

REPORT DOCUMENTATION PAGE

Form Approved
OMB No. 0704-0188

Public reporting burden for this collection of information is estimated to average 1 hour per response, including the time for reviewing instructions, searching existing data sources, gathering and maintaining the data needed, and completing and reviewing the collection of information. Send comments regarding this burden estimate or any other aspect of this collection of information, including suggestions for reducing this burden, to Washington Headquarters Services, Directorate for Information Operations and Reports, 1215 Jefferson Davis Highway, Suite 1204, Arlington, VA 22202-4302, and to the Office of Management and Budget, Paperwork Reduction Project (0704-0188), Washington, DC 20503.

1. AGENCY USE ONLY (Leave blank)	2. REPORT DATE	3. REPORT TYPE AND DATES COVERED	
		10/1/95 - 9/30/96	
4. TITLE AND SUBTITLE		5. FUNDING NUMBERS	
The Chemistry and Transformations of Mercury and Arsenic in Anaerobic Sediments		Award No.: N00014-96-1-0036	
6. AUTHOR(S)		8. PERFORMING ORGANIZATION REPORT NUMBER	
Francois M. M. Morel		001-96	
7. PERFORMING ORGANIZATION NAME(S) AND ADDRESS(ES)		10. SPONSORING/MONITORING AGENCY REPORT NUMBER	
Department of Geosciences Princeton University Guyot Hall Princeton, New Jersey 08544			
9. SPONSORING/MONITORING AGENCY NAME(S) AND ADDRESS(ES)			
Office of Naval Research, ONR 252: Diane Gales Ballston Centre Tower One 800 North Quincy Street Arlington, VA 22217-5660			
11. SUPPLEMENTARY NOTES			
12a. DISTRIBUTION / AVAILABILITY STATEMENT		12b. DISTRIBUTION CODE	
Approved for public release distribution unlimited			
13. ABSTRACT (Maximum 200 words)			
<p>The objectives of this project are to elucidate the chemical and biological mechanisms that control the precipitation and dissolution of arsenic and mercury in anaerobic coastal sediments and to quantify the consequences of these processes in determining the potential release of these toxic elements to the water column and their accumulation in marine organisms.</p> <p>Based on the preliminary research described in the proposal, rapid progress has been made on both the arsenic and the mercury aspects of this project. In particular, the conditions for the microbial reduction of arsenate to arsenite and the precipitation of arsenite as the arsenic trisulfide solid have been documented. These two processes (reduction of arsenate and precipitation of arsenite) largely determine the environmental mobility of arsenic in anaerobic sediments. The rate of dissolution of mercuric sulfide under various conditions and the rates of oxidation and reduction of dissolved mercury are also being quantified. In addition, according to preliminary data, it appears that, as hypothesized in the proposal, the presence of polysulfides can enhance many fold the rate of microbial methylation of mercury in anaerobic sediments.</p>			
14. SUBJECT TERMS		15. NUMBER OF PAGES	
Arsenic, Mercury, Sediments, Mobility, Bioaccumulation		4	
		16. PRICE CODE	
17. SECURITY CLASSIFICATION OF REPORT	18. SECURITY CLASSIFICATION OF THIS PAGE	19. SECURITY CLASSIFICATION OF ABSTRACT	20. LIMITATION OF ABSTRACT
unclassified	unclassified	unclassified	unlimited

19960827 080

GENERAL INSTRUCTIONS FOR COMPLETING SF 298

The Report Documentation Page (RDP) is used in announcing and cataloging reports. It is important that this information be consistent with the rest of the report, particularly the cover and title page. Instructions for filling in each block of the form follow. It is important to *stay within the lines* to meet optical scanning requirements.

Block 1. Agency Use Only (Leave blank).

Block 2. Report Date. Full publication date including day, month, and year, if available (e.g. 1 Jan 88). Must cite at least the year.

Block 3. Type of Report and Dates Covered. State whether report is interim, final, etc. If applicable, enter inclusive report dates (e.g. 10 Jun 87 - 30 Jun 88).

Block 4. Title and Subtitle. A title is taken from the part of the report that provides the most meaningful and complete information. When a report is prepared in more than one volume, repeat the primary title, add volume number, and include subtitle for the specific volume. On classified documents enter the title classification in parentheses.

Block 5. Funding Numbers. To include contract and grant numbers; may include program element number(s), project number(s), task number(s), and work unit number(s). Use the following labels:

C - Contract	PR - Project
G - Grant	TA - Task
PE - Program Element	WU - Work Unit Accession No.

Block 6. Author(s). Name(s) of person(s) responsible for writing the report, performing the research, or credited with the content of the report. If editor or compiler, this should follow the name(s).

Block 7. Performing Organization Name(s) and Address(es). Self-explanatory.

Block 8. Performing Organization Report Number. Enter the unique alphanumeric report number(s) assigned by the organization performing the report.

Block 9. Sponsoring/Monitoring Agency Name(s) and Address(es). Self-explanatory.

Block 10. Sponsoring/Monitoring Agency Report Number. (If known)

Block 11. Supplementary Notes. Enter information not included elsewhere such as: Prepared in cooperation with...; Trans. of...; To be published in.... When a report is revised, include a statement whether the new report supersedes or supplements the older report.

Block 12a. Distribution/Availability Statement. Denotes public availability or limitations. Cite any availability to the public. Enter additional limitations or special markings in all capitals (e.g. NOFORN, REL, ITAR).

