Chapter 1

Organometallic compounds in the environment: An overview

P. J. Craig and R. O. Jenkins

General points

In this chapter organometallic compounds are defined as those which have a carbon to metal single sigma bond polarized $M^{\delta+}$ - $C^{\delta-}$ (some useful sources are listed in the References Craig 2003; Abel et al. 1995; Bennett et al. 1994, Crompton 2002; Ebdon et al: 2001; Elschenbroich and Salzer 1992; Sigel and Sigel 1993; Hock 2001; Ure and Davidson 1995). The metals of interest are usually main group metals in environmental matters (They are shown in Tables 1 and 2). For useful information to be derived, these substances need to be analysed. In most cases a full speciation analysis is not possible; the organometallic fragment is usually bound to a complex environmental moiety which may not be identifiable. Nevertheless much progress in speciation analysis has been made in recent years (see references above). For speciation analysis in the environment to be possible the organometallic fragment has to be separated from its environmental binding and then measured.

(i) Methods of Separation

a. Gas chromatography
b. Thermal desorption methods
c. High performance liquid chromatography
d. Flow injection methods
e. Ion exchange chromatography
f. Ion chromatography

(ii) Methods of Detection

a. Atomic absorption spectroscopy
b. Atomic fluorescence spectroscopy (sometimes with hydride generation)
c. Atomic emission spectroscopy
d. Voltammetry
e. Mass spectrometry
f. X-ray and neutron methods

Table 1. Stability of methylmetals to oxygen [a]

Stable	Unstable [b]
Me_2Hg	$MePbX_3$
Me_4Si, $[Me_2SiO]_n$, $(Me)_nSi^{(4-n)+}$, Me_6Si_2	$MeTl^+$
Me_4Ge,$Me_4Ge^{(4\ n)+}$, Me_6Ge_2	Me_2Zn, $MeZn^+$
Me_4Sn	Me_2Cd, $MeCd^+$
Me_4Pb§	Me_3B
MeHgX (Ph and Et also stable)	Me_3Al
$Me_{4\ n}SnX_n$	Me_3Ga
Me_3PbX	Me_3In
Me_2PbX_2	Me_3Tl
$Me(C_5H_4)Mn(CO)_3$ [c]	Me_3As [e]
$MeM_n(CO)_4L$ [d]	Me_3Sb [e]
$Me_2AsO(OH)$	Me_3Bi [e]
$MeAsO(OH)_2$	Me_2AsH
Me_2S	$MeAsX_2$
Me_2Se	$MeSbX_2$
MeHgSeMe	$Me_{4n}SnH_n$ [e]
$MeCoB_{12}$ (solid state)	Me_6Sn_2 (At RT gives $[Me_3Sn]_2O$)
Me_3SbO	Me_6Pb_2 (to methyl lead products)
$Me_2SbO(OH)$	Me_3Sb
$MeSbO(OH)_2$	Me_3AsO
Me_2Tl^+, Me_2Ga^+	Me_3P
Me_3S^+	Me_4SiH_{4-n}
Me_3Se^+	Me_4GeH_{4-n}
Me_3PO	

a At room temperature in bulk as against rapid (seconds, minutes) oxidation. Assume similar but lesser environmental stability for ethyls.

b Variously unstable because of empty low lying orbitals on the metal, polar metal-carbon bonds and/or lone electron pairs on the metal.

c Gasoline additive.

d To exemplify ligand-complexed transition metal organometallics. Many of these synthetic compounds are oxygen-stable but none have been found in the natural environment.

