturally occurring strong ligands or unknown competitive electrophiles, available trimethyltin species will be more efficient mercury(II) methylators than possible (as yet unidentified) transition metal methylators with the possible exception of biogenic methylcob(III)alamin [5].

In addition to large changes in transmethylation rates as a function of aquatic salinity, it should be noted that the reactions summarized in Figure 2 represent true ionic processes. As such, these are subject to changes in ionic strength, a property of natural water systems that undergoes drastic fluctuation depending on local environmental factors, such as tidal flow and rainfall. According to the basic tenets on the Brønsted-Hückel-Debye relationship, the bimolecular rate constant k_2 is proportional to $\sqrt{\mu}$ and the algebraic product of the charges of the two reaction partners in the transition state [44]. Those reactions which involve a neutral species, such as $HgCl_2^o$ and Me_3SnCl^o, or 3-PyH^+-$CH_2Mn(CO)_5$ at high pH [37], will be unaffected by such environmental gradients in ionic strength. That is, $\ln k_2/k_2^o = 0$ where k_2^o is the rate constant for such reactions at infinite dilution.

On similar grounds, it was shown [25] that the effect of a change in ionic strength $\Delta\mu$ causes a change in the rate constant for charged reaction partners,

$$\ln (k_2^1/k_2^2) = 2z_+z_- [\sqrt{\mu_1}-\sqrt{\mu_2}] \quad , \qquad \underline{\text{Equation 1}}.$$

where it is presumed that no change in the transmethylation mechanism occurs over $\Delta\mu$.

In comparing available methylelement reaction rate profiles (Figure 2), we note that for charged reaction partners, such as X-$CH_2Cr(H_2O)_5^{3+}$ and Hg^{2+} or Me_3Sn^+ and $HgCl_3^-$, the natural flow of waters from land (rivers) through estuaries to the sea results in an increased μ which decreases their reaction rates. Various authors indicate that μ ranges from about 0.65 in oceans to 0.3 in estuaries to perhaps $10^{-2.6}$ molal in rivers [25,42, 43,45]. This implies an overall rate reduction of about two to twelve-fold for any of the singly and multiply charged methyl donors reacting with charged electrophiles. Moreover, the overall rate for methylation of these various electrophiles depicted will depend not only upon their effective charge (e.g., effect of salinity on ionic species of X-$CH_2Cr(H_2O)_5^{3+}$,

etc.), but on the sum of the concurrent reactions with available chloromercury(II) electrophiles. In general, without additional information on the stability coefficients for Cl^- complexes with charged Cr or Co methyl donors, we only conclude that salinity will play a far greater role in methylmercury formation from these in fresh or brackish waters. For trimethyltin species, we conclude that for their principle reactions contributing to mercury methylation (k_{02}, k_{12} and k_{13} listed in SCHEME 2) the usual overall gradients in ionic strength play no great role, but rather only increases in salinity or Cl^- yielding higher relative concentrations of $HgCl_2$ and $HgCl_3^-$ species will be significant. These considerations and conclusions signify the importance of trace organometal speciation in environmental aquatic systems, whether by indirect estimations from stability-coefficient calculations of competitive equilibria or by direct instrumental speciation.

Recent progress in the speciation of environmental organotins

Over the past decade, considerable effort in coupling trace molecular separation schemes directly to sensitive element- or compound-specific detectors has provided tools of great value to environmental organometallic chemistry [46,47]. Prior methods for research and industrial analysis of organotins at $\mu g\ mL^{-1}$ (ppm) concentrations had mainly relied upon single- or two-dimensional thin layer chromatography (TLC) for separation, followed with formidable methods of tin-specific quantitation by colorimetric or electrometric analyses of isolated spots physically removed from the TLC plates. Increased availability of commercial atomic absorption spectrophotometers (AA) has greatly improved the sensitivity and selectivity for such organotin analyses [48], but such procedures are not susceptible to ready on-line or automatic operations.

In addition to the long-familiar detection means of mass spectrometry (MS), two rapidly emerging commercial developments for tin-specific detection are generating exciting new applications. Fully automatic electrothermal or graphite furnace atomic absorption (GFAA) detection units,

nominally capable of detecting tin in gases, liquids or solids at ng mL^{-1} concentrations [49] are available from suppliers world wide. Similarly, rapid commericalization of stable flame photometric detectors (FPD), specific for gaseous Sn-H emission derived from plasma decomposition of organotin analytes in hydrogen-rich flames, now offers widely based marketing. Consequently, of special interest are the reported combinations of gas chromatography (GC) with AA [50] and GFAA [51] or FPD [52]. More recently, high performance liquid chromatography (HPLC) has been efficiently coupled directly to flame AA [53], GFAA [54] and FPD [55] in automatic modes of operation.

All of these methods must provide means to isolate from complex natural matrices trace amounts of individual organotin molecules, hopefully with minimum perturbation of the original form of the tin-containing moieties. Effective application of either gas or liquid chromatographic separations must overcome or exploit the long-known hydrolysis or ionization of organotins in water [9],

$$R_nSnX_{4-n} + H_2O \longrightarrow R_nSn^{(4-n)+}{}_{aq} + (4-n)\ X^- \quad .$$

For GC-AA or GC-FPD methods, the substantial aquation energies associated with this reaction impose highly unfavorable partition coefficients; that is, direct gas detection by sparging or conventional headspace analysis [56] is inappropriate because of the very low volatility of the solvated organotin ions. For the same reasons, hydrophobic $R_nSnR'_{4-n}$ species, either occurring naturally or formed by analytical derivatization, very favorably partition into headspace gases and can be effeciently speciated by GC methods. A novel variation on this last approach will be examined more fully below.

