Arsenic Species in the Environment. W. R. Cullen, Environmental Chemistry Group, Chemistry Department, University of British Columbia, Vancouver, B.C. Canada, V6T 1Z1, wrc@chem.ubc.ca.

The principal soluble or volatile arsenic species found in the terrestrial and fresh water environment are listed in Table 1. Those found in the marine environment are listed in Table 2. It is important to note that the organic derivatives can exist in two oxidization states equivalent to the inorganic species arsenate and arsenite. The history of their discovery parallels the development of analytical methodology. The first compound to be properly characterized was trimethylarsine, a gas produced by microorganisms. Volatilization of the compound separated it from the matrix and made identification possible, even in 1933, by using classical techniques.

The next big breakthrough had to wait until 1973 when it was found that volatile arsines could be produced by treatment of environmental samples with borohydride. This is a derivatization method, and the products, which initially were separated by boiling point differences, were taken as indicating the number of organic groups attached to arsenic. Thus dimethylarsine was assumed to originate from dimethylarsinic acid in the sample, although it could equally well have come from dimethylarsinous acid. Modern refinements of this methodology employ gas chromatography for separation of arsines coupled to detectors such as atomic absorption (HG/AA). The enthusiastic, but often uncritical, application of this method revealed that mainly methylarsenic species were found in the terrestrial and fresh water environment, and in the urine of individuals exposed to arsenic via drinking water and food. The limitation of HG methodology is that it cannot detect species that are not reducible by borohydride.

The discovery of new species was slow and initially based on a careful “natural product” approach that involved the tedious isolation of specific arsenic species from large amounts of material. Once isolated the compounds were identified by conventional means. Samples were chosen from the marine environment because they had high natural concentrations of arsenic, 1-100 ppm. Arsenobetaine the main arsenical in marine fish was first discovered in this way followed by the arsenosugars. These ribose derivatives are the main arsenicals in marine algae.

The development of high performance liquid chromatography, HPLC, allowed the next big advance in arsenic speciation. Most of the known arsenicals could be separated by this means, and ICP/MS provided a detector of the necessary sensitivity for element specific detection. Application of this methodology HPLC/ICP/MS has now allowed the identification of arsenicals in most environmental compartments, as shown in the Figures. However, this methodology does not allow identification of species in the absence of known standards so we can expect to see more emphasis on HPLC/MS^n for speciation studies in the near future.

Methylation of arsenic proceeds via a stepwise oxidation/reduction sequence involving first oxidative addition of a methyl group from S-adenosylmethionine, SAM, to an arsenic(III) species to afford a methylarsenic(V) product. A two electron reduction follows, probably involving thiol groups, and results in a methylarsenic(III) species that is ready for the next oxidative addition. SAM probably delivers the adenosyl group to arsenic in the same way to afford the arsenosugars. The pathway to arsenobetaine is yet to be elucidated.

Arsines are produced by microbial action from sites such as landfills and hot springs. They are very acutely toxic if an As-H bond is present; however, Me_3As, Gosio Gas, seems to be less toxic in spite of its historical association with illness, and the more recent hypothesis that its production in the nursery environment is one of the causes of Sudden Infant Death Syndrome. It has been generally accepted that the methylation of arsenic is a detoxification step but this was based on the measured acute toxicities of the methylarsenic(V) species. Recent studies reveal that methylarsenic(III) species can be more toxic than arsenite, and in fact are genotoxic.

The accepted method for the analysis of arsenic species in water and food (EPA Method 1632) is based on hydride generation methodology and can be inadequate and misleading. Much more information is obtained by the application of HPLC/ICP/MS provided extracts can be obtained under mild conditions (Unfortunately many samples be do not meet this criterion, and the speciation of these samples remains a challenge). Arsenobetaine the main arsenical in marine fish is known to be non toxic to humans, it is excreted unchanged after consumption, and it has been assumed that this is the “organic arsenic” that is found in all fish and related food. However, the speciation in marine and freshwater biota can be quite different with arsenosugars and inorganic arsenic comprising most of the arsenic species in fresh water samples. Humans (and sheep) metabolize the arsenosugars, mainly to dimethylarsinic acid. This metabolite which is excreted in the urine could be a cause for concern because of the possibility of reduction to genotoxic arsenic(III) species (The acid itself has been studied in connection with bladder cancer).