e But stable in dilute form and detected in the environment

Reproduced in part from Craig (2003) with permission

Table 2 Stability of organometallic species to water

Organometallic	Stability, comments
R_2Hg, R_4Sn, R_4Pb	Only slightly soluble, stable, diffuse to atmosphere. Higher alkyls less stable and less volatile. Species generally hydrophobic and variously volatile
MeHgX	Stable, slightly soluble depending on X
$(Me)_nSn^{(4-n)+}$	Soluble, methyltin units stable but made hexa- and penta-coordinate by H_2O, OH^-. Species are solvated, partly hydrolysed to various hydroxo species. At high pH polynuclear bridged hydroxo species form for $(Me)_2Sn^{2+}$
Me_3Pb^+	Soluble, hydrolysis as methyltins above. Also dismutates to Me_4Pb and Me_2Pb^{2+} at 20 ^oC
Me_2Pb^{2+}	Soluble as for Me_3Pb^+ above. Disproportionates to Me_3Pb^+ and CH^+_3 slowly. These reactions cause eventual total loss of Me_3Pb^+ and Me_2Pb^{2+} from water.
Me_2As^+	Hydrolyses to Me_2AsOH then to slightly soluble $[Me_2As]_2O$
$MeAs^{2+}$	Hydrolyses to $MeAs(OH)_2$ then to soluble $(MeAsO)_n$
$Me_2AsO(OH)$	Stable and soluble (330 g dm^{-3}). Acidic pKa = 6.27. i.e. cacodylic acid, dimethylarsinic acid. Detected in oceans
$MeAsO(OH)_2$	Stable and soluble. Strong acid $pK_1 = 3.6$, $pK_2 = 8.3$ – methylarsonic acid. Detected in oceans
Me_3S^+, Me_3Se^+	Stable and slightly soluble
Me_nSlCl_{4-n}	Hydrolyse and condense, but methylsilicon groups retained
$Me_nGe^{(4-n)+}$	Stable, soluble, has been discovered in oceans. Hydrolyses but Me_nGe moiety preserved
Me_2Tl^+	Very stable, soluble, but not been detected as a natural environment product
Me_3AsO, Me_3SbO	Stable and soluble
MeAsH, CH_3AsH_2	Insoluble, diffuses to atmosphere, air unstable
MeSbO(OH)	Stable and soluble. Detected in oceans
$CH_3SbO(OH)_2$	Stable and soluble. Detected in oceans

Solubility refers to air-free distilled water, no complexing ligands. Range of solubility is from mg dm^{-3} to g dm^{-3}.

Other species
Stable and insoluble – R_4Si, $(R_2SiO)_n$,$H_3HgSeCH$, most PhHg derivatives, Me_2S, Me_2Se, Me_4Ge, Me_3B
Unstable – $MePb^+$ (has not been detected in the environment), R_2Zn, R_2Cd, R_3Al, R_3Ga, Me_6Sn_2, Me_6Pb_2, $MeTl^{2+}$, $MeCd^+$, Me_2Cd, Me_2Sb^+, $MeSb^{2+}$.

Reproduced in part from Craig (2003) with permission

Separation and detection of organometallics in the environment presupposes that the species are stable. Stability is not discussed here but it is discussed in detail in a recent work (Craig 2003). Toxicology is also covered elsewhere in this work.

As many organometallic moieties are tightly bound in the environment, they may not be volatile and susceptible to separation as above. For such cases separation by derivatization is usually carried out.

This is generally achieved by (formal) SN_2 attack by hydride (from $NaBH_4$), ethyl (NaBEt) or other alkyl group (e.g. from a Gignard reagent), e.g. (Eqn. 1)

$$Bu_3SnX \xrightarrow{NaBH_4} Bu_3SnH \qquad [1]$$

X = environmental counter ion

Organometallic compounds may be found in the natural environment because they are *formed* or because they are *introduced*. The chemistry of the latter group is better known, and their environmental impact has been widely discussed. Organometallic compounds introduced to the environment directly may enter *via* use as products whose properties relate to the environment (e.g. biocides) or they may enter additionally to a separate, main function (e.g. gasoline additives, polymer stabilizers). Compounds of arsenic, mercury, tin and lead have important environmental roles as organometallic compounds.

Where organometallics are formed in the environment it is usually as a result of a methylation process, "biomethylation". This process is discussed below.

As mentioned above, stabilities will be little discussed here (but are shown in Tables 1 and 2), but it should be pointed out that the metal carbon bond is not necessarily weak (i.e. leading to decay for thermodynamic reasons), but there are often low energy routes for metal-carbon decomposition (i.e. kinetic decay). In the latter case the activation energy for decay is low.

In a similar way, all organometallic compounds are thermodynamically unstable to oxidation because of the lower free energies of the products of oxidation. However, some do not oxidise (or are not inflammable) for kinetic reasons. Compounds which in bulk may e.g. ignite are sometimes stable at high attenuation. Most organometallics are thermodynamically unstable to hydrolysis to the metal hydroxide and hydrocarbon. Again many are kinetically stable e.g. if nucleophilic attack by water on the metal cannot take place because lack of suitable orbitals on the metal or if the attack is physically blocked by ligands.

Stability to light for organometallics is most important for those volatile species which enter the atmosphere, and less relevant for those coordinated to biological or environmental ligands in organisms or water. Chemistry, decay and toxicity of organometallic species in biological systems is discussed elsewhere (see above) and in the present work.