Liquid chromatography, especially modern HPLC [57], provides a more direct method which relies upon the ionization reactions of aquated organotins. The method is limited to those species which are in solution and not

bound to microparticulates or cellular detritus, unless these moieties are readily desorbed by solvation. In typical, aprotic organic solvents, such as n-hexane, a common commercial organotin biocide, triphenyltin chloride, remains undissociated as a neutral molecule. Consequently, as Figure 3A illustrates, conventional normal partition chromatography permits separation of this species from another neutral chromophoric aryl derivative, benzene. With an ultra-violet (UV) detector monitoring (254 nm) the HPLC effluent, two well-separated peaks are observed, but their identity can only be inferred by comparison with retention times of authentic analytes, if available. Collection of the total eluent in equal, serial portions, followed by off-line tin-specific quantitation by GFAA spectrophotometry unambiguously resolved (Figure 3A, bottom) which of the two aromatic species contained tin. This represents, however, a tedious procedure susceptible to contamination and it places unnecessary constraints on the remarkable detection limits of GFAA detectors. Figure 3B depicts an automated approach developed in our laboratory [54]. Here, the HPLC eluent, after passing through the UV detector (upper chromatogram), is periodically sampled by a commercial autosampler micropipette and periodic aliquots thereby subjected to GFAA analysis for tin. Only 2-6 percent of total analyte is consumed, hence additional off-line characterization is possible for organotin molecules thus separated.

The resulting histogrammic output (lower chromatogram) clearly features the peak shapes of triphenyl-, tri-n-butyl- and tri-n-propyltin cations separated on a C-2 reverse bonded-phase column employing water-methanol solvent systems. It is very important to note here that the UV detector alone provides no chemical information since either the phenyltin species is at too low concentration, or the alkyltins bear no chromophoric functions. Moreover, the retention time for all three R_3Sn^+ species shown in Figure 3B is independent of original gegenion, e.g., Cl^-, OAc^- or Br^-, since the separation mechanism depends upon both the individual carbophilicity of each organotin cation for the reverse bonded phase and some form of ion-pairing release from the column substrate (presumably by OH^-) [57].

