



## Project Summary

# GC/MS Analysis of Organics in Drinking Water Concentrates and Advanced Waste Treatment Concentrates

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The major goal of this research was to characterize organic material concentrated from large volumes (1,500 liters to 15,000 liters) of finished drinking water (DW) and finished water from advanced waste treatment (AWT) plants. Organic compounds were identified based on glass capillary gas chromatography-mass spectrometry (GC-MS) analysis of the fractionated concentrate. The complex organic concentrates were partitioned into less complex fractions by liquid-liquid partitioning, methylation of acidic components, and fractionation of neutral species on silica gel. One of the purposes of this research was to enable EPA scientists to correlate the results of the detailed chemical characterization with those from other programs that test the potential biological activity (i.e., mutagenicity) of the concentrates. Fifteen DW concentrates, sixteen AWT concentrates, and five concentrate production method blanks were analyzed.

The cities represented by the DW samplings were Cincinnati, Miami, New Orleans, Ottumwa (Iowa), Philadelphia, and Seattle. Only 20 percent of the organic material in the DW concentrates for a given sampling was recovered in analyzed fractions, and only one half of that material was chemically suitable for GC-MS analysis. Most of the unrecovered organic portion, and the extracted material not amenable to GC-MS analysis, appeared to be humic. In the 15 DW concentrates, 1,091 organic

compounds were identified in 2,383 detection instances.

The AWT plants sampled were located in Escondido, Lake Tahoe, Orange County, and Pomona, California; Dallas, Texas; and Washington, DC, (Blue Plains). Less humic material was present in the AWT concentrates; thus, about 50 percent of the organic material was recovered in the GC-MS analyzed fractions. In the 16 AWT concentrates, 991 organic compounds were identified in 2,097 detection instances.

The GC-MS data were surveyed by computer for 53 compounds with potential health effects significance. For DW concentrates, 31 of these compounds were present in 108 detection instances. For the AWT concentrates, 33 compounds were found in 117 detection instances. The DW concentrates uniformly contained more and higher concentrations of materials attributable either to pollution from the organic chemical industry or consumer products containing chemicals than AWT concentrates. This difference was probably due to the use of granular activated carbon (GAC) or reverse osmosis (RO) as a final treatment step in the AWT plants but not in the DW treatment plants. All DW samples contained some indicators of water reuse (i.e., drugs or metabolites).

Small volume samples (10 to 30 liters) were also analyzed to determine the effectiveness of the RO and GAC treatment in retaining organic mole-

cules. These results, together with some of the DW concentrate results, indicate that RO membranes do not effectively retain apolar organic molecules.

*This Project Summary was developed by EPA's Health Effects Research Laboratory, Research Triangle Park, NC, to announce key findings of the research project that is fully documented in a separate report of the same title (see Project Report ordering information at back).*

## Introduction

Assessing the health effects of trace (parts per billion, ppb) levels of organic material in water is an important, if not determining, factor in establishing maximum permissible contamination levels for drinking water (DW) and finished water from advanced waste treatment (AWT) plants. The issue of trace-level organic chemical contamination of DW will continue to be emphasized in environmental health effects research. In the western states, the use of potable or other high-quality AWT finished water is certain to assume a major role. Pilot- and production-scale AWT plants are already providing high-quality water for use in ground-water injection--either to prevent sea water intrusion into coastal aquifers or simply as aquifer replenishment. In addition, direct potable reuse of AWT finished water is now being planned for some municipalities for which unlimited supplies of fresh surface water or ground water are not presently assured. Detection and control of trace-level organic contamination in these AWT reuse waters is obviously important for the ultimate protection of DW sources.

The Toxicology and Microbiology Division of the Health Effects Research Laboratory of the U.S. EPA in Cincinnati, Ohio (HERL-CI) is pursuing a research program to characterize the trace-level organic materials in DW and AWT water and to test the biological activity of these materials for their potential health effects. The goal of this research was to characterize the organic materials in sufficient detail to enable EPA to correlate the compound identification results with the biological test results. This correlation may suggest which of the organic compounds or classes of compounds have sufficient potential health effect significance to warrant future regulation and monitoring.