Biomethylation

Biomethylation is the process whereby living organisms produce a direct linkage of a methyl group to a metal or metalloid, thus forming metal-carbon bonds. Methylation has been extensively studied and biomethylation activity has been found in soil, but mainly occurs in sediments in e.g. estuaries, harbours, rivers, lakes and oceans. The addition of a methyl group to a metall(oid) changes the chemical and physical properties of that element, and this then influences toxicity. The organisms responsible for metall(oid) biomethylation are nearly all microorganisms. Anaerobic bacteria are believed to be the main agents of biomethylation in sediments and other anoxic environments. Some aerobic and facultatively anaerobic bacteria, as well as certain fungi and lower algae, may also methylate metals. With the exception of vitamin B_{12} higher organisms, containing a methyl-cobalt bond, do not seem to be able to methylate genuine metals. The situation is different for the metalloids arsenic, selenium and tellurium: many higher organisms have been shown to form methyl derivatives of these elements, e.g. methylarsenicals are formed in a wide range of organisms, including marine biota and mammals (and man).

Volatile methyl and hydride derivatives of metal(loids) can often be found in gases released from natural and anthropogenic environments (Feldmann and Hirner 1999; Feldmann et al. 1999; Hirner et al. 1998; Feldmann et al. 1994), e.g. geothermal gases, sewage treatment plants, marine sediments, landfill deposits), and biological production of volatile compounds is believed to be an important part of the biogeological cycles of metal(loids)s, such as arsenic, mercury, selenium and tin. With the exception of arsenic and selenium (and perhaps antimony), biomethylation increases toxicity, because methyl derivates are more lipophilic and therefore more biologically active.

Biomethylation of organic molecules – e.g. such as proteins, nucleic acid bases, polysaccharides and fatty acids – occurs in all living cells and is an essential part of normal intracellular metabolism. The three main biological methylating agents for organic molecules – S-adenosylmethionine (SAM), methylcobalamine and N-methyltetrahydrofolate – have all been shown to be capable of involvement in the biomethylation of metall(oids). SAM is a ubiquitous methylating agent and is synthesised by the transfer of an adenosyl group from ATP to the sulphur atom of methionine.

A positive charge on the sulphur atom activates the methyl group of methionine, making SAM a methyl carbonium ion donor. The methyl group in biochemistry is transferred as a radical (CH_3•) or as a carbonium ion (CH_3^+) and the atom receiving the methyl group must be nucleophilic, which requires a lone pair of electrons in the metal valency shell; i.e. oxidative addition, where there is alternation of M^{n+} and $M^{(n+2)+}$ oxidation states. The reaction (involving carbonium ions) is usually referred to as the Challenger mechanism, devised originally to account for the methylation of arsenic (Challenger et al. 1933; Brinckman and Bellama 1978) (Figure 1). SAM has subsequently been shown also to be the methylating agent for selenium, tellurium, phosphorus (Fatoki 1997) and antimony (Andrewes

et al. 1999a), all of which have lone paid of electrons. N-Methyltetrahydrofolate like SAM, is thought to transfer methyl groups as carbonium ions or an intermediate radical, but its transfer potential is not as high as SAM. Conversely, for methylcobalamin in the environment – a derivative of vitamin B_{12} – the methyl group is transferred as a carbanion (CH_3^-) and the recipient atoms must be electrophilic e.g. mercury (II). Methylcobalamin is well established as a methylating agent for mercury and can also be involved in (in vitro) methylation for lead, tin, palladium, platinum, gold and thallium (Fatoki 1997). Although methylcobalamin appears to be the only carbanion methylating agent, in the natural environment, a carbanion may also be transferred to metals from other organometallic species which may be present, e.g. Me_3Pb^+, Me_3Sn^+. Regardless of the methylating agent, only one methyl group transfers to the metal(loids) in each step, although further groups may then be transferred to the same receiving atom. Methylation of some individual elements is now discussed.

Arsenic

Many microorganisms can methylate arsenic and methylarsenic compounds are produced, under both aerobic and anaerobic conditions (Cullen and Reimer 1989). Fungal methylation of arsenic was reported in the nineteenth century, when several poisoning incidents in England and Germany were associated with arsenic containing wall papers. Gosio in 1901, reported that a garlic-smelling, methylated arsenic compound was released from moulds growing in the presence of inorganic arsenic. Challenger et al. (1933) identified this as trimethylarsine (Me_3As). Several fungi have been shown to methylate arsenic under aerobic conditions, including *Scopulariopsis brevicaulis, Penicillium* sp.*, Gliocladium roseum* and the yeast *Cryptococcus humicola* (Brinckman and Bellama 1978; Thayer 1984; Andreae 1986). The mechanism of arsenic methylation in fungi was established by Challenger et al 1933 and involves a series of reductions and oxidative methylations, using SAM (Figure 1.) as a methyl donor.

