Environmental Assessment and Risk Analysis Element

Research Project Summary

NJDEP

March, 2003

The Characterization of Tentatively Identified Compounds (TICs) in Water Samples Collected from Public Water Systems in New Jersey

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Abstract

This is a summary report of a detailed investigation in which the analysis of synthetic organic chemicals by Gas Chromatography (GC) and Liquid Chromatography (LC) was conducted on raw and finished water samples collected from public water supplies using ground water as a source of drinking water. All water systems sampled are known to be contaminated by volatile organic chemicals except for one (the "control" system). This work investigated the potential presence of non-volatile and semi-volatile organic chemicals in those water supplies. Five bottled waters were also sampled. Several generalizations can be made: 1) water serving systems impacted by identified hazardous waste sites have distinct and sometimes unique TICs associated with them; 2) TICs are generally low in concentration, most being estimated at a concentration below a part per billion (microgram per liter, mg/L); and 3) many organic chemicals reported as TICs were not actually in the water sampled but were found in the analysis due to sampling and/or laboratory contamination.

Introduction

Presently, certain conventional analytical methods for analyzing drinking water samples from public water supplies for specific, or targeted, organic chemical contamination are required by the NJ Safe Drinking Water Act. For the most part, this routine testing is adequate for the determination of commonly occurring volatile organic chemicals (VOCs). It was always known that VOCs, which are the current regulatory focus of analysis for organics in drinking water, may serve as markers for the presence of mostly unregulated non- and semi-volatile contaminants in addition to being significant in their own right. In situations where impacted water is being used as a potable source, this issue is very important. In the past, reliable analytical methods were not available to determine the presence or the nature of many non-volatile (e.g., some pharmaceuticals, dyes, inks) and semi-volatile (e.g., plasticizers, fragrances, some components of fuel oils) contaminants, with the exception of certain types of semi-volatiles (i.e., some pesticides and plasticizers).

A volatile compound is defined chemically as one with a relatively low boiling point. That is, a volatile compound "evaporates" readily into the air. Whereas, a non-volatile compound evaporates much more slowly or not at all. A semi-volatile compound falls in between. Thus, due to the historical focus on VOCs, the full picture of exposure and health risk from contaminated drinking water may not have been adequately determined. With the emergence of more sensitive analytical capabilities for non- and semi-volatile organic contaminants, a more complete assessment of this additional contamination, if and where it exists, can be made, and appropriate steps can be taken to protect public health.

This study was able to address the potential detection of hundreds of chemicals because the instrumentation was set up to screen for tentatively identified compounds (TICs). A TIC is a compound that can be seen by the analytical testing method, but its identity and concentration cannot be confirmed without further analytical investigation. An analogy is when a photograph is taken of a subject. The picture also captures the information in the background, and often this information is fuzzy, but the focus of the picture is the subject. The subject (i.e., target item) is clear, but the background components (i.e., the tentatively identified items), while captured in the picture, are fuzzy.

Objectives

There were three related objectives to this multi-year project.

1. Tentatively identify and possibly quantify chemicals present in raw and treated water samples collected from water supply systems impacted by hazardous waste sites.
2. In instances where chemicals are present in the raw water, determine if existing water treatment is effective at removing them.
3. Characterize the types of unregulated compounds present in water samples due to sampling and laboratory contamination.

Methods

Data on organic analyses from public community water systems that use ground water as their water source was generated and delivered to the project investigators by the NJ Department of Environmental Protection's (NJDEP)

Bureau of Safe Drinking Water (BSDW). Review of this data showed which systems had historical organic contamination above appropriate maximum contaminant levels (MCLs) and which systems had water treatment technologies in place to remove the contamination. This became the candidate list from which systems were selected for participation in the study. There were 96 individual facilities (points-of-entry to the water distribution system), serving approximately 54 community water systems, identified in 1997 where volatile contamination above MCLs occurred in the untreated source water and where some type of water treatment was in place to remove the contamination before the water was distributed to customers.

