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Division of Science and Research
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RESEARCH PROJECT SUMMARY

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Analysis of Mercury Species in New Jersey Ground water Using Inductively Coupled Plasma - Mass Spectrometry and Gas Chromatography

Research Project Summary Prepared By:

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ABSTRACT

Water samples from 78 private potable wells in southern NJ were collected for mercury analysis in 1991-1992. The wells are located in Atlantic, Burlington, Camden, Cape May and Ocean Counties. Total mercury concentrations varied from 1 ng/L to over 36 µg/L. The dominant form in which mercury occurred in the wells sampled was inorganic, although monomethylmercury was present in some wells comprising up to 8% of the total mercury in one ground-water sample. Mercury analyses performed using the EPA Method 245.1 should be interpreted with caution. While this method is generally suited for analyzing waters having elevated mercury concentrations (total mercury levels above 2000 ng/L or 2 µg/L), it is less sensitive and even inadequate for characterizing background mercury levels.

INTRODUCTION

In the late 1980's, private drinking water wells in Atlantic County, NJ were found to contain levels of mercury above the 2 micrograms per liter (µg/L or parts per billion) maximum contaminant level (MCL) set by US Environmental Protection Agency (USEPA). As a result of these findings, the Atlantic County Department of Health (ACDOH) instituted an aggressive county-wide sampling program to determine the magnitude and extent of this contamination. Results of their sampling showed that mercury contamination is widely distributed

throughout Atlantic County. Mercury levels as high as 40 µg/L have been observed by ACDOH since the contamination was first discovered. The levels found by local health officials in this county are the highest reported in the state. In fact, there are no reports in the available literature showing similar levels of mercury in ground water.

NJ Department of Environmental Protection and Energy (NJDEPE) responded to the Atlantic County findings by launching an intensive sampling campaign in cooperation with local health officials. To date, water samples collected from NJDEPE and county health departments from more than 250 potable domestic wells completed in the upper Kirkwood-Cohansey aquifer system in the NJ Coastal

Plain have been found to exceed the 2 µg/L MCL for mercury. There are no known point source(s) of mercury to account for the extensive contamination of wells.

In addition, the NJDEPE began investigating potential sources of mercury to ground water, the mechanism of travel of mercury in ground water, the most effective treatment system for removal of mercury, and the evaluation of the species of mercury present in ground water. The study described here focuses on the evaluation of analytical methodologies for the detection, quantification and speciation of mercury water from contaminated as well as "pristine" wells in the Kirkwood-Cohansey aquifer system. Most laboratories that analyze for mercury in water do not differentiate among species. The species or form of mercury is important to identify because different mercury species behave differently in the environment as well as in the human body. The predominant form of the mercury could have a substantial impact on recommendations regarding various water uses. Preliminary results of the research indicate that background mercury levels in this aquifer are within levels reported in the literature (less than 10 ng/L) (Jonasson & Boyle, 1972; USEPA, 1980; Bloom, 1989; and Dooley, 1992), while contaminated wells may have total mercury levels up to 36 µg/L. Trace amounts of monomethylmercury were detected in water samples taken, and potentially significant concentrations of volatile (elemental) mercury were present in some of the contaminated wells.

OBJECTIVES

The general objectives of this analytical research project were:

- 1) to develop and apply a reliable analytical technique using inductively coupled plasma mass spectrometry (ICP-MS) to determine the mercury concentrations and speciation in southern NJ ground water;
- 2) to compare this ICP-MS technique to other methods that are currently used by certified laboratories for the analysis of total mercury, specifically EPA Method 245.1; and
- 3) to develop a better understanding of the distribution of mercury among different organic and inorganic forms in ground water.

PROJECT DESIGN/METHODS

Water samples from 78 wells in southern NJ were collected in October 1991 and March 1992. Sample preservation based on the analytical technique to be used was conducted in the field. Purging of water samples with nitrogen and analysis for volatile mercury was also performed in the field. Of the water samples collected for this study, 24 were known to have been contaminated with mercury from prior analysis. The remaining 54 wells were selected to represent uncontaminated or "pristine" ground water; they were located in undeveloped, forested areas with no known potential sources of mercury within two miles.