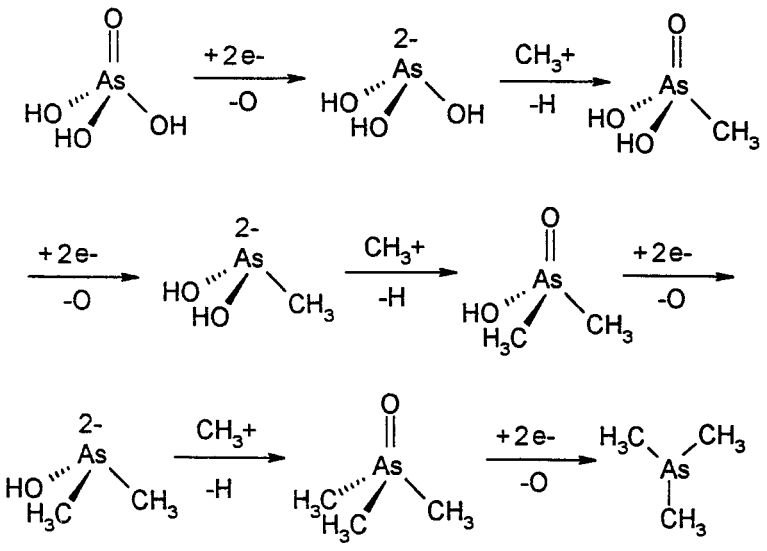

Fig. 1. Arsenic methylation according to the Challenger mechanism

Certain bacteria have also been shown to methylate arsenic under aerobic conditions, including *Flavobacterium* sp., *Escherichia coli* and *Aeromonas* sp. (Thayer 1984).

Arsenic biomethylation can also be catalysed by obligate anaerobic bacteria, e.g. *Methanobacterium* sp. can reduce AsO_3^- to AsO_2^-, with subsequent methylation to methylarsonic acid, dimethylarsenic acid and dimethylarsine (Takahashi et al. 1990). Methylcobalamin is the methyl donor for arsenic methylation by methanogenic archaea (McBride and Wolfe 1971). Michalke et al. (2000) have reported trimethylarsine in the gas phase above anaerobic cultures of *Methanobacterium formicicum, Clostridium collagenovorans* and two *Desulfovibrio* spp. For *C. collagenovorans* and *D*, *vulgaris*, trimethylarsine was the only volatile arsenic species detected. Conversely, *M. formicicum* volatilised arsenic as mono- di- and trimethylarsine and as arsine (AsH_3), while *Methanobacterium thermoautotrophicum* produced only arsine. This data serves to illustrate the key role of the organism for metal(loid) microbial transformations.

There is an extensive marine chemistry for arsenic with many methylarsenic riboside species identified and analogous compounds are now being found in terrestrial situations.

Antimony

Mono- and dimethylantimony species have been found to be formed in both marine and terrestrial natural waters (Andreae 1981; Andreae 1984). Freshwater plants from two lakes contaminated by mine effluent, and plant material from an abandoned antimony mine have also been shown to contain methylantimony species (Craig et al. 1999; Dodd et al. 1996).

Biomethylation of inorganic antimony by the aerobic fungus *Scopulariopsis brevicaulis* is documented (Craig et al. 1998; Jenkins et al. 1998a; Jenkins et al. 1998b; Andrewes et al. 1998; Andrewes et al. 1999b; Andrewes et al. 2000) and is thought to involve methyl transfer *via* SAM (Andrewes et al. 1999a). Recently, the fungus *Phaeolus schweinitzii* has also been shown able to biomethylate antimony (Andrewes et al. 2001). Mixed cultures of bacteria growing under anaerobic conditions have been shown to generate volatile trimethylantimony as the sole volatilised antimony species (Gates et al. 1997, Gurleyuk et al 1997, Jenkins et al 1998c). Volatilisation of antimony from environmental sediments and municipal waste sites also suggests that certain anaerobic and/or facultatively anaerobic bacteria can biomethylate (Hirner et al. 1994; Feldmann et al. 1994) antimony. Michalke et al. (2000) reported biomethylation of inorganic antimony by pure cultures of anaerobic bacteria. *C. collagenovorans*, *D. vulgaris* and three species of methanogenic archaea, were shown to produce trimethylantimony in culture headspace gases. *M. formicium* was shown to produce SbH_3 together with $Me_{3-n}SbH_n$ (n = 0,72) into culture headspace gases.