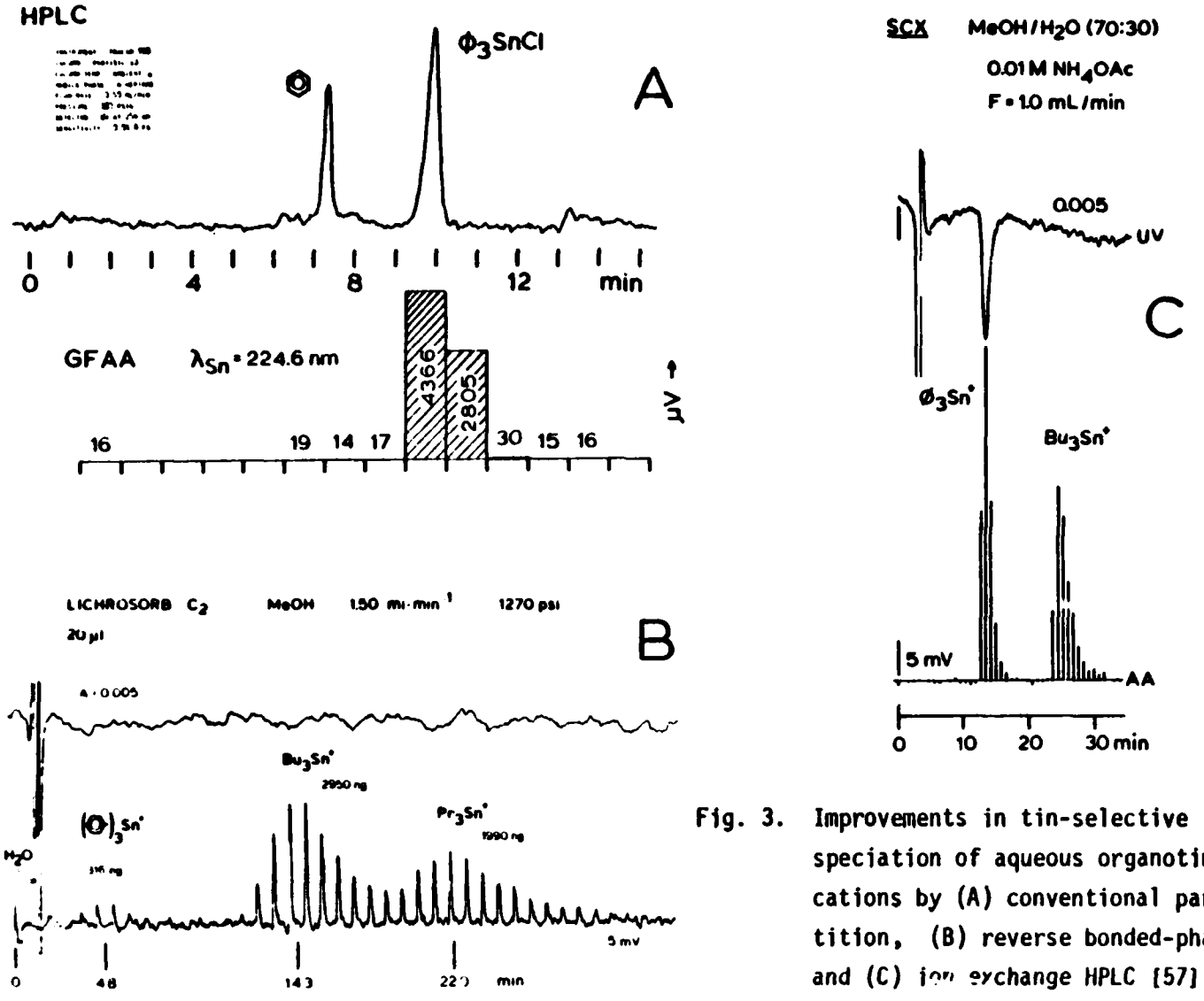


Fig. 3. Improvements in tin-selective speciation of aqueous organotin cations by (A) conventional partition, (B) reverse bonded-phase and (C) ion exchange HPLC [57].

More precise and efficient use of such ionic exchange processes is illustrated in Figure 3C. Here, organotin cations, again irrespective of the original anionic groups, display very reproducible retention parameters dependent solely upon the kind and number of R groups bound to tin(IV) [15]. Not only is column resolution greatly improved, but detection limits for the complete HPLC-GFAA system result which permit direct speciation, for example, of aqueous leachates from organotin-contaminated materials associated with marine antifoulants [15], or from cell-free nutrient solutions exposed to organotin-resistant microorganisms [58]. Presently, the HPLC-GFAA systems routinely in use in our laboratory yield detection limits of 40 to 800 $\mu g\ L^{-1}$ for organotins, depending upon the size of R with Me being least favorable because of greater sample volatilization during the GFAA thermal cycle [15,54]. These limits will doubtless improve in the near future.

Separations of organotin species by HPLC-GFAA on commercial strong cation exchange columns were shown to obey the basic ion exchange relationship, $k' \sim 1/\mu$, where k' is the column capacity factor, a true thermodynamic property of the column separation process [57,59], and μ is the ionic strength of the mobile phase. Consequently, prospects for correlating molecular substituent constants of the organic functions R on the organotins with chromatographic retention indices appear good. Since ln k' was shown to be, in effect, a linear free energy term, several workers have examined various models related to the expression,

$$\ln k' = m(\mathrm{QSAR}) + \mathrm{constant}, \qquad \underline{\text{Equation 2}}.$$

where QSAR represents a "quantitative structure-activity relationship" [60], including Taft-Hammett functions for example. We conducted a preliminary survey of several possible QSAR sources and found one series developed by Mastryukova and Kabachnik [61] for aqueous pK_a of organophosphonic acids to provide highly significant correlations for organotins in the above expression [15]. Not only do such results presage possibilities

for predicting retention properties of known organotin cations on new column materials or with new mobile phases after simple calibration with several known compounds, the possibility of identifying R groups on unknown environmental organotin species separated on calibrated ion exchange columns appears likely.

Though usually requiring derivatization, gas phase speciation of aquatic organotins, particularly the methyltins, offers a more sensitive method than HPLC. Several important procedures for achieving both volatility and molecular fidelity were obtained by exhaustive hydridization with aqueous BH_4^- [62,63] or permethylation with excess methyl Grignard reagent [64]. Thus, the hydrophobic R_nSnH_{4-n} or R_nSnMe_{4-n} (n = 1-3) so formed are reported to be detectable in natural waters at concentrations (as tin) of ~ 0.1 ng L^{-1} by low-temperature evaporative separation into a FPD [62] or AA detector [63], where R = Me or Bu with the hydrides, and at 10 µg L^{-1} by GC-MS where R = Bu with the methylated derivatives [64]. Hydridization was also found to be a sensitive means for speciation of agricultural organotin residues with a GC-electron capture detector (ECD), giving detection limits of 10 µg L^{-1} [14a]. It should be noted that the ECD is not element-selective for tin, however, and careful cleanup procedures are needed to insure that interferences are minimized.

A deficiency common to all the above gas phase speciation techniques above lies in their failure to separate and quantitate environmental tetramethylstannane. Though less volatile than many of the hydrides formed during derivatization, the above procedures are not designed to collect and preconcentrate this species prior to GC or thermal separation into AA and FP detectors, or the extraction solvent interferes with Me_4Sn determination by GC-MS. Clearly, tetramethylstannane is a potential biogenic and chemical end-product from known formation of methyltins in natural waters, and it represents the likely hydrophobic transport agent for tin between oceans and atmosphere as is suggested for mercury [4,65]. Prior to this time tetramethyltin had not been reported in natural waters, although recent

reports suggest biological formation of tetramethyllead in estuarine tidal flats with subsequent transport into the atmosphere over substantial distances [66].

In view of our need to complete the picture of methyltin redistribution in aquatic systems, we recently developed a hybrid procedure which permits both tetramethyltin and all the solvated intermediate methyltins, $R_nSn^{(4-n)+}_{aq}$, along with inorganic tin(IV), to be separated and quantitated from a single aqueous sample at environmental concentrations [67]. Basically, the procedure employs a programmable purge and trap assembly (P/T) which directs a prescribed flow of inert gas through 10-50 mL of sample water into which an excess of aqueous $NaBH_4$ solution is added. The tin(IV) hydrides thus formed, along with any tetramethyltin present, are swept into a proprietary polymer absorbant ("Tenax GC") maintained at room temperature. Automatically, following this purging cycle, the absorbant column is rapidly heated while the gas flow is redirected into the GC-PFD system. Thereby, all volatile organotins are recovered in good yields, there being no evidence for loss of original tetramethyltin present during hydridization. Detection limits for the complete P/T-GC-FPD system at the present stage of development are 30 ng L^{-1} for Me_4Sn and 10 ng L^{-1} for the other methylstannanes.