DOD - See DoDD 5230.24, "Distribution Statements on Technical Documents."
DOE - See authorities.
NASA - See Handbook NHB 2200.2.
NTIS - Leave blank.

Block 12b. Distribution Code:

DOD - Leave blank.
DOE - Enter DOE distribution categories from the Standard Distribution for Unclassified Scientific and Technical Reports.
NASA - Leave blank.
NTIS - Leave blank.

Block 13. Abstract. Include a brief (Maximum 200 words) factual summary of the most significant information contained in the report.

Block 14. Subject Terms. Keywords or phrases identifying major subjects in the report.

Block 15. Number of Pages. Enter the total number of pages.

Block 16. Price Code. Enter appropriate price code (NTIS only).

Blocks 17. - 19. Security Classifications. Self-explanatory. Enter U.S. Security Classification in accordance with U.S. Security Regulations (i.e., UNCLASSIFIED). If form contains classified information, stamp classification on the top and bottom of the page.

Block 20. Limitation of Abstract. This block must be completed to assign a limitation to the abstract. Enter either UL (unlimited) or SAR (same as report). An entry in this block is necessary if the abstract is to be limited. If blank, the abstract is assumed to be unlimited.

The Chemistry and Transformations of Mercury and Arsenic in
Anaerobic Sediments

Principal Investigator: François M. M. Morel

Department of Geosciences, Princeton University

Princeton, New Jersey 08544

ONR Grant #: N00014-96-1-0036

First Year Report

The objectives of this project are to elucidate the chemical and biological mechanisms that control the precipitation and dissolution of arsenic and mercury in anaerobic coastal sediments and to quantify the consequences of these processes in determining the potential release of these toxic elements to the water column and their accumulation in marine organisms.

Building on the preliminary research described in the proposal to ONR, we have been able to make rapid progress on both the arsenic and the mercury aspects of this project. In particular we have documented the microbial reduction of arsenate to arsenite and studied the conditions for precipitation of arsenite as the arsenic trisulfide solid. These two processes (reduction of arsenate and precipitation of arsenite) largely determine the environmental mobility of arsenic in anaerobic sediments. We have also begun to quantify the rate of dissolution of mercuric sulfide under various conditions and the rates of oxidation and reduction of dissolved mercury. In addition, according to our preliminary data, it appears that, as hypothesized in the proposal, the presence of polysulfides can enhance many fold the rate of microbial methylation of mercury in anaerobic sediments. These achievements are described succinctly below.

Arsenic: Arsenic occurs in the environment principally in two forms, arsenate, As(V), which forms stable precipitates mainly with iron, and arsenite, As(III), which in contrast has been generally considered quite soluble and hence mobile. The chemical and biological transformations between As(V) and As(III) in oxic and anoxic environments are thus of particular interest. Following our previous work with MIT-13 (now *Geospirillum arsenophilus*), we have

now isolated a second strain, OREX-4 (now *Desulfitobacterium orex*) that grows by dissimilatory reduction of As(V), and characterized both organisms in terms of their metabolic capabilities. One organism can reduce N(V) as well as As(V), while the other can grow on N(VI) as well as As(V). While MIT-13 is gram-negative, OREX-4 is gram-positive and, according to 16S ribosomal RNA sequencing, the two organisms are phylogenetically quite distant. These results, which are being written-up for publication, demonstrate that As(V) reduction is likely widespread among bacterial phyla and common in contaminated anoxic environs.

In addition to reducing As(V), OREX-4 precipitates As(III) as As_2S_3 in S-containing medium. This precipitation occurs, at least in part, intracellularly and under conditions where no chemical precipitation is observed. This finding puts into question the general assumption that reduction of As(V) to As(III) makes As more mobile in the environment. On the contrary, As_2S_3 precipitation may provide a permanent sink for As in anaerobic sediments. A manuscript on this topic is being submitted to Applied and Environmental Microbiology.

Mercury: The major form of mercury in anoxic sediments is mercuric sulfide (HgS), as cinnabar (red) or metacinnabar (black). These minerals are extremely insoluble and a major question relating to the mobility of Hg in anoxic environments is that of the mechanisms and rate of dissolution of HgS. We have begun a systematic study of the kinetics of HgS dissolution examining the effects of such factors as pH, oxygen concentration, light and the presence of organic acids. At present, it is clear that, as we hypothesized, visible light greatly enhances the kinetics of dissolution as does oxygen. The dissolution process is complicated by the possible reduction of Hg(II) (by sulfur or organic species) and rapid re-oxidation of Hg(0) (ultimately by O_2). The rapid oxidation of Hg(0) in the presence of oxygen seems to have been ignored in the environmental literature and, in many aquatic systems, this process should effectively decrease the net rate of Hg(0) volatilization into the atmosphere. We are in the process of quantifying the rates of each of these chemical reactions under conditions typical of natural sediments.

In addition to the difficulties posed by facile redox reactions, the chemistry of mercury in sediments is complicated by the multiple forms of inorganic sulfur. In particular we have

hypothesized that Hg(II) complexes with polysulfides, S_n^{2-} , may facilitate the bacterial uptake and hence the methylation of mercury. Indeed we have found that addition of 0.1mM polysulfide increases the solubility of HgS about 10 fold at pH's 8-10. Further, in preliminary experiments, the same addition of polysulfides to cultures of methylating bacteria grown under fermentating conditions in the presence of HgS increases many fold the rate of Hg methylation. If these results are confirmed, they will constitute a breakthrough in our understanding of the mechanisms of Hg methylation in anaerobic sediments and of the factors that control it.