Mercury

Biomethylation of mercury has been studied extensively. Methylation of mercury increases lipid solubility and thus enhances bioaccumulation in living organisms. This can lead to mercury entering the food chain and to mercury poisoning incidents, e.g. in Japan and Iraq (Craig 2003). Many different bacteria in aerobic and anaerobic environments are known to cause mercury biomethylation, although anaerobic sediments are the main sites of environmental methylmercury formation (Fatoki 1997). Sulphur-reducing bacteria, such as *Desulfovibrio desulfuricans*, are thought to be the most important methylators of mercury (Compeau and Bartha 1985; Compeau and Bartha 1987; Kerry et al. 1991). Both low pH and high sulfate concentrations promote mercury biomethylation activity within environmental sediments (Winfrey and Rudd 1990; Craig and Moreton 1984). Methylcobalamin is the methyl donor, giving rise to monomethylmercury and (in a slower step) dimethylmercury (volatile) products in a transfer to electrophilic mercury (II) of a methyl carbonium ion (Eqn 2) viz.

$$CH_3CoB_{12} + Hg^{2+} \xrightarrow{H_2O} CH_3Hg^+ + H_2OCoB_{12} \qquad [2]$$

Further reaction of methylmercury can occur *via* various biotic mechanisms (e.g. disproportionation reaction involving H_2S) also giving rise to dimethylmercury (Eqn 3) (Craig and Moreton 1984).

$$2CH_3Hg^+ + S^{2-} \rightarrow (CH_3Hg)_2S \rightarrow (CH_3)_2Hg + HgS \quad [3]$$

An important factor governing the concentration of mercury in biota is the concentration of methyl mercury in environmental waters, which is determined by the relative efficiencies of methylation and demethylation processes.

Several other metals and metalloids can undergo methylation and these systems have been discussed in detail in a recent work (Craig 2003). The elements involved include tin, bismuth, selenium and others. An example of a biogeochemical cycle for tin is shown in Figure 2.

