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PRACTITIONER COMMENT

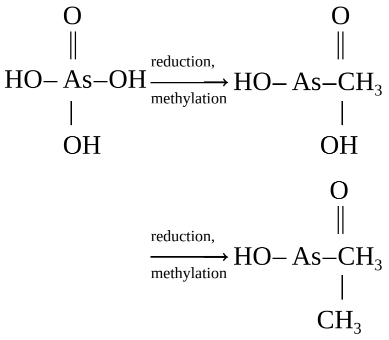
# Accuracy in Speciation

In recent years our understanding of the biogeochemical cycling of elements through the environment has been greatly enhanced by the development of increasingly sophisticated procedures for the identification of chemical species. However, a worrying problem has developed, arising from confusion in the literature about the exact nature of the species which have been demonstrated to be present in the environment. Such difficulties result from three main sources, the adoption of postulates as truth, the over-interpretaton of experimental data by investigators and the removal of cautionary statements by reviewers.

Most scientific advances are made by following a classical approach in which a postulate is made and then tested. Frequently, however, it is necessary in the testing stage to employ an investigative procedure that produces supporting evidence but that cannot, in itself, provide a definitive identification. Progress in all scientific disciplines is constrained by the state of knowledge at the time. Scientific progress is made by the development of ideas, procedures and instrumentation; a scientist must employ currently available tools or develop new ones to test a hypothesis. At any one time the available tools may provide only a partial answer; the limitations of a set of results must be accepted alongside the progress which has been made possible. The remaining uncertainty provides the basis for the next stage of the work.

Problems also arise from the reporting of a study. A mechanism may be suggested and without confirmation become accepted wisdom. Whilst the original researchers may clearly state the limitations of their work, once transferred into reviews and books such reservations are lost, leading to the adoption of suggested mechanisms as having been proven and statements that particular species have been demonstrated to be present. This note sets out to raise an awareness of how easy it is for a result to be over-interpreted and for one investigator's postulate to become a subsequent reviewer's fact. Two examples come to mind from the environmental field which illustrate these problems.

It is now well established that a significant proportion of the dissolved arsenic which is present in the marine environment is methylated. The study of arsenic species can be traced back to investigations into the nature of Gossio gas and the work by Challenger on the generation of volatile arsenicals by mould. In 1945 Challenger[1] summarized the results of his work in a suggested scheme for the sequential methylation of arsenic (Scheme 1).



**Scheme 1**

Despite subsequent advances in our understanding of the biochemical transformations of arsenic, this scheme is still being presented in review articles as if it were currently believed to represent accurately the formation of the methylated arsenicals which are present in the environment. The important discovery of dissolved methylated arsenic species in aquatic systems was initially made by Braman and Foreback[2] in 1978 using a 'hydride generation' technique which converted some of the marine methylated arsenic species to $CH_3$ $AsH_2$ and $(CH_3)_2AsH$. As the exact nature of the dissolved methylated arsenic species in the sea was not then established, their work is most accurately described as having discovered the presence of 'dimethylarsenic' (DMA). The step which caused confusion in many subsequent reports and reviews was that in their initial paper Braman and Foreback reported that they had found the oxyanion dimethylarsinate (DMAA). This was not in fact the case as they had employed an analytical procedure which is incapable of distinguishing

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the dimethylarsinate ion from other molecules containing the structural moiety dimethylarsenic. Throughout modern literature dimethylarsinate is still being cited as a major dissolved methylated marine arsenic species in seawater without questions being asked as to whether DMAA has in fact ever been shown to be present.

Dimethyl sulphoniopropionate (DMSP) is an example of a species which is at risk of potential misidentification. DMSP is an algal precursor of dimethyl sulphide, and as such is an important natural source of material which can contribute to the acidity of precipitation and which has been proposed as a factor influencing climate change. The history of the measurement of DMSP goes back to its initial isolation from the alga *Pollysiphonia fastigiata* in 1948.[3] Since then a logical non-sequitur seems to have become adopted. The measurement of DMSP is based on the dimethyl sulphide released on base hydrolysis. DMSP undergoes base hydrolysis to dimethyl sulphide (DMS), base hydrolysis of seawater gives dimethyl sulphide, therefore *dissolved* DMSP is present in the sea.

Measurements based on the release of DMS have provided an invaluable insight into the origins of atmospheric DMS and at present the only procedures having sufficient sensitivity to measure dissolved DMS-precursors such as DMSP are those which are based on the base hydrolysis. With the only options being to use current instrumentation to measure DMS-precursors, or to stop work in the area until improved techniques are developed which can measure true DMSP, it is not surprising that the reliable indirect measurement techniques are still employed. The problem is not that the base hydrolysis procedure is not specific to DMSP, but that it is now frequently implied in the literature that DMSP has been measured and that DMSP is the only dissolved DMS-precursor which is present in the world's oceans. Such indirect measurements must therefore be distinguished in nomenclature from true DMSP determinations; there are other potential DMS-precursors to be found in marine algae which might be expected to respond in this hydrolysis procedure. DMSP has been definitively identified as being present in surprisingly few algae and the definitive characterization of the dissolved DMS-precursors which are present in the sea has yet to be carried out.

The problems identified in these two examples do not arise from intrinsic problems with the techniques which are employed, just from the words which are used to express the results. In most cases the best available means of measurement is not definitive. It is important, therefore, when presenting the results of such studies that greater clarity is employed and that unjustified claims are not made. This is particularly true for the authors of review articles, who should decide carefully whether the information contained in an article to be cited is still considered to be accurate and whether the reported chemical species have actually ever been demonstrated to be present.

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## REFERENCES

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2. R. S. Braman and C. C. Foreback, *Science* **182**, 1247 (1973).
3. F. Challenger and M. I. Simpson, *J. Chem. Soc.* **43**, 1591 (1948).