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**ORGANOMETALLIC COMPOUNDS OF Sb, Bi, Cd,  
Ge, Mn, P, Se, AND TI IN THE ENVIRONMENT  
- A REVIEW**

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**NWRI Contribution No. 99-094**

**Organometallic Compounds of Sb, Bi, Cd, Ge, Mn, P, Se, and Tl  
in the Environment - A Review**

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## **MANAGEMENT PERSPECTIVE**

Studies of organometallic compounds in the environment have gained much attention in recent years because of their unique properties, being highly toxic and bioaccumulative. The most studied organometallic compounds are those of mercury, lead and tin. Recent reports on environmental occurrence of organometallic compounds of antimony, bismuth, germanium, selenium have caused concern that many other organometallic compounds are present in our environment. It is the purpose of the present review to summarize the knowledge and current status of research of some less common organometallic compounds in order to provide background information for further work.

## **SOMMAIRE À L'INTENTION DE LA DIRECTION**

Les études sur les composés organométalliques dans l'environnement, qui sont fortement toxiques et bioaccumulatifs, ont reçu beaucoup d'attention au cours des dernières années à cause des propriétés uniques de ces composés. Les plus étudiés d'entre eux sont ceux du mercure, du plomb et de l'étain. Des rapports récents sur l'occurrence dans l'environnement de composés organométalliques d'antimoine, de bismuth, de germanium et de sélénium ont soulevé des inquiétudes parce que beaucoup d'autres composés organométalliques sont présents dans notre environnement. La présente étude, qui doit résumer les connaissances sur ce sujet et faire le point sur les recherches portant sur des composés organométalliques plus rares, doit fournir des informations de base pour des travaux ultérieurs.

## **ABSTRACT**

Since the discovery of biomethylation of mercury almost thirty years ago, studies on environmental aspects of organometallic compounds have swiftly gained momentum. The development of highly sensitive and specific analytical techniques has enabled detection of organometallic species at ultra-trace levels in the environment. Because of their wide industrial usage and applications, studies particularly on mercury, lead and tin are plentiful. Research on less common organometallic compounds such as those of antimony, bismuth, cadmium, germanium, manganese, phosphorus, selenium and thallium are relatively sparse. It is the purpose of the present review to summarize the development and current status of organometallic compounds of these elements and to provide background information for researchers interested in this field.

## **Keywords**

Organometallic compounds, antimony, bismuth, cadmium, germanium, manganese, phosphorus, selenium, thallium

## **RÉSUMÉ**

Depuis la découverte de la biométhylation du mercure il y a presque 30 ans, les études sur les aspects environnementaux des composés organométalliques ont pris assez rapidement une importance croissante. Le développement de techniques d'analyse très sensibles et très spécifiques a permis la détection d'espèces de composés organométalliques présents à l'état d'ultratraces dans l'environnement. À cause de la grande diversité de leurs usages et de leurs applications dans l'industrie, il existe un grand nombre d'études de ce type, notamment sur le mercure, le plomb et l'étain. Par contre, les recherches sur les composés organométalliques moins communs, comme ceux de l'antimoine, du bismuth, du cadmium, du germanium, du manganèse, du phosphore, du sélénium et du thallium, sont relativement rares. La présente étude, qui doit résumer les connaissances sur ce sujet et faire le point sur les composés organométalliques de ces éléments, doit fournir des informations de base utiles aux chercheurs de ce domaine.

### **Mots clés**

composés organométalliques, antimoine, bismuth, cadmium, germanium, manganèse, phosphore, sélénium, thallium

## INTRODUCTION

Natural formation of organometallic compounds has been known for almost two centuries, but systematic study of the phenomena was only carried out after more than a hundred years. The first case of the formation of an organometallic compound of environmental concern is probably the biomethylation of arsenic leading to the formation of a toxic gas, later known as methylarsine in 1810 in Germany. The large-scale environmental catastrophes were the mercury poisoning cases in Japan in 1950, in Iraq in 1971 and in South America, etc. where hundred of people were poisoned. Apart from the natural formation, many organometallic compounds are man-made. It was the wonder of chemistry in the 30's which represented the advancement of chemical technology. Their uses and applications are extensive, from medicinal and pharmaceutical applications to industrial usage. Typical ones are alkyltin compounds in biocidal uses, and alkyllead as anti-knocking agents in gasoline. Needless to say that there are many other organometallic compounds being used in our daily life. Comprehensive treatises of the environmental aspects of organometallic compounds and on the history and applications of organometallic compounds have been given by Thayer<sup>1</sup> and Craig<sup>2</sup>.