Environmental organotin chemistry today: current problems and trends

The central problem for organometallic chemists in defining meaningful and practical experiments involving environmental media stems from the micro-heterogeneity and diversity of reaction sites and conditions that prevail [43b]. If one considers, in light of the foregoing discussion, the passage of an element of interest, such as tin, through a typical aquatic microenvironment, it is apparent from Figure 4 that severe gaps in both qualitative and quantitative information remain [68]. We can say with some certainty that homogeneous transmethylation reactions should occur between both long-lived and transient methylmetal(loid)s and appropriate electrophiles, depending upon the form and availability of methyltins. The

overall rates of such processes in the water column will be dictated by

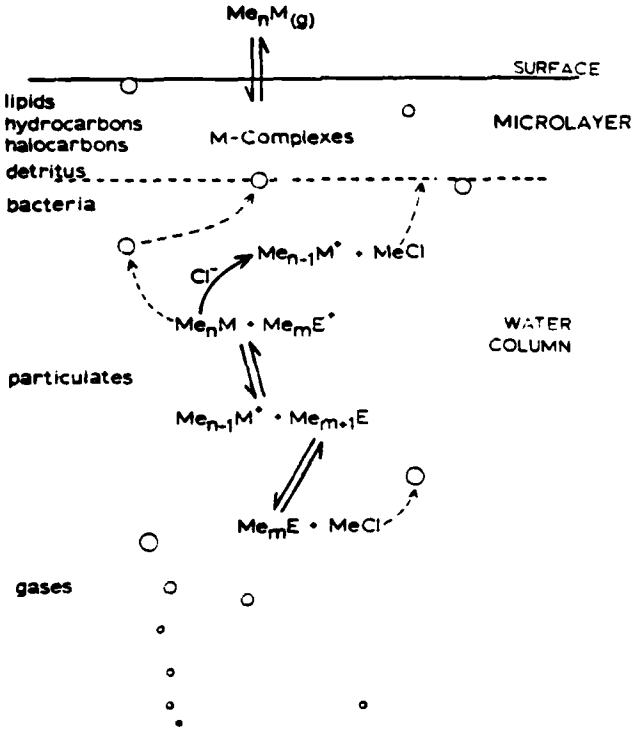


Figure 4. Representative aquatic system shows vertical redistribution pathways for methylmetal(loid)s, Me_nM, and methyl acceptors, Me_mE, with respect to outgassing through the microlayer [72-75].

species concentrations, salinity, pH, and ionic strengths, as well as a number of unresolved factors involving competing ligands [43a,45], photolysis, and unimolecular decomposition rates among others. Many of the unstable intermediate methylelement carriers involved in methyltin redistribution, may serve only to transport chemically and biologically active methyl groups from sedimentary or particulate reservoirs into the atmosphere

as volatile hydrophobic methanes, thus irreversibly reducing the metal "methylation potential" [69] in the locale. Evidence for biogenesis of halomethanes is strong [70] and marine CH_3I production is suggested to involve biogenic methylcob(III)alamin [5a]. Presumably, the carrier metals, so reduced by demethylation, are either precipitated into sediments or incorporated into new biogeochemical cycles [4,43b,71].

Further, Figure 4 suggests that the presence of particulates, both of mineral and biological origin, as well as microbubbles of gases in the water column insures a high degree of surface activity and adsorption processes, along with local mixing. A very large chemical gradient is encountered, however, at the "microlayer". These are ubiquitous surface films (usually 50-600 μm thick) found on the earth's fresh and saline waters [72], and they provide a unique zone of chemical and biological transformations which undoubtedly can alter transport of mobile methyl-metals. Here, not only do microbial populations, potentially capable of transforming organometals, occur in sharply increased abundance [73], the concentrations of many toxic elements are reported to amplify [74]. The microlayer consists of many simple and complex organic molecules, as is suggested in Figure 4. Both the nutrient value of such materials and their ability to favorably ligate environmental metal(loid) species explains the observed intensification and bioactivity of metals in these films [75].

An obvious precaution to be considered by environmental chemists involves measurements attempting to relate the abundance of hydrophobic methylmetal(loid)s evolved from the sediment into the water column and through the surface layer into the atmosphere. The underlying problem is to insure that both abundances and individual species' lifetimes are assessed within all of the principal compartments noted in the figure. Accordingly, isolated measurements of headspace gases above natural waters cannot alone reveal the nature of flux or responsible transport agents in the environmental movement of organometals. Additionally, the relative contribution of chemical and biological forces contributing to the forma-

tion and translocation of a given diagnostic organometallic species must be established in order to reliably correlate both laboratory and field experimental data, and to thereby generate a predictive model. A partial, but unfortunately very speculative, attempt based upon available data will follow for methyltins in concluding this paper.