Most living organisms take up arsenate inadvertently via the phosphate transport system and eliminate this unwanted species following reduction to arsenite. So what is the reason for the formation of the wide range of species seen in the Tables? We now report that scallops preferentially accumulate arsenic, but not other elements, in their gonads. There are also differences in the species present and their concentrations during the reproductive cycle. Thus female gonads have higher total arsenic concentrations than males, have much higher concentrations of one arsenosugar (the sulfate), but have the same concentration of arsenobetaine. Over the spawning cycle the total arsenic concentration in the female gonad is constant but the total content decreases, whereas the reverse is true for the male gonad. Why?

Table 1

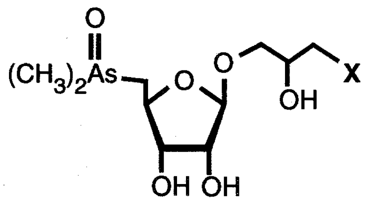
Arsenic in the Freshwater/ Terrestrial Environment

As (III)	**As (V)**
$As(OH)_3$,	H_3AsO_4
"$CH_3As(OH)_2$" "$(CH_3)_2AsOH$"	$CH_3AsO(OH)_2$ $(CH_3)_2AsO(OH)$ $(CH_3)_3AsO$ $(CH_3)_4As^+$
AsH_3 CH_3AsH_2,$(CH_3)_2AsH$ $(CH_3)_3As$	$(CH_3)_3As^+CH_2COO^-$ $(CH_3)_3As^+CH_2CH_2OH$ arsenosugars (Table 2)
$As(C_2H_5)_3$ $CH_3As(C_2H_5)_2$ $(CH_3)_2AsC_2H_5$	$C_6H_5AsO(OH)_2$

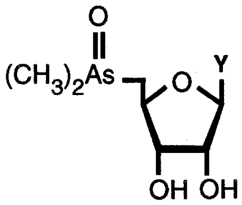
Table 2

Arsenic in the Marine Environment

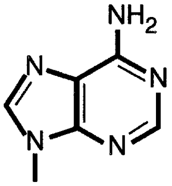
H_3AsO_4, $As(OH)_3$, $CH_3AsO(OH)_2$, $(CH_3)_2AsO(OH)$, $(CH_3)_3AsO$,
$(CH_3)_3As^+CH_2COO^-$, $(CH_3)_3As^+CH_2CH_2OH$, $(CH_3)_4As^+$.

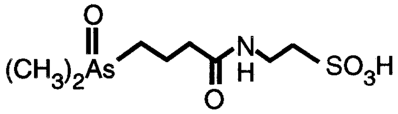


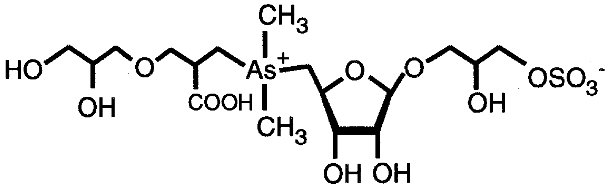
X = SO_3H,OH,OSO_3H
$OPO(OH)OCH_2CHRCH_2R$
$(R{=}OH,OOC(CH_2)_nCH_3)$



Y = OCH_3, $OCH_2(CHOH)_4CH_2OH$
$OCH_2CH(OH)COOH$,
$OC(O)NHCH_2COOH$







K.A. Francesconi and J.S. Edmonds
Oceanogr. Mar Biol. Annu. Rev
1993, **31,** 111