Using the candidate list, the investigators selected appropriate water systems to sample as part of this study. There were several exceptions. Two of the water systems were very small (one is a church and the other is a school) with no water treatment. They were included as part of the study because historical results showed the presence of unusual organic chemical contamination, according to BSDW records. One surface water system was selected for comparison purposes, and one system used both surface as well as ground water. One ground water system was selected as a control system (i.e., no known impacts and no treatment to remove organic contamination). Ultimately, 21 water systems were sampled during this study. The sample bottles for one system (NJ American – Atlantic City) were broken in the laboratory. No resample was collected. Therefore, results for 20 systems are reported here.

Conventional Analytical Methods
All water samples were sent to the NJ Department of Health and Senior Services (NJDHSS) laboratory for analysis by conventional USEPA Methods 524.2 (84 target volatile chemical analytes) and 525.2 (42 target semi-volatile chemical analytes) and for arsenic and mercury.

General Nonconventional Methods
Nonconventional analytical methods were developed at the NJ Environmental and Occupational Health Sciences Institute (EOHSI) and the NJ Center for Advanced Food Technology (CAFT) of Rutgers University. The EOHSI method utilized gas chromatography to analyze for volatile and semi-volatile compounds. The CAFT method utilized high pressure liquid chromatography to analyze for non-volatile compounds. All water samples were run through these methods at least once to screen for classes of chemical compounds present.
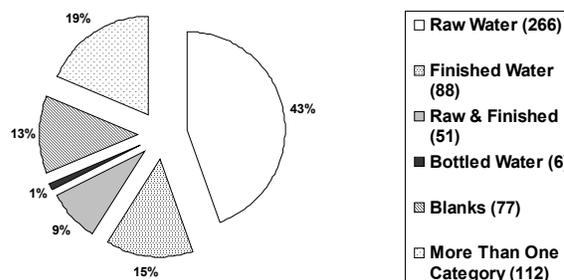
Results
CONVENTIONAL ANALYSIS:
The volatile organic compounds most frequently detected above maximum contaminant levels in the raw waters were trichloroethylene, tetrachloroethylene, and 1,1,1-trichloroethane. Water samples collected after the air treatment systems indicated that these compounds were removed to levels below the MCLs, mostly below method detection levels. However, several instances, levels of trichloroethylene and tetrachloroethylene were detected at levels close to their MCLs of 1.0 μg/L. The results of the conventional analysis validated the historical data collected at the water systems, indicating that raw water is contaminated

with volatile organic chemicals and that air treatment installed to remove these contaminants is effective at removing them. Also, trihalomethanes and other types of disinfection by-products were detected in chlorinated water samples at levels greatly below appropriate existing MCLs.

Figure 1. Distribution of TICs (unique to the group) by type of water sample.

Legend:
- Raw Water (266)
- Finished Water (88)
- Raw & Finished (51)
- Bottled Water (6)
- Blanks (77)
- More Than One Category (112)

Pie values: 43%, 15%, 9%, 1%, 13%, 19%

NONCONVENTIONAL ANALYSIS:
High Pressure Liquid Chromatography (HPLC)
During the first two years of the study, no non-volatile compounds were detected using HPLC. During the third year of the study, larger sample sizes were analyzed. Two liters of sample were used instead of one to improve the overall method detection limit. Even with the larger sample size, almost all of the samples reported a non-detect result.

Gas Chromatography Over the course of the 4 year study, approximately 600 TICs were detected in 199 water samples collected: 108 raw water samples (3 raw surface water and 105 raw ground water), 51 finished water samples, 35 blank samples, and 5 bottled water samples. Of the 600 TICs, 112 were detected frequently among the types of samples collected and among the systems sampled. For instance, butylated hydroxytoluene was detected in raw, finished, bottled and blank water samples, so it is included under "more than one category". The remaining 488 TICs were detected in the distribution shown in Figure 1, which delineates TIC distribution in raw, finished, raw & finished, bottled and blank samples. The distribution of TICs by water supply system and type of sample is shown in Figure 2. TICs unique to water supply systems are shown in Figure 3.