Studies on biological and environmental aspects of organometals have gained much impetus since the discovery of mercury methylation by microorganisms to a highly neurotoxic methylmercury species.<sup>3</sup> Studies on biotransformation of elements and their environmental impact soon extended to cover lead, tin, selenium. Because of their industrial usage and applications, studies and literature on mercury, lead and tin are particularly plentiful during the last two decades. With the advent of new speciation analytical techniques, not only trace concentrations of many organometallic compounds have been discovered in the environment, knowledge of the pathways and toxicity were significantly enhanced. The speciation technique

has opened up a new frontier of analytical chemistry which has become one of the most flourishing and fast growing research areas.

The present review summarizes the development and current status of the environmental aspects of some lesser-known organometallic compounds. It is hoped that the information will be useful to researchers interested in this field.

### **Antimony**

Early work showed that the methylantimony(V) species, monomethylstibonic acid (MSA) and dimethylstibonic acid (DMSA) were detected in natural water at the ng Sn/L level in several rivers in USA, Gulf of Mexico and Main River in Frankfurt.<sup>4,5</sup> Volatile species of many elements including Sb, Te, V, Si, As, Sn, Hg and Bi were reported to be present in gases released from domestic waste deposits.<sup>6</sup> In recent experiments with anaerobic soil enrichment cultures spiked with potassium antimony tartrate or potassium hexahydroxyantimonate, a volatile antimony compound was detected in the headspace gases which was confirmed to be trimethylantimony (TMA) by GC-MS.<sup>7</sup> The TMA production was linked to the culture's cell population and the mechanism was suggested as biomethylation. Later in another laboratory, the  $\text{Me}_3\text{Sb}$  together with  $\text{Me}_4\text{Sn}$  and  $\text{Et}_2\text{Me}_2\text{Sn}$  species were positively identified in landfill and sewage sludge fermentation gases.<sup>8</sup> Apart from volatile trimethylantimony ( $\text{Me}_3\text{Sb}^{2+}$ ) found in the headspace nonvolatile antimony compounds, dimethylantimony ( $\text{Me}_2\text{Sb}^{3+}$ ) and trimethylantimony ( $\text{Me}_3\text{Sb}^{2+}$ ) species were also found in cultures of the fungus *Scopulariopsis brevicaulis* grown in culture media containing Sb (III), but not Sb (V) compounds under aerobic conditions.<sup>9</sup> In these experiments, hydride generation gas chromatography-atomic absorption spectrometry (HG-GC-AAS) was used for antimony determinations and gas chromatography-inductively coupled plasma mass spectrometry (HG-GC-ICP-MS) system was used to provide



complementary information on the volatile organometallic species. Later, the presence of trimethylantimony (TMA) only in headspace gases over anaerobic soil enrichment cultures spiked with potassium antimony tartrate was also reported.<sup>10</sup> Their results suggested that the capability to generate TMA was widely distributed in the terrestrial environment and was attributable to different metabolic types of micro-organisms. At the same time biomethylation of inorganic antimony compounds by an aerobic fungus *Scopulariopsis brevicaulis* was confirmed by the same research group.<sup>11</sup> Both these studies employed GC-AAS techniques for analysis and GC-MS for identification of the volatile antimony compound. No systematic survey work, however, have yet been carried out to study the occurrence of methylated antimony compounds in the environment.