Craig stated [76], "there is circumstantial, but no direct evidence so far, that tin compounds may be methylated under environmental conditions." So matters stood following our first discussion of *in vitro* microbial methylation of tin(IV) in 1973 [28]. No additional direct or inferential support for *in situ* production or presence of methyltins in environmental media appeared until 1979, when improved speciation methods revealed widespread occurrence of $Me_nSn^{(4-n)+}_{aq}$ (n = 0-3) in fresh and marine waters, and even in human urine [62,63]. Our proposal that biomethylation of inorganic tin(IV) might occur in aerobic estuarine sediments and also mediate methylmercury(II) production [77] had received partial support by the studies of Wood and his coworkers [5,27] who extensively examined the methylcob(III)alamin-tin transmethylation system, but no direct evidence for biogenesis of methyltins from incubated sediments was available. Independent reports last year of widespread distribution of aquatic methyltins has now rekindled interest in this problem.

During the preparation of this paper, three separate groups have reported on the sedimentary biotransformations of tin. Chesapeake Bay bacteria (17 percent of the total population) were found to be resistant to dimethyltin dichloride at nine varied sites, and the sediments yielded microorganisms capable of volatilizing inorganic tin [78]. Similarly, in estuarine sediments from San Francisco Bay, viable microbiota were found to convert trimethyltin hydroxide to tetramethyltin slowly, but sulfur-containing ligands and reducing agents also catalyzed the formation of Me_4Sn non-biologically [79]. Equally important results were reported for microbial transformations of Sn(II), Sn(IV), and several organotin compounds to methyltins in freshwater lake sediments. Chau *et al.* employed

hydride derivatization in combination with GC-AA [50] to demonstrate that Me_4Sn production was confined to Me_3SnCl additions to sediments, but that Me_3Sn^+ production occurred with additions of both inorganic tin salts and methyl-, butyl-, or phenyltin compounds to incubated sediments [80].

We have reported also on a series of in vivo laboratory and in situ field measurements which respectively incorporate methyltin speciation by GC-MS and the new purge/trap GC-FPD method [67]. Repeating our previous work with the pure aerobic Pseudomonas 244 strain [28], we reexamined the respirant atmospheres above sterile and inoculated agar slants contained in grease-free, closed vessels which can be attached directly to the GC-MS system. A number of such controls were imposed on Pseudomonas inocula stressed with either Sn(II) or Sn(IV) at 10 ppm. Representative GC-MS mass chromatograms are reproduced in Figure 5. The mass spectra of tetramethyltin and its derivatives are complex, owing to ion multiplets arising from the presence of many stable tin isotopes in a characteristic abundance patterns. In general, these are reported or can be deduced from data available in computer networks [81]. In the figure, the characteristic principal gaseous ions of Sn^+ (m/e = 120) and Me_3Sn^+ (m/e = 165) are employed to visualize the respective chromatograms from four such vessels after a week's incubation. Slight Me_4Sn production was detected from sterile Sn(II) controls, but no volatile methyltins were generated from sterile Sn(IV). In sharp contrast, volatile methyltin species incorporating three methyl groups were detected at significant concentrations in the metabolic gases above the inoculated Sn(IV) medium, and to a considerably lesser extent from the corresponding Sn(II) medium. The retention time of 0.95 min with the Sn(IV) experiment corresponds to that obtained with authentic tetramethyltin. The earlier retention envelope of unresolved (probably decomposing) peaks at 0.5 to 0.8 min were closely simulated by gaseous mixtures of trace Me_2SnH_2 and Me_3SnH prepared by treatment of the corresponding chlorides with Bu_3SnH [82] in similar slant vessels and injected into the GC-MS system.

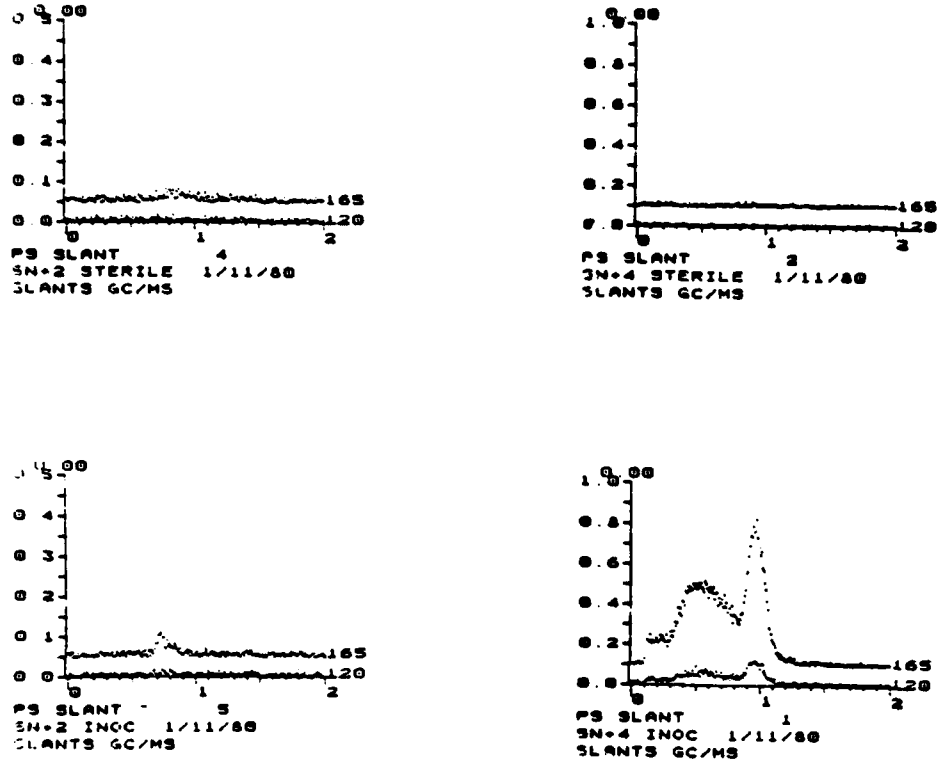


Figure 5. Reproductions of CRT displays from the GC-MS computer show four mass chromatograms specific for Sn^+ (m/e = 120) and Me_3Sn^+ (m/e = 165) obtained from sterile slants or Pseudomonas 244 [28] inocula stressed with either Sn(II) or Sn(IV), as noted. The retention times were compared with injections of authentic Me_4Sn and Me_3SnH/Me_2SnH_2 mixtures [67].