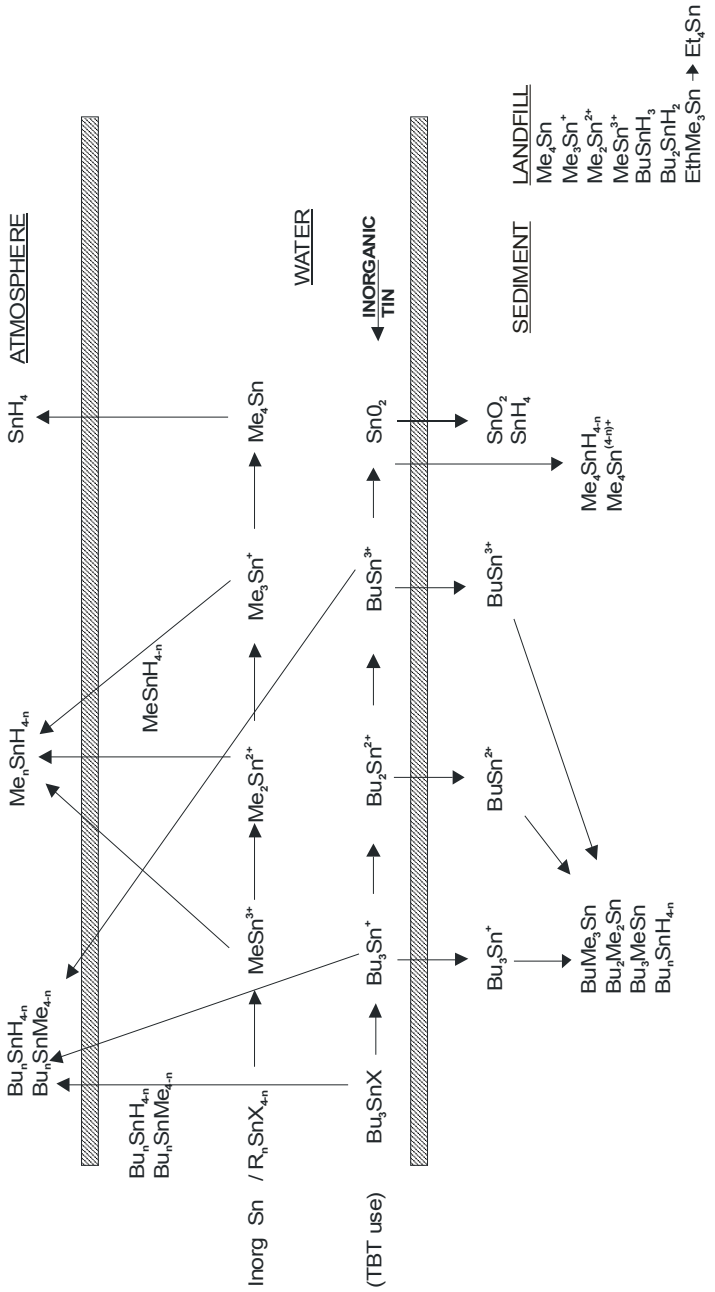

Fig. 2. The biogeochemical cycle of tin

Microbial demethylation/dealkylation

For some metals, such as mercury and tin, microbial demethylation or dealkylation of organometallic forms are important in detoxication mechanisms. Bacterial mercury (II) resistance, for example, involves reduction of Hg(II) to Hg(O) *via* mercuric reductase (MR). The reduced form of the metal is less toxic, more volatile and is rapidly removed to the atmospheric. Detoxification of organomercurials proceeds *via* organomercurial lyase (OL), a product of the *Mer* B gene, that enzymatically cleaves the Hg-C bond to form Hg(II), which is then removed *via* mercuric reductase (Gadd 1993; Losi and Frankenberger 1997) (Eqns 4 and 5). For example

$$CH_3Hg^+ \xrightarrow{OL} CH_4 + Hg^{2+} \xrightarrow{MR} Hg^0 \qquad [4]$$

$$C_2H_5Hg^+ \xrightarrow{OL} C_2H_6 + Hg^{2+} \xrightarrow{MR} Hg^0 \qquad [5]$$

Oxidative demethylation of methylmercury, involving bacterial liberation of carbon dioxide, also occurs. The mechanism is thought to involve enzymes associated with bacterial metabolism of C-1 compounds (Oremland et al. 1991) and is believed to occur widely in freshwater and aqueous environments, under both aerobic and anaerobic conditions.

Degradation of organotin compounds has been shown for a wide range of microorganisms, including bacteria, fungi and algae (Gadd 2000). Organotin degradation (Eqn.6) is thought to involve sequential cleavage of tin-carbon bonds, resulting in removal of organic groups and a reduction in toxicity (Cooney and Wuertz 1989; Crompton 1998; Cooney 1988a; Cooney et al. 1988b). Cleavage is initiated by hydroxo attack (Eqn. 6).

$$R_4Sn \rightarrow R_3SnX \rightarrow R_2SnX_2 \rightarrow RSnX_3 \rightarrow SnX_4 \qquad [6]$$

Tributyltin oxide (TBTO) and tributyltin napthenate (TBTN) have been shown to be degraded by fungal action to di- and monobutyltins. Certain gram-negative bacteria and the green alga *Ankistrodesmuc falcatus* can also dealkylate tributyltin, giving rise to dibutyl-, monobutyl- and inorganic tin products; the alga was able to metabolise around 50% of the accumulated tributyl over a four-week period (Maguire 1984). Similar end-products are formed by the action of soil microorganisms on triphenyltin acetate (Barnes et al. 1973). Tin-carbon bonds are also cleaved abiotically, for example by UV, and it has been difficult to establish the relative importance of abiotic and biotic mechanisms of degradation in the natural environment (Gadd 2000). In some circumstances, environmental conditions (e.g. pH or redox potential), established by microbial activity, strongly

pH or redox potential), established by microbial activity, strongly influence the extent of abiotic degradation of organotins (Gadd 2000). This discussion relating to abiotic and biotic organotin degradation also apply to other organometal(loids).

Bacterial demethylation of methylarsenicals is known to occur in aerobic aqueous and terrestrial environments, giving CO_2 and arsenate (Andreae et al. 1986). Several soil bacteria, such as *Achromobacter, Flavobacterium* and *Pseudomonas*, have been shown to possess organoarsenical demethylation ability. Bacterial demethylation of methylarsenic acids excreted by marine algae is an important part of the biogeochemical cycling of arsenic.

Dimethylselenide has been shown to be demethylated in anaerobic environments by methanogenic and suphate reducing bacteria, producing CO_2 and CH_4 (Newman et al. 1997). Several bacterial isolates form aerobic soils, - including members of the genera *Pseudomonas*, *Xanthmononas* and *Corynebacterium* – have been shown to use methylselenides as sole source of carbon (Doran and Alexander 1977).