In HERL-CI's approach to this research problem, large quantities (1,500 to

15,000 liters) of DW and AWT water were concentrated, principally by reverse osmosis, to yield gram-quantity amounts of concentrated organic material. Eighty percent of each organic concentrate was reserved for biological testing. Half of the remaining 20 percent was analyzed for organic compounds by glass capillary gas chromatography-mass spectrometry (GC-MS). Thus, the sample aliquot analyzed represents between 150 and 1,500 liters of the original water for a theoretical concentration factor of 150,000.1 to 1,500,000.1. This extremely high concentration, coupled with fractionation of the sample into five separately analyzed organic polarity groups (thereby adding another order of magnitude to the concentration factor), allowed for a more detailed characterization of the portion of organic material amenable to GC-MS analysis in these clean waters than any previous approach. Theoretical sensitivities of some identified compounds reached below the 0.1 part per trillion (ppt) level (0.1 nanogram per liter).

The following is a brief description of the analytical scheme employed:

- Fractionation of the concentrate into five different polarity groups
- Glass capillary GC-MS analysis of four of the fractions on two different GC phases with all generated data archived on 9-track magnetic tape
- Residue weight analysis of the unpartitioned concentrate and the five fractions
- Attempted identification based on mass spectra of all chromatographic peaks and shoulders in the GC-MS data
- Automated searching of GC-MS data filed for 53 high-interest compounds and quantification of those found
- Confirmation of tentative identifications by comparison with GC-MS data generated from commercially obtained reference compounds
- Entry of compound identification results and other pertinent concentrate information into Battelle's mainframe computer for automated data management and generation of tabular listings of results
- Concentrate analysis report generation

## Conclusions

The results of this research have shown that the fractionation of complex organic concentrates followed by glass capillary GC-MS analysis enables the identification of hundreds of organic compounds present in these samples. Moreover, concentration techniques in which thousands of liters of water are used to produce the analyzed sample, together with computerized GC-MS data searching, have enabled theoretical sensitivities toward individual pollutant species which extend well below the ppt (nanogram per liter) level. Thus, results of this research have produced more detailed chemical characterizations of very clean drinking waters and advanced waste treatment finished waters than previously possible.

The results for drinking water (DW) provide the following conclusions:

- Most of the organic material in the analyzed concentrates consisted of humic-related substances which are not amenable to GC-MS analysis. On the average, more than 90 percent of the organic material present in the concentrates was not recovered through the fractionation scheme. Part of the recovered material is not suitable for characterization by GC-MS analysis, and it is estimated that only 30 to 60 percent of the material recovered into fractions (i.e., 3 to 6 percent of the original concentrates) can be characterized by GC-MS analysis.
- All of the DW samples (except for one case which served as a blank) contained many identified organic compounds, generally between 150 and 400 different species.
- The species identified at the highest levels and greatest numbers were non-aromatic and aromatic carboxylic acids.
- All DW concentrates contained some evidence of the presence of re-use water via the identification of drug metabolites and other materials expected to originate from domestic sewage.
- All DW concentrates showed some evidence for contamination by organic compounds from industrial discharges (organic solvents and chemical industry commodities, intermediates and wastes), and

consumer use of organic chemical-containing products including herbicides and pesticides. Concentrates from Cincinnati, Philadelphia, and New Orleans contained the highest levels of these substances.

- All DW concentrates contained halogenated species which probably originated from the chlorination of naturally occurring organic material in the source water. This result was the most pronounced for the Seattle and Miami concentrates.
- A tentative conclusion that the reverse osmosis membranes used for pre-concentration did not effectively retain (or, perhaps, absorbed) highly apolar species was based on a comparison of the reverse osmosis-produced concentrates from a Cincinnati sampling with the concentrate produced by direct XAD-2 adsorption/elution prepared from the same volume of identical water. Based on the limited evidence, RO was more effective for recovering highly polar, water soluble materials, especially humic material.

For the AWT concentrate analysis results, the use of contact with granular activated carbon (GAC) was obviously effective in reducing the amount of organic material recoverable in the final concentrate. Almost without exception, the AWT concentrates contained less organic material in the analyzed fractions and resulted in fewer identified compounds and lower detected levels than the DW concentrates. For some of the AWT concentrates, these comparative differences were substantial. However, the sampled finished AWT water contained higher total organic carbon (TOC) levels than the sampled finished DW, it can therefore be concluded that the finished AWT water contained higher levels of material not recoverable by RO or not suitable for GC-MS analysis than did the finished DW.