In spite of all these work, a controversial opinion was raised in a recent work with the aerobes, *Scopulariopsis brevicaulis* or other *Bacillus* sp. in culture with water-insoluble antimony compounds, or soluble antimony derivatives, that no evidence could be found to support the production, in culture, of methylated antimony compounds.<sup>12</sup> Only anaerobic cultures from a polluted pond generated trimethyl-antimony from potassium antimony tartrate.

### **Bismuth**

Literature on the occurrence of organometallic compounds of bismuth in the environment is sparse. Among many other volatile species such as those of Si, V, As, Br, Sn, Sb, Te, I, Hg, Pb, volatile Bi compounds were released from domestic waste deposits.<sup>6</sup> Volatile Bi compounds were also reported in gases released in landfill and sewage digester.<sup>8</sup> Among several volatile metal compounds, Me<sub>3</sub>Bi is the major compound in the gases of sewage sludge digester. The volatile Bi compound was identified as Me<sub>3</sub>Bi by using element-specific detection (ICP-MS) and

matching retention time with a  $\text{Me}_3\text{Bi}$  standard. The highest concentration of  $25 \mu\text{g}/\text{m}^3$  was observed in a survey of seven sewage treatment plants.<sup>13</sup> The authors also suggested that primary evidence was obtained for the occurrence of methylated bismuth compounds in freshwater sediments. However, occurrence of methylbismuth compounds in the environment has not yet been comprehensively studied.

### **Cadmium**

There has been little research of the formation of organocadmium compounds in the environment due to the well-known unstable properties of mono- and dialkylcadmium species in air and water. The first laboratory experiment by Huey and Brinckman<sup>14</sup> in (1975) suggested the methylation of cadmium based on the indirect evidence of transmethylation of Hg (II) by a volatile cadmium species generated by a bacterium *Pseudomonas sp.* in the presence of a vitamin  $\text{B}_{12}$  complex. There was no direct identification of the methylcadmium species. Later in another experiment with  $\text{CH}_3\text{CoB}_{12}$  and a saturated solution of cadmium (II) chloride, it was reported to produce low concentrations ( $2 \times 10^{-9}$  g Cd) of a volatile cadmium species at pH 9.6 in water at  $37^\circ\text{C}$ .<sup>15</sup> Nothing has been done since these experiments until recently the evolution of several volatile metals from sewage gases including Cd was reported.<sup>16</sup> However, all these are circumstantial evidences which do not discern the molecular form of Cd being transported.

Recently a breakthrough experiment reported the determination and verification of the monomethylcadmium species in sea water by a differential pulse anodic stripping voltammetric technique.<sup>17</sup> In eight samples of Arctic ice-floes in South Atlantic, the concentration range of  $\text{MeCd}^+$  was 520-1300 pg Cd/L (detection limit 470 pg Cd/L). A positive correlation with the bioactivity parameter, adenosine triphosphate (ATP) measurement, of the sampling sites was found with the  $\text{MeCd}^+$  concentrations. Other bioactivity indicator such as algal growth as in the

case of pack-ice border also supported this relationship. The authors concluded the production of  $\text{MeCd}^+$  was biological. The  $\text{MeCd}^+$  concentrations were low, but significant enough as evidence for the methylation of Cd.

## Germanium

Methylated Ge compounds Mono- and dimethyl-germanium species was first reported in sea water such as Sargasso Sea, Bering Sea, in concentrations of 10-24.5 ng Ge/L, whereas the trimethylgermanium species was only found in rainwater samples in Florida<sup>18</sup> and in other natural waters with concentrations in the ng Ge/l level.<sup>19</sup> However, these investigators considered the values reported for all these samples to be artifacts resulting from contamination in the laboratory or from biomethylation of naturally-occurring Ge in rain water by fungi growing in the sample storage bottles. Oceanic vertical profiles of monomethylgermanium (MMGe) and dimethylgermanium (DMGe) were consistent with concentrations of  $326 \pm 14$  pmol/L and  $97 \pm 9$  pmol/L respectively. There is no evidence of biological activity of methylgermanium in seawater and no apparent inter-ocean differences. The sources of methylgermanium are not yet known, but it is only known that they are stable.<sup>20</sup> In a recent investigation of the behaviour of germanium species in three sampling stations in the Pacific Ocean,<sup>21</sup> the MMGe species was found uniformly distributed throughout the water column at a concentration of approximately 16 ng/L, indicating that MMGe was not involved in the biogeochemical cycling of inorganic germanium. In an attempt to understand the mechanism of methylation, chemical methylation experiments of germanium (II) in model aqueous solutions have been carried out.<sup>22</sup> It was concluded that monomethylgermanium was the only product in methylation by methyl iodide and methylcobalamin. The first mechanism was an oxidative