Water samples were stored at 4°C until ready for analysis. Samples were analyzed within four weeks of delivery to the lab.

For a detailed description of the five analytical methodologies employed, the reader is advised to read the full final report. The techniques performed on water samples were: 1) isotope dilution ICP-MS for reactive mercury and for total mercury; 2) EPA Method 245.1 (cold vapor atomic absorption) for total mercury; 3) a modified cold vapor atomic absorption technique for reactive mercury; 4) laboratory data control (LDC) atomic absorption for volatile mercury; and 5) gas chromatography with electron capture detector for methyl mercury.

RESULTS

As a result of this research project, mercury contamination in wells in southern NJ was confirmed. That is, it was determined that the elevated levels being found by the State and by local health agencies were not due to field or laboratory contamination. Mercury was present at elevated levels.

Ambient, natural total mercury concentrations in southern NJ ground water fell within the range of background surface water levels reported in the literature, <1-10 ng/L. Background mercury concentrations in this study are in the range <1-42 ng/L. Kraffenhof & Babiarz (1992) report ground water concentrations for mercury in Wisconsin of 2-4 ng/L, and Lindqvist *et al.* (1991) reports levels in Swedish ground water of 11.9 ng/L. These are the only known reported values in the literature. Total mercury levels in contaminated areas in southern NJ ranged from approximately 25 ng/L to 36400 ng/L. For the purposes of this report, "contaminated" wells are those whose mercury levels equalled or exceeded

the maximum contaminant level (MCL), or drinking water standard, of 2 µg/L (or 2000 ng/L). Data ranges are reported in Table 1.

In order to evaluate the relationships of the analytical methods used, statistical correlations were performed on the data sets. Linear relationships between analytical methods for total mercury and reactive mercury are strong in ground waters exceeding the MCL (2000 ng/L). Linearity between methods' results was lost in water samples whose total mercury was below the MCL of 2000 ng/L, with one exception. The ICP-MS method continued to show a linear relationship between total and reactive mercury even at these lower concentrations.

The EPA method was adequate for identifying contamination of ground water above or near the MCL of 2000 ng/L but was inadequate for measurement of mercury levels below 2000 ng/L. The EPA method tended to overestimate mercury concentrations in water samples especially in samples containing higher levels of mercury (i.e., above 2000 ng/L). This is due probably to contaminants in reagents and to interferences with the instrumentation. Background mercury concentrations of 1-10 ng/L could not be measured using the EPA method. The modified cold vapor technique seemed more suitable for background analyses of reactive mercury in water samples containing greater than 10 ng/L of mercury. The isotope dilution ICP-MS technique is specific for mercury, therefore interferences such as those common in the cold vapor technique are minimized.

Most of the mercury present in water samples was in the reactive, or inorganic, form. There was no significant difference between reactive mercury and total mercury for either the ICP-MS or the EPA method when levels were ≥ 2000 ng/L, although there was a significant difference between the EPA Method 245.1 for total mercury and the modified cold vapor method for reactive mercury at levels < 2000 ng/L. Median values for wells containing total mercury above the MCL of 2000 were 4600 and 6750 ng/L using the ICP-MS method and the EPA cold vapor method, respectively. For wells containing total mercury below the MCL of 2000 ng/L, they were 5.0 and 55 ng/L, respectively.

Volatile mercury levels in waters containing total mercury above 2000 ng/L accounted for up to 10% of the total mercury in the sample.

The results of the methylmercury analyses suggest that methylmercury may be present up to 8% of the total but in most cases was under 3%.

RECOMMENDATIONS

Additional research on the species of mercury present in drinking water wells in southern NJ is needed in order to better assess human exposure to toxic forms of this metal. Of the 78 wells sampled in this study, only 16 had levels of mercury above the MCL. In assessing human exposure to volatile and organic forms of mercury, a wider database is needed. Since volatile forms of mercury are readily absorbed into the human body via inhalation, this route of exposure represents a potential concern for homeowners whose total mercury levels exceed the current drinking water standard of 2000 ng/L. Further, methylmercury may pose a health threat via direct ingestion of potable water containing this form of mercury.