These results basically confirm our earlier study [28] and provide clear evidence for the generation of methyltin species of the type expected [77] to methylate any Hg^{2+} present in the Pseudomonas--Sn(IV)--Hg(II) medium [20, 25]. It cannot be inferred from these results that

Me_4Sn is a direct bacterial metabolite, since many intervening non-biological methyl disporportionation reactions could ensue following biogenesis of the initial methyl-tin bonds. This possibility was mentioned by Coleman et al. [79] and is regarded as an important consideration in the environmental formation of tetramethyllead [83,84]. We find the apparent biological production of methylstannanes, Me_nSnH_{4-n} (n = 2,3) seen in these experiments to be more surprising, primarily because most chemists regard the longevity of organotin hydrides in aqueous or aerobic environments as very brief [82]. Nonetheless, it is already clear that trace (c. ng) quantities of stannanes can be generated in acidic water (pH ~ 6.5) with excess hydride present and successfully degassed into GC-FPD systems.

The question thus to be considered has two parts. First, we must presume that pseudo-first-order decomposition rates involving methylstannanes and dissolved oxygen or protons may be relatively slow. Preliminary data for half lives of Bu_3SnH in water (~ 42 min) or methanol (~ 149 min) [15] suggest that additional rate studies are needed. Second, it should be recognized that bioreduction of metals and metalloids is commonplace in the environment. The Pseudomonas 244 strain is well-known to rapidly reduce inorganic Hg^{2+} to elemental Hg^0 gas [28,85] aerobically at conditions of pH and pCl which involve a redox couple of E^0 ~ +0.8 V [5,86]. Similar bioreductions, involving from 2- to 4-electron steps, occur at lower potentials, and these result not only in the production of free elements, but also produce detectable quantities of trimethylarsine [87] and even dimethylarsine [88] from AsO_4^{3-} (for $As^V \rightarrow As^{III}$, E^0 = +0.56 V). The observed reduction of Sn^{4+} in our experiments, does not formally accord with the 2-electron redox couple, Sn(IV) → Sn(II) (E^0 = +0.15) [5,86], but is well within the physiological range. Schwarz et al. point out that it is close to the redox potential of flavone enzymes [7a], and the formation of As-H bonds additionally suggests that "hydridase" enzymic sites may be available in microorganisms [87].

Concurrent field studies were also rationalized in terms of bioreduction and biomethylation of environmental tin to form methylstannanes of

relatively long lifetimes [67]. We examined Chesapeake Bay water samples at polluted sites. Surface (0.1-1 m depth) and near-bottom samples examined by the P/T-GC-FPD system showed a sustained presence of tetramethyltin with a maximum concentration of 900 ng L^{-1} in early Spring. Even more variable was the appearance of tin-containing species in the GC-FPD , which eluted earlier than Me_4Sn. Figure 6 summarizes experiments which compare a Bay water sample displaying the maximum methyltin content with laboratory calibration solutions. These contain the same composition of Sn^{4+}, $MeSn^{3+}$, Me_2Sn^{2+}, Me_3Sn^{+} and Me_4Sn, and were either subjected to the BH_4^- treatment described above or introduced directly via the P/T into the GC-FPD without hydridization, as with the field sample. Very satisfactory simulation of this field sample was obtained only by hydridization of known methyltin ions. Similar results were obtained with other Chesapeake Bay waters, though usually variable in methyltin concentrations. Insufficient sampling limits any trend analysis at this time. We found maximum concentrations (ng L^{-1}) for the series Sn^{4+} ($\sim$ 0), $MeSn^{3+}$ ($\sim$ 0), Me_2Sn^{2+} (200), Me_3Sn^{+} (398) and Me_4Sn (480) at a Baltimore Harbor sewage outfall. These concentrations are substantially higher than those reported in well-mixed estuarine situations [62,63], and no doubt reflect the local influence of anthropogenic influxes.

The <u>in vivo</u> biomethylation and methyltin hydride production by an aerobic microbe prevalent in the Chesapeake Bay along with the preliminary evidence reported for methylstannanes in sub-surface waters from that estuary does not demonstrate a direct causal relationship [67]. What was shown is that the capacity for biogenesis of methyltins, in forms quite unexpected by organometallic chemists, may occur in environmental circumstances and that quantitative information concerning the stability and likely reactions of such reactive species in aqueous media is prerequisite to future studies on environmental tin chemistry. The occurrence of methyltin hydrides in sub-surface waters may not result from biological events, but the chemical alternatives are not apparent from the literature.