addition and the latter was through a free-radical transfer. There is no report on the environmental aspects of methylgermanium compounds since these studies.

## **Manganese**

Methylcyclopentadienylmanganese tricarbonyl (MMT) has been used in gasoline as a partial substitute for alkyllead antiknocking agents in unleaded gasoline to improve the octane rating. It is also used extensively as a boiler or gas turbine fuel additive to reduce deposits, smoke, particulates and sulphur trioxide formation. The concentrations in gasoline range from 0 to 17.2 mg Mn/l for individual samples depending on the grade of gasoline, season and geographical areas.<sup>23</sup> Based on MMT sales in Canada, total annual manganese used in Canadian gasoline was in the level of 306 thousand kg in 1994.<sup>24</sup>

MMT itself is highly toxic. The combustion of MMT lead to the formation of manganese oxides, especially manganese tetroxide  $Mn_3O_4$ .<sup>25,26</sup> The vast majority of cases of manganese poisoning have occurred as a result of exposure to airborne manganese. The major area of environment concern for manganese is the role of aerosol-size manganese oxide particles in the atmosphere. It is evident that Mn from MMT source is an important constituent of the urban air pollution which is related to traffic density on a local scale.<sup>27</sup> In an assessment of the at-work and off-work manganese exposure of two potentially at-risk groups in Montreal, taxi drivers and garage mechanics, the mean manganese concentrations in the workplace of taxi drivers and mechanics were  $0.024 \mu\text{g Mn/m}^3$  and  $0.250 \mu\text{g Mn/m}^3$  respectively, which were significantly higher than the off-work levels of  $0.007 \mu\text{g Mn/m}^3$  and  $0.011 \mu\text{g Mn/m}^3$ , respectively for the two groups.<sup>28</sup> The emission of manganese to the atmosphere may cause chronic manganese poisoning leading to Parkinsonism-like effects.<sup>29,30</sup>

MMT has a solubility of about  $29 \pm 3$  mg/L and a relatively low vapour pressure ( $5.0 \times 10^{-2}$  mm Hg at  $20^\circ\text{C}$ ).<sup>31</sup> It photolyzes rapidly in the presence of light. The disappearance of MMT followed the first order kinetic with a half life of 0.93 min. MMT can be persistent in natural aquatic environment if light is absent. Its half-life in the aquifer and sediment system was found to range from 0.2 to 1.5 years at  $25^\circ\text{C}$ .<sup>31</sup> In a recent study of the occurrence of MMT in environmental samples, it was found that air samples collected at underground car parks contained significant amounts of MMT. It was also found frequently in storm runoff waters collected at highways immediately after rain, and also in runoff samples stored in amber-glass bottles in refrigerator over periods of 2-3 weeks.<sup>32</sup> Table 1 summarizes some data on occurrence of MMT in environmental samples. Its occurrence in highway runoff rain samples is not understood as MMT photodegrades almost instantly under light. Its occurrence and persistence in groundwater warrants future investigation.