Literature

Abel EW, Stone FGA, Wilkinson G (1995) Comprehensive organometallic chemistry II, Vols 1-14, Pergamon (Elsevier), Oxford, UK

Andreae MO (1986) Arsenic Compounds in the Environment, in Craig, PJ, Organometallic Compounds in the Environment, Longman, Harlow, UK, 198-228 pp

Andreae MO, Asmode J-F, Foster P, van't Dack L (1981) Determination of antimony(III), antimony (V), and methylantimony species in natural waters by atomic absorption spectrometry with hydride generation. Anal Chem 53: 1766-1771

Andreae MO, Froelich P N (1984) Arsenic, antimony, and germanium biogeochemistry in the Baltic Sea. Tellus 36b:101-117

Andrewes P, Cullen WR, Feldmann J, Koch I, Polishchuk E, Reimer K J (1998) The production of methylated organoantimony compounds by *Scopulariopsis brevicaulis*. Appl Organometal Chem 12:827-842

Andrewes P, Cullen WR, Feldmann J, Koch I, Polishchuk E (1999a) Methylantimony compound formation in the medium of *Scopulariopsis brevicaulis* cultures: $^{13}CD_3$-L-methionine as a source of the methyl group.Applied Organometallic Chemistry 13:681-687

Andrewes P, Cullen WR, Polishchuk E (1999b) Confirmation of the aerobic production of trimethylstibine by Scopulariopsis brevicaulis. Appl Organometal Chem13:659-664

Andrewes P, Cullen WR, Polishchuk E (2000) Arsenic and antimony biomethylation by *S.brevicaulis*: Interactions of arsenic and antimony compounds. Environ Sci Technol 34:2249-2253

Andrewes P, Cullen WR, Polishchuk E, Reimer KJ (2001) Antimony biomethylation by the wood rotting fungus *Phaeolus schweinitzii*. Appl Organometal Chem 6:473-480

Barnes RD, Bull AT, Poller RC (1973) Persistence of the organotin fungicide fentin acetate (triphenyltin acetate) in the soil and on surfaces exposed to light. Pesticide Sci 4:305-317

Bennet S (1994) The Open University, Science, a Third Level Course, S343, Inorganic Chemistry, Block 6, Open University Press, second edition

Brinckman F, Bellama JM (1978) Organometals and organometalloids; occurrence and fate in the environment, American Chemical Society, Washington DC

Challenger F, Higginbottom C, Ellis L (1933) The formation of organometalloidal compounds by microorganisms. Part 1: Trimethylarsine. J Chem Soc Transact 32:95-101

Compeau GC, Bartha, R (1985) Sulfate-reducing bacteria: principal methylators of mercury in anoxic estuarine sediment. Appl Environ Microbiol 50:498-502

Compeau GC, Bartha R (1987) of salinity on mercury-methylating activity of sulfate-reducing bacteria in estuarine sediments. Appl Environ Microbiol 53:261-265

Cooney JJ (1988a) Ineractions between microorganisms and tin compounds. In: Craig P J, Glockling F (eds) The biological alkylation of heavy elements. Royal Society of Chemistry, London, UK, 92-104pp

Cooney JJ (1988b) Microbial transformations of tin and tin compounds. J Ind Microbiol 3:195-204

Cooney JJ, Wuertz S (1989) effects of tin compounds on microorganisms. J Ind Microbiol 4:375-402

Craig PJ, Moreton PA (1984) Total mercury, methyl mercury and sulphide in River Carron sediments. Marine Poll Bull 15:406-408

Craig PJ, Forster SN, Jenkins RO, Miller DP (1999) An analytical method for the detection of methylantimony species in environmental matrices: methylantimony levels in some UK plant material. Analyst 124:1243-1248

Craig PJ (2003) (ed), Organometallic compounds in the environment, second edition, John Wiley, Chichester, UK

Crompton TR (1998) Occurrence and analysis of organometallic compounds in the environment, John Wiley, Chichester, UK

Crompton TR (2002) Determination of metals in natural and treated waters, Spon Press (Taylor and Francis), London, UK

Cullen WR, Reimer KJ (1989) Arsenic speciation in the environment. Chem Rev 89:731-764

Dodd MS, Pergantis S, Cullen WR, Li H, Eigendorf GK, Reimer KJ (1996) Antimony speciation in freshwater plant extracts by using hydride generation-gas chromatography-mass spectrometry. Analyst 121:223-228

Doran JW, Alexander M (1977) Microbial transformations of selenium. Appl Environ Microbiol 33:31-37

Ebdon L, Pitts L, Cornelis R, Crews H, Donard OFX, Quevauviller Ph, (eds) (2001) Trace Elements Speciation for Environment, Food and Health, Royal Society of Chemistry, London, UK

Elschenbroich CH, Salzer A (1992) Organometallics, a concise introduction, second edition, VCH Press, Weinheim, Germany

Fatoki OS (1997) Biomethylation in the natural environment: A review. S Afr J Sci 93:366-370