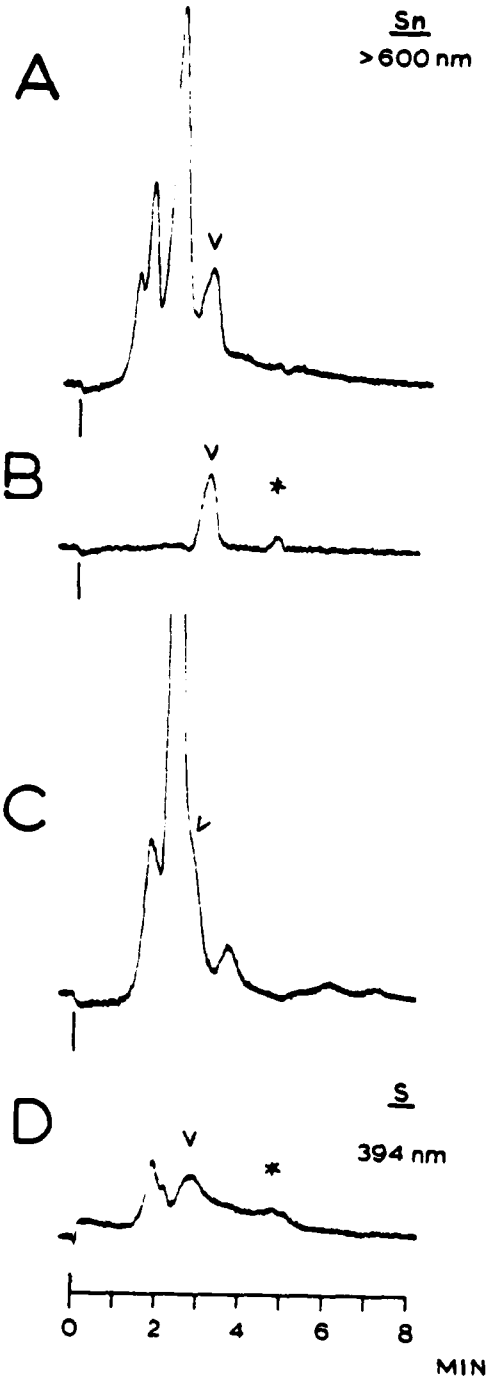


Figure 6.

Tin-selective (> 600 nm) purge and trap GC-FPD chromatograms compare two laboratory calibration solutions (10 mL) containing (ng L^{-1}) Sn^{4+} (0), $MeSn^{3+}$ (384), Me_2Sn^{2+} (200), Me_3Sn^{+} (199), and Me_4Sn (480) (V). Solution A was treated with 100 µL 4% aqueous $NaBH_4$ solution prior to initiating the P/T cycle. Solution B was purged without BH_4^- treatment; Solution C was a surface water sample collected from a polluted Chesapeake Bay site and cycled through the P/T-GC-FPD [67] without BH_4^- treatment. Sample D was taken from the same Bay site, but was examined with the FPD in the sulfur-selective mode [52] at 394 nm. Aquatic Me_2S_2 (*) seen in D may be compared with a large spike added to both samples A and B. The order of retention follows the order of increasing methyl substitution [62,63].

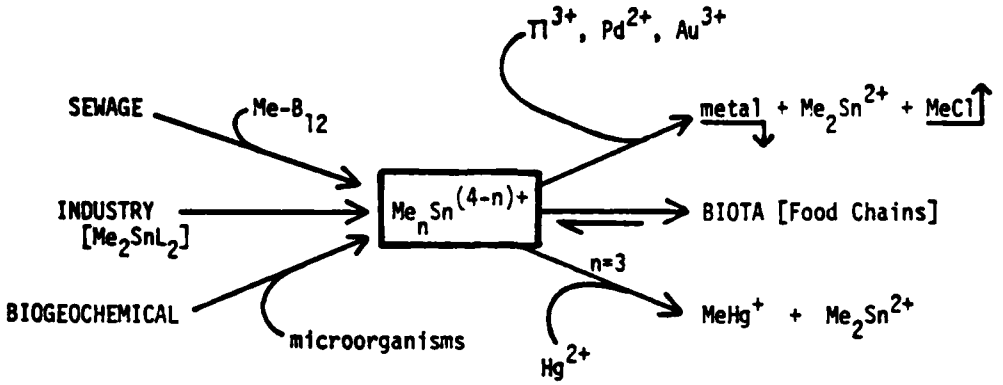
The fate of such stannanes may involve mainly biological sinks, though competative abiotic reactions with dissolved oxygen (in turn dependent on season, pH, salinity, plankton bloom, etc.) or electrophiles (H^+, metal ions) should be important. No reports are yet available regarding the involvement or fate of organometals (as opposed to "metallo-organics" [74,75]) in the microlayer. Speciation of methyltins in that critical compartment by the new techniques will be of great significance to evaluating the potential for dispersal of methyltin precursors into the atmosphere as with tetramethyllead [66,84].

Occurrence and fate of methyltins in the environment

It is appropriate to conclude this paper with a consideration of the environmental dynamics of methyltins. Some writers note concerns for possible threats to human health, based upon certain formal similarities between methyltins and aquatic methylmercury [5,76]. These concerns are surely amplified by findings on biomethylation of innocuous inorganic tin substrates. The mammalian toxicity of triorganotin species, particularly the trimethyl and triethyl derivatives, is well established [3,18,89] and a safety criterion for workplace exposures in organotin production has been promulgated in the United States [90]. Balanced against such concerns, we are reminded that substantial evidence for the essentiality of tin, albeit in unspecified molecular forms, to mammalian metabolism was earlier presented by Schwarz et al. [7a]. It is equally significant that trimethyltin species appear in human urine at much higher concentrations than in natural waters, possibly reflecting a metabolic elimination pathway similar to that found for human detoxification of arsenic via methylarsonates [91].