### Phosphorus

Methylphosphorus compounds have been isolated from natural waters,<sup>33,34</sup> and identified by gas chromatography as dimethylmethylphosphonate. Although biomethylation of phosphorus was theoretically feasible by comparison of its chemistry with the mechanisms of As and Sb,<sup>1</sup> there is to date no evidence for phosphorus (III) as a biochemical intermediate to support its biological methylation.<sup>2</sup> Release of phosphine from the anaerobic biosphere and by bio-corrosion of phosphide-rich iron has been reported.<sup>35,36</sup> Although phosphine is not an organometalloidal phosphorus species, its release by microorganisms from compost processing, sewage sludge and river sediments can have significant consequences in providing pathways for methylation. Other organophosphorus compound that has been isolated in marine species includes 2-aminoethylphosphonic acid (ciliatine),  $\text{H}_2\text{NCH}_2\text{CH}_2\text{PO}(\text{OH})_2$ .<sup>37</sup> At present, there is no evidence of

methylation of phosphorus in the environment. The relevant phosphorus chemistry in this aspect and the use of organophosphorus derivatives in medicine have been reviewed in the work by Thayer<sup>1</sup> and Craig.<sup>2</sup>

## Selenium

The methylation of selenium by organisms has been known since the beginning of the century. It is known that several genera of fungi produce dimethyl selenide from inorganic selenium compounds.<sup>38,39</sup> Experiments with higher animals such as rats fed with selenite or selenate salts showed the presence of volatile dimethylselenide and dimethyl- diselenide in their exhaled gases,<sup>40,41</sup> and trimethyl-selenonium ion was present in the urine.<sup>42</sup>

Environmental methylation of inorganic selenides was first reported by Chau & Wong<sup>43</sup> in 1976 that dimethyl selenides, dimethyl diselenide and an unknown organoselenium compound were produced in lake sediments incubated with inorganic selenite and selenate and organic selenium compounds. The unknown volatile selenium species was also produced in soils and sewage sludge, and was identified as dimethyl selenone ((CH<sub>3</sub>)<sub>2</sub>SeO<sub>2</sub>).<sup>44</sup> Recently the identification was refuted by other researcher who proposed dimethyl selenyl sulfide (CH<sub>3</sub>SeSCH<sub>3</sub>) to be the correct identity of the unknown compound, using mass spectral, chromatographic, and boiling-point data.<sup>45,46</sup>

Organoselenium compounds have also been found in natural waters and sediment.<sup>47,48</sup> Five different volatile forms of selenium have been detected in laboratory experiments, namely, hydrogen selenide (H<sub>2</sub>Se), methaneselenol (CH<sub>3</sub>SeH), dimethyl selenide (CH<sub>3</sub>SeCH<sub>3</sub>), dimethyl

selenyl sulfide ( $\text{CH}_3\text{SeSCH}_3$ ), and dimethyl diselenide ( $\text{CH}_3\text{SeSeCH}_3$ ), the last three compounds have been determined in the environment samples. (Table 2)

Apart from the volatile compounds, selenium in tissues of marine animals was found to be associated with the proteins as selenocysteine.<sup>55,56</sup>

### **Thallium**

Not much work has been done since the early incubation experiments carried out by Huber and Kirchmann<sup>57</sup> in 1978 with Tl(I) compound (TlOAc) under anaerobic conditions in the dark with anaerobic bacteria from sediment of a natural lake. Dimethylthallium ions ( $(\text{CH}_3)_2\text{Tl}^+$ ) was the only product. The biomethylation of thallium was suggested to be a detoxification mechanism for thallium because the dimethylthallium ion is less toxic than thallos ion.<sup>58</sup> The reaction mechanism proposed was an oxidative methylation. There is no report to date on the occurrence of methylthallium species in the natural environment.

In conclusion, the organometallic compounds of the reviewed elements have been shown to occur in the environment but most of them are not systematically investigated. It is anticipated that more effort will be directed to the study of their environmental aspects in the years to come.