Assuming that the AWT influent contained organic material suitable for GC-MS analysis at levels at least as high as those for the finished DW, one must conclude that the GAC contact step in the AWT process was effective in reducing the levels of GC-MS analyzable organic substances to below those for the sampled DW. Compared to the DW concentrates, the AWT concentrates contained higher levels of fatty and other acids, phthalates, and poly glycol ethers

(relatively polar species) but generally lower levels of apolar species attributable to the use or production of industrial organic chemicals. This observation supports the conclusion about the effectiveness of GAC contact stages in the AWT plants. Higher efficiency for removing the apolar species (which are more suitable for GC-MS analysis) than the polar, more highly water-soluble species is consistent with expected chemical behavior. One AWT plant (Escondido, California) employed RO rather than GAC contactor treatment. Since the Escondido concentrate contained less organic material and fewer species identifiable by GC-MS, the tentative conclusion is that RO is highly effective for final treatment for AWT systems. However, insufficient data are available to compare RO effectiveness to GAC treatment.

### Recommendations

Future work in correlating potential health effects of organic contamination in DW and AWT water with the nature of the organic materials present should employ biological testing of individual chemical group fractions of the organic concentrates rather than bulk concentrates. Such a strategy could greatly reduce the amount of chemical analysis required. Results from the DW concentrates indicated that more than 80 percent of the organic material present was humic, which was not suitable for characterization by GC-MS, yet these materials may be responsible for a significant amount of biological activity. Standard methods are available for isolating the humic materials in concentrates. Separate biological testing of a humic/fulvic acid fraction as well as the fractions isolated for GC-MS analysis would greatly simplify the task of correlating the organic compounds in the concentrate with the biological testing results. For example, the polar neutral fraction always contained a plethora of alcohols, ketones, diester plasticizers and mixed functionality species, many of which are difficult to identify by GC-MS analysis. Certainly, many of these compounds are biologically inactive, and if this polar fraction consistently failed to show biological activity, GC-MS analysis could be omitted. The opposite may be true for the aromatic fraction, which represented only 0.05 to 1.0 percent of organic material in the concentrate.

Comparison of analysis results for concentrates prepared from identical DW samples by the RO-based method and by the direct XAD-2 adsorption/elution

method suggested that much and possibly most of the apolar anthropogenic species in the sampled water were not recovered by RO. These anthropogenic species are of the highest interest for potential health effects investigation. On the other hand, direct XAD-2 adsorption/elution did not recover ionized, highly polar and macromolecular species such as humic/fulvic acids and poly glycols so well as the method employing RO pre-concentration. Development of a combination of these two methods could provide a concentrate more representative of the organic material present in the original water, so that more reliable health effects conclusions could be drawn.

The results represented in this work constitute the most detailed chemical characterization of a wide variety of clean waters such as DW and finished AWT water from various sources. However, the results also show that only a small fraction of the organic material recovered into the concentrate is suitable for characterization by GC-MS methods. Detailed characterization of the major part of the organic material which was not suitable for direct GC-MS analysis should be performed to complete this work. Because the completion of this work would have great importance in health effects evaluations and intrinsic scientific value, present work should be continued.

In future analyses of this type, the following minor modifications would be more cost effective.

- The use of polar capillary GC columns capable of higher temperature limits could eliminate the necessity for analyzing the high polarity, medium polarity and acid fractions on the apolar phase.
- GC-MS analysis of the aromatic fraction should be restricted to the apolar GC column.
- Based on the compound identification results of this study, additional compounds could be selected for computerized data searching. These compounds could be selected to profile different characteristics of source waters.

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The complete report consists of three volumes, entitled "GC/MS Analysis of Organics in Drinking Water Concentrates and Advanced Waste Treatment Concentrates;" (Set Order No. PB 85-128 213; Cost: \$61.50)

"Volume 1. Analysis Results for 17 Drinking Water, 16 Advanced Waste Treatment and 3 Process Blank Concentrates;" (Order No. PB 85-128-221; Cost \$25.00)

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"Volume 3. Batch Liquid-Liquid Extraction and Analysis of 10-Liter Sample and Analysis of Concentrates from Small Volumes (10 to 50 Liters) of Drinking Water;" (Order No. PB 85-128 247; Cost: \$17.50)

The above reports will be available only from: (cost subject to change)

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