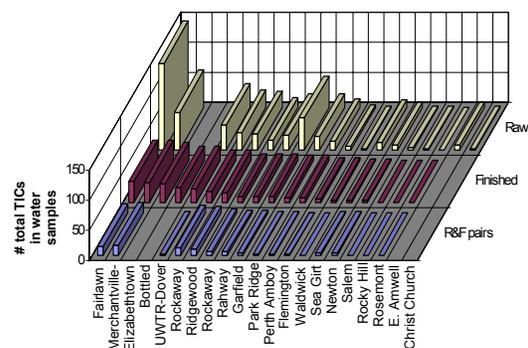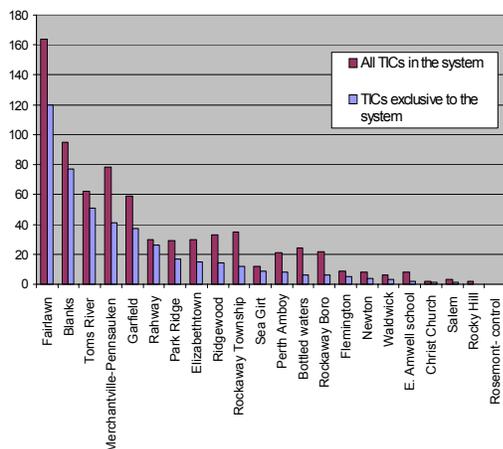Figure 2. TICs in Water Samples (not including TICs that were detected in blanks)

Figure 3. Number of TICs Found by System

Raw & Finished Sample Pairs

In general, when TICs were detected in both raw and finished water from the same system, it was in systems where carbon treatment was not present. This is not surprising because air-based treatment technologies are designed specifically to remove volatile organic chemicals (and many are capable of removing some semi-volatile compounds). Carbon treatment technologies can remove many types of volatile, semi-volatile and non-volatile chemicals.

Finished Drinking Water Samples

Finished drinking water contained some TICs that were never detected in raw water samples, indicating that they may enter the distribution system through the treatment process, chemical transformation of other compounds during treatment, or addition of disinfection reagents.

While 88 unique TICs were detected in finished water samples, only 8 of these appeared in more than one finished water sample. The appearance of compounds in finished water is not unusual in and of itself – the conventional analyses showed disinfection by-products appearing in finished water samples and not in raw water samples. Similarly, the treatment of water by air, carbon, or the addition of disinfectants may introduce compounds that would not necessarily be present in raw water.

Raw water samples

Of the 600 TICs detected in this study, 338 were detected in raw water samples (and not in blanks). Of these 338, a subset of 266 TICs were detected in raw water samples only, and not in finished water samples or any other category. The wells sampled as part of this study were selected because they had historical volatile chemical contamination. Another criteria for selection was proximity of the wells to known contaminated sites. In several instances, the contaminated site influencing the wells had been identified and, in fact, the responsible party paid for installation and maintenance of the treatment technology at the water system. It was not surprising, therefore, to see that semi-volatile compounds were present in the raw water samples, as these samples also contained the highest numbers of and highest concentrations of volatile organic chemicals of the groups.
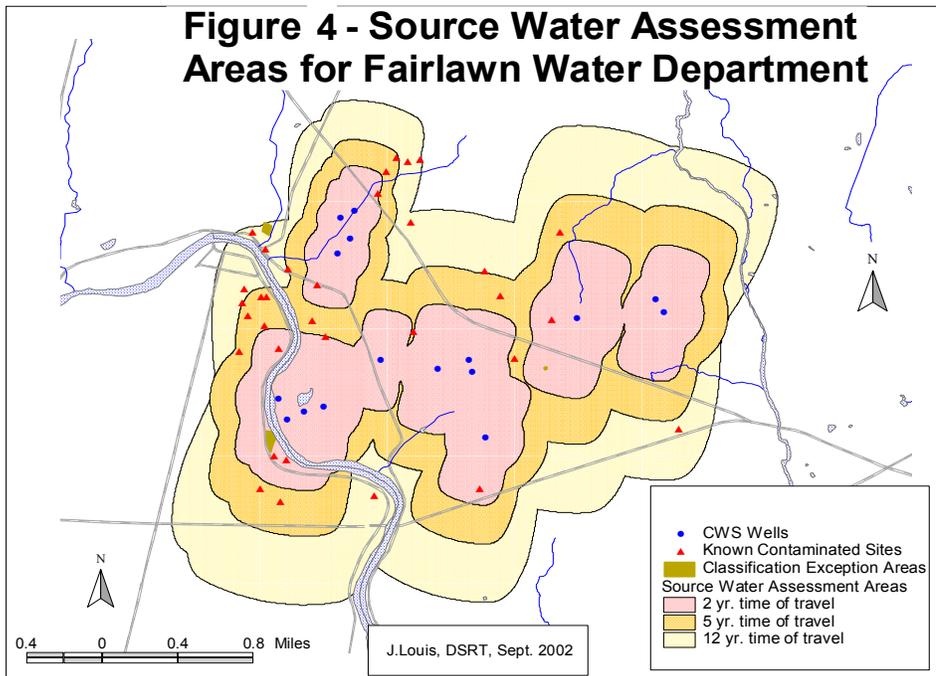
Bottled Water Samples