The current drinking water standard of 2000 ng/L is based on ingestion of inorganic mercury salts (USEPA, 1992). This was indeed the predominant form found in this study. The discovery of percentages of volatile mercury in drinking water has led to the initiation of research regarding alternate water uses (i.e., showering and washing dishes) by the State. The drinking water standard may need to be revisited if volatile and methylated forms of mercury continue to be detected in southern NJ potable wells.

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This work was funded by the A-280 Safe Drinking Water Research Program. A NJDEPE/DSR technical report on this project can be ordered (609-292-9373). A duplication fee may be charged. General information about the environmental research program at the Division of Science and Research is available (609-984-6071). DSR Reference No. 9300

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Table 1. Mercury Concentrations in Selected Drinking Water Wells in Southern NJ.

Mercury Concentrations in Wells With Total Mercury Concentrations Exceeding 2000 ng/L.

Parameter	MDL (ng/L)	Median (ng/L)	Range (ng/L)	Mean (ng/L)	Number of Samples
Mercury _{total} ICP-MS	1	4600	2700-36100	8424	16
Mercury _{total} EPA 245.1	50	6750	4000-31650	10715	13
Mercury _{reactive} ICP-MS	1	5345	2400-36400	8142	16
Mercury _{reactive} modified EPA 245.1	10	4730	2770-12270	5754	13
Volatile Mercury LDC	1	312	<1-403.5	245	14
Methyl Mercury GC-ECD	0.2	0.9	<0.2-137	24.75	15

MDL - method detection limit

Mercury Concentrations in Wells With Total Mercury Concentrations Below 2000 ng/L.

Parameter	MDL (ng/L)	Median (ng/L)	Range (ng/L)	Mean (ng/L)	Number of Samples
Mercury _{total} ICP-MS	1	5.0	<1-1650	101	62
Mercury _{total} EPA 245.1	50	55	<50-1220	143	33
Mercury _{reactive} ICP-MS	1	5.0	<1-1740	129	62
Mercury _{reactive} modified EPA 245.1	10	10.0	<10-3580	521	16
Volatile Mercury LDC	1	<1.0	<1-54	4.5	44
Methyl Mercury GC-ECD	0.2	0.55	<0.2-124	16.09	8

MDL - method detection limit

Table 2. Pearson's Correlations for Linear Relationships for Mercury Analyses.

All ground water samples.

Parameter	Mercury _{total} ICP-MS	Mercury _{reactive} ICP-MS	Mercury _{total} EPA 245.1	Mercury _{reactive} EPA 245.1*
Mercury _{total} ICP-MS	1.0	0.996	0.980	0.684
Mercury _{reactive} ICP-MS	0.996	1.0	0.99	0.713
Mercury _{total} EPA 245.1	0.98	0.99	1.0	0.75
Mercury _{reactive} EPA 245.1*	0.684	0.713	0.75	1.0

* Method 245.1 modified for reactive mercury determinations (see text)

Ground-water samples whose total ICP-MS mercury exceeded or equalled 2000 ng/L.

Parameter	Mercury _{total} ICP-MS	Mercury _{reactive} ICP-MS	Mercury _{total} EPA 245.1	Mercury _{reactive} EPA 245.1*
Mercury _{total} ICP-MS	1.0	0.994	0.946	1.0
Mercury _{reactive} ICP-MS	0.994	1.0	0.935	0.974
Mercury _{total} EPA 245.1	0.946	0.935	1.0	0.975
Mercury _{reactive} EPA 245.1*	1.0	0.974	0.975	1.0

* Method 245.1 modified for reactive mercury determinations (see text)

Ground-water samples whose total ICP-MS mercury was less than 2000 ng/L.

Parameter	Mercury _{total} ICP-MS	Mercury _{reactive} ICP-MS	Mercury _{total} EPA 245.1	Mercury _{reactive} EPA 245.1*
Mercury _{total} ICP-MS	1.0	0.944	0.644	0.684
Mercury _{reactive} ICP-MS	0.944	1.0	0.642	0.713
Mercury _{total} EPA 245.1	0.644	0.642	1.0	0.272
Mercury _{reactive} EPA 245.1*	0.684	0.713	0.272	1.0

* Method 245.1 modified for reactive mercury determinations (see text)