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**Table 1. Concentration of MMT in Environmental Samples in Canada (1997-98)**

<b>Sample</b>	<b>MMT</b>	<b>CMT</b>
<b>Underground Car Park (6 samples)</b>	<b>2.0-23.0</b>	<b>d-7.4</b>
<b>Air Samples* (3 samples)</b>	<b>0.33-0.50</b>	<b>d</b>
<b>Soil Samples* (3 samples)</b>	<b>0.26 - 0.44</b>	<b>d</b>
<b>* samples taken at locations near Ethyl Corp. Corunna, Ontario. d - detected but not quantified; concentrations, air in pg Mn/L; soil in pg Mn/g</b>		
<b>Highway Runoff (6 samples)</b>	<b>1.0-18.3 (<math>\pm 0.2</math>)</b>	<b>nd</b>
<b>Sewage Samples#</b>		
<b>Raw</b>	<b>50.0 <math>\pm</math> 5.1</b>	<b>nd</b>
<b>Final</b>	<b>12.0 <math>\pm</math> 1.3</b>	
<b>Lake water Samples (2 samples, L. Ontario)</b>	<b>nd</b>	<b>nd</b>

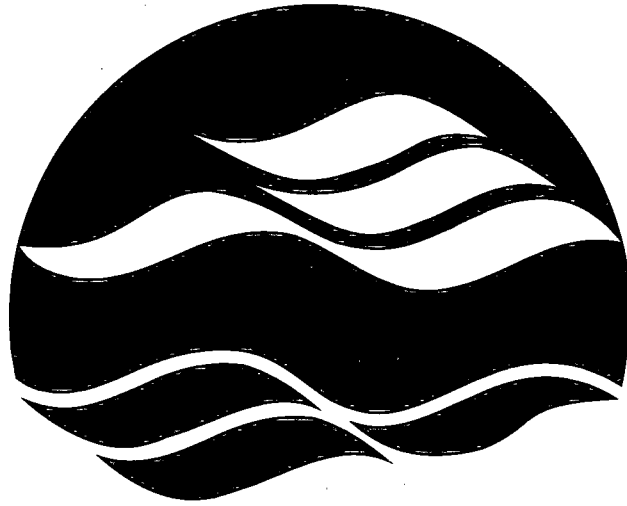
**Highway runoff collected at Skyway, Burlington Bay; n= 3; # Hamilton Sewage Treatment Plant, concentrations in pg Mn/L; nd - not detected;  
MMT - methylcyclopentadienylmanganese tricarbonyl  
CMT - cyclopentadienylmanganese tricarbonyl**

**Table 2. Volatile Organoselenium Compounds in the Environment**

<b>CH<sub>3</sub>SeCH<sub>3</sub></b>	Lake water-sediment	Chau et al. (1976) <sup>43</sup>
	Soil, sewage sludge, headspace	Reamer & Zoller (1980) <sup>44</sup>
	Soil	Karlson & Frankenberger, Jr. (1989) <sup>49,50</sup>
	Atmosphere	Jiang et al. (1983;1989) <sup>47,48</sup>
	Sea water	Tanzer & Heumann (1990;1992) <sup>51,52</sup>
	Human breath	Feldmann et al.(1996) <sup>53</sup>
<b>CH<sub>3</sub>SeSeCH<sub>3</sub></b>	Lake water-sediment	Chau et al. 1976 <sup>43</sup>
	Soil, sewage sludge, headspace	Reamer and Zoller (1980) <sup>44</sup>
	Soil	Karlson & Frankenberger, Jr. (1989) <sup>49,50</sup>
	Atmosphere	Jiang et al. (1983;1989) <sup>47,48</sup>
	Groundwater	Cooke & Bruland (1987) <sup>54</sup>
	<b>CH<sub>3</sub>SeSCH<sub>3</sub>*</b>	
	Soil, sewage sludge headspace	Reamer and Zoller (1980) <sup>44</sup>
	Atmospheric	Jiang et al. (1983;1989) <sup>47,48</sup>
	Lake water-sediment	Chau et al. (1976) <sup>43</sup>

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\*It was proposed as dimethylselenone (CH<sub>3</sub>)<sub>2</sub>SeO<sub>2</sub> by all these investigators, it is now identified as dimethyl selenyl sulfide (CH<sub>3</sub>SeSCH<sub>3</sub>)<sup>45</sup>



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