For brevity, we shall deal with the occurrence and fate of methyltins in a simplistic "though-put" model [92], indicated by SCHEME 3. Industrial influxes, especially organotins including dimethyltin plastics stabilizers, represent the major direct environmental contribution to the aquatic $Me_nSn^{(4-n)+}$ reservoir (box). The organotins represent perhaps four percent of the total anthropogenic influx of tin, which in 1976 amounted to a con-

ENVIRONMENTAL THROUGHPUT OF METHYLTINS



SCHEME 3

sumption of 2.26×10^8 kg [93,94]. In addition to this, substantial quantities of potentially bioactive tin presumably are released into waterways via urban and industrial sewage disposal as a recent multi-element survey of United States cities implies [95]. The evidence for biological production of corrinoids in such sewage [96], possibly including methylcob(III)-alamin, must not be discounted as another route to methyltin formation in these sources. Additionally, the evidence noted before concerning sedimentary biomethylation of inorganic and organo-tin substrates in marine and fresh water locales (from whatever source the tin arises) should be considered a natural biogeochemical "background" influx to the aquatic methyltin reservoir.

Losses of methyltins from the aquatic reservoir can occur by many routes, including irreversible chemical or biological events. In addition to photodecomposition, often suggested as a primary degradation pathway for industrial organotin biocides [14,16,17,97], biological demethylation of methyltin moieties to inert mineral forms may be possible. This kind of process was found to be important in demethylation of methylmercurials by sediment bacterial communities [98]. Homogeneous transmethylation reac-

tions involving metal electrophiles could also be significant, but the relative rates of such bimolecular decompositions in natural waters, as previously discussed, will be very dependent upon the prevalent metal ions and their respective concentrations. In SCHEME 3, the demethylation of Me_3Sn^+ by Hg^{2+} is singled out because both species occur in natural ocean waters at levels which may mediate the steady-state concentration of methyltin in the reservoir.

It is possible at this point with currently available data to make rough estimations of the significance of abiotic demethylation of aquatic Me_3Sn^+ by oceanic mercury(II), and to calculate the residence time of Me_3Sn^+ from these approximations. The principal supporting values and comparative residence times for Me_3Sn^+, Sn and Hg are summarized in Table II.

Table II

GLOBAL OCEAN[a] BURDENS--TIN AND MERCURY SPECIES

Metal Species	Concentration ng L^{-1}	Total in Oceans kg	Residence Time, yr
Sn	9.0[b]	1.2×10^{10}	1×10^{5}[c]
Sn^{IV}	4.2[d]	5.8×10^{9}	---
$Me_nSn^{(4-n)+}$	2.5[d]	3.4×10^{9}	---
Me_3Sn^+	0.5[d]	6.8×10^{8}	5.8×10^{5}[e]
Hg	30.[c]	4.1×10^{10}	4.2×10^{4}[c]
$MeHg^+$	1.5[f]	2.1×10^{9}	---

1976 World Consumption Sn: 226,000 metric tons = 2.26×10^8 kg [94].

[a]Volume = 1.37×10^{21} L [43a]; [b]Ref. 99; [c]Goldberg, 1963, 1965 in Ref. 43a; [d]Ref. 62; [e]This work; [f]Ref. 100.

Thus, based upon average oceanic concentrations reported for total Me_3Sn^+ [62] and Hg [43b], the latter taken as Hg(II), we can estimate relative concentrations of reactive species in seawater at usual conditions of pH, pCl, temperature and ionic strength [43,45]. CHEMSPECIES computations [25] indicate that > 99 percent of all reactants appear in the profiles: $HgCl_2^0$ (3%), $HgCl_3^-$ (15%), and $HgCl_4^{2-}$ (82%), or Me_3Sn^+ (72%), and Me_3SnCl^0 (28%). Applying the rate constants summarized in SCHEME 2 and the $\Delta\mu$ correction Equation 1 for the change in ion c strength from the laboratory-based rates and ocean μ, k_2 is estimated as 13.2×10^{-3} $\underline{M}^{-1}s^{-1}$. From the reported concentrations of mercury and Me_3Sn^+, the half-life residence of Me_3Sn^+ is calculated to be 5.8×10^5 yr. It is interesting to note from Table II that related turnover values for total dissolved tin (1×10^5 yr) and total mercury (4.2×10^4 yr) agree fairly well with this initial estimation. That total mercury turns over in the oceanic environment more quickly than Me_3Sn^+ probably has no kinetic basis, but rather accumulative errors in all the numbers and the likely prospect that other pathways afford turnover of Me_3Sn^+ should be considered.

Finally, in SCHEME 3 is presented the idea that some reversible uptake and reentry of methyltins between the aquatic reservoir and the food chain (BIOTA) may exist. This postulate is reasonable on the basis that mixed methyltins in aquatic environments display no special trends toward degree of substitution. While removal of trimethyltin cation may be important, either by chemical demethylation or bioaccumulation, the substantially greater abundance of Sn(IV) as inorganic tin and lower methyltins (Table II) must be reckoned with in terms of different aqueous organometallic reactions or biotransformations as yet undiscovered. These tasks will surely occupy the attention of chemists for years to come.

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