Feldmann J, Gruemping R, Hirner AV (1994) Determination of volatile metal and metalloid compounds in gases from domestic waste deposits with GC/ICP-MS. Fresenius J Anal Chem, 350:228-234

Feldmann J, Hirner AV (1995) Occurence of volatile metal and metalloid species in landfill and sewage gases. Int J Environ Anal Chem 60:339-359

Feldmann J, Krupp E, Glindemann D, Hirner AV, Cullen W R (1999) Methylated bismuth in the environment. Appl Organometal Chem 13:739-748

Gadd GM (2000) Microbial interactions with tributyltin compounds: detoxification, accumulation, and environmental fate. Sci Total Environ 258:119-127

Gates PN, Harrop HA, Pridham JB, Smethurst B (1997) Can microorganisms convert methylated antimony trioxide or potassium antimonyl tartrate to methylated stibines? Sci Total Environ 205:215-222

Gurleyuk H, Van Fleet-Stadler V, Chasteen TG (1997) Confirmation of the biomethylation of antimony compounds. Appl Organometal Chem11:471-483

Hirner AV, Feldmann J, Goguel R, Rapsomanikis S, Fischer R, Andreae M (1994) Volatile metal and metalloid species in gases from municipal waste deposits. Appl Organometal Chem 8:65-69

Hirner AV, Feldmann J, Krupp E, Gruemping R, Goguel R, Cullen WR (1999) Metal(loid)organic compounds in geothermal gases and waters. Org Geochem 29:1765-1778

Hock CB (2001) Thermochemical proceses, principles and models, Butterworth-Heinemann, Oxford, UK

Jenkins RO, Craig PJ, Goessler W, Irgolic KJ (1998a) Biovolatilization of antimony and sudden infant death syndrome (SIDS). Human Exp Toxicol 17:231-238

Jenkins RO, Craig PJ, Goessler W, Miller D, Ostah N, Irgolic KJ (1998b) Biomethylation of inorganic antimony compounds by an aerobic fungus: *Scopulariopsis brevicaulis*. Environ Sci Technol 32:882-885

Jenkins RO, Craig PJ, Miller DP, Stoop LCAM, Ostah N, Morris T-A (1998c) Antimony biomethylation by mixed cultures of micro-organisms under anaerobic conditions. Appl Organometal Chem 12:449-455

Kerry A, Welbourn PM, Prucha B, Mierle G (1991) Mercury methylation sulphate- reducing bacteria from sediments of an acid stressed lake. Water Air Soil Pollut 56:565-575

Losi ME, Frankenburger WT (1997) Bioremediation of selenium in soil and water. Soil Sci 162:692-702

McBride BC, Wolfe RS (1971) Biosynthesis of dimethylarsine by Methanobacterium. Biochemistry 10:4312-4317

Maguire RJ (1984) Butyltin compounds and inorganic tin in sediments in Ontario. Environ Sci Technol 18:291-294

Michalke K, Wickenheiser A , Mehring A, Hirner AV, Hensel R (2000) Production of volatile derivatives of metal(loid)s by microflora involved in anaerobic digestion of sewage sludge. Appl Environ Microbiol 66:2791-2796

Newman DK, Kennedy EK, Coates JD, Ahmann D, Ellis DJ, Lovley DR, Morel FMM (1997) Dissimilatory arsenate and sulfate reduction in *Desulfotomaculum auripigmentum* sp. nov. Arch Microbiol 168:380-388

Oremland RS, Culbertson CW, Winfrey MR (1991) *In situ* bacterial selenate reduction in the agricultural drainage systems of western Nevada. Appl Environ Microbiol 578:130-137

Sigel H, Sigel A, (eds) (1993) Metal ions in biological systems, Vol 29, Biological properties of metal alkyl derivatives, Marcel Dekker, New York

Takahashi K, Yamauchi H, Mashiko M, Yamamura Y (1990) Effect of S-adenosylmethionine on methylation of inorganic arsenic. *Nippon Eiseigaku Zasshi* 45:613-618

Thayer JS (1984) Organometallic compounds and living organisms, Academic Press, New York

Ure AM, Davidson CM, (eds) (1995) Chemical speciation in the environment, Blackie Academic and Professional, Glasgow

Winfrey MR, Rudd JMW (1990) Environmental factors affecting the formation of methylmercury in low pH lakes. Environ Toxicol Chem 9:853-869

http://www.springer.com/978-3-540-20829-7

Organic Metal and Metalloid Species in the Environment
Analysis, Distribution, Processes and Toxicological Evaluation
Hirner, A.V.; Emons, H. (Eds.)
2004, XVIII, 328 p., Hardcover
ISBN: 978-3-540-20829-7