Thirty-two TICs were found in the five bottled water samples. Twenty-four of these were not detected in the corresponding blank water samples. There were six (6) TICs unique to bottled water. Only one of the six TICS unique to bottled water was detected in more than one bottled water and not detected in the blanks. It was 3,5-di-tert-butyl-4-hydroxybenzyl alcohol.

Blank Samples

Because of the prevalence of TICs in blank water, it is difficult to interpret their presence in environmental water samples. However, several patterns emerge when investigating the data of TICs in blank water samples: there is a population of TICs that occur only in blanks; there are TICs that occur frequently in blanks and environmental samples; and there are TICs that sometimes appear in a blank and sometimes appear in an unrelated environmental sample. What it implies is that when regulators look at TIC information from environmental samples, it is vital that they also look at the corresponding blank sample information. The detection of a TIC in a water supply sample does not directly imply that there is an environmental contamination problem if the TIC also appears in the field or trip blank. Similarly, the fact that a compound appears in a blank does not preclude its presence in an environmental sample. The data need to be evaluated side-by-side in order for an assessment to be made about the actual occurrence of a contaminant in a sample.

Discussion

Source Water Assessment Areas (SWAs) have been delineated and are available for several of the water systems sampled as part of this study. One is shown in Figure 4. When looking at the map, it is clear that there are potential sources of contamination near some of the community supply wells sampled. The NJDEP should continue its work on assessing the potential impacts from hazardous waste sites to drinking water sources in the state. As a result of this study, the NJDEP may want to consider more intensive scrutiny of the inventory of chemicals reported by hazardous waste site operators. Currently, the site inventories are very broad. It may be useful to have site operators generate more specific types of waste lists in order for NJDEP staff to determine if there is the potential for contaminants to reach drinking water wells. This study shows that contamination by hazardous waste sites may not be limited to volatile organic chemicals and that treatment to remove volatile chemicals may not be sufficient to remove semi- and non-volatile chemicals. Evidence from the control system shows that water systems not impacted by sources of contamination do not appear to contain unique TICs.

Figure 4 - Source Water Assessment Areas for Fairlawn Water Department

Legend:
- CWS Wells
- Known Contaminated Sites
- Classification Exception Areas
- Source Water Assessment Areas
  - 2 yr. time of travel
  - 5 yr. time of travel
  - 12 yr. time of travel

0.4   0   0.4   0.8 Miles

J.Louis, DSRT, Sept. 2002

Next Steps

Further work is underway to definitively identify and quantify some of the TICs seen in this study. While it is impossible to pursue positive identifications for all 600 TICs reported, it is possible to cull the list and focus on a more manageable number of TICs. The criteria for selection of which TICs to pursue include: availability of an analytical standard, frequency of occurrence in water samples not likely to be present due to sampling or laboratory contamination, and potential human toxicity. A report is expected on this work in 2003.

The study described herein focused on the occurrence of TICs in water samples from water supply systems using ground water as their water sources. Presently, water samples collected from surface water systems are being collected and will be analyzed using the same GC-MS screening methods described here. A report on this work is expected by the spring of 2004.

A report on the preliminary assessment of health information on the TICs found in this study is expected in 2003. Researchers from the University of Medicine and Dentistry, NJ have reviewed the available literature to find chemical, industrial and health information on as many of the TICs as possible. Further, a preliminary assessment of potential human risk based on toxicity data (when available) will be included.

Funding

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