



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



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Acronyms and abbreviations used in this report:

BAT: Best Available Treatment
BSDW: NJDEP's Bureau of Safe Drinking Water
CAFT: Center for Advanced Food Technology
DSRT: NJDEP's Division of Science, Research and Technology
EOHSI: Environmental and Occupational Health Sciences Institute
GAC: Granular Activated Carbon
GC: Gas Chromatography
GCITMS: Gas Chromatography with Ion Trap and Mass Spectrometry
HPLC-MS: High Pressure Liquid Chromatography-Mass Spectrometry
KCSL: Known Contaminated Site List
LC: Liquid Chromatography
MCL: Maximum Contaminant Level
MS: Mass Spectrometry
NIST: National Institute for Standards and Technology
NJDEP: New Jersey Department of Environmental Protection
NJDHSS: New Jersey Department of Health and Senior Services
POE: Point-of-Entry
PWS: Public Water Supply
PWSID: Public Water System Identification number
ROD: Record of Decision
SWAP: Source Water Assessment Program
TIC: Tentatively Identified Compound
µg/L: micrograms per liter
USEPA: United State Environmental Protection Agency
USGS: United State Geological Survey
VOC: Volatile Organic Chemical

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Abstract

This is the interpretive 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, $\mu\text{g/L}$); and 3) many synthetic and natural 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

In NJ, there are 54 community water systems (of approximately 600 in the state) that have organic chemical removal treatment systems due to the presence of elevated levels of volatile organic chemicals in the source ground water. The significance of the contamination varies, and the source(s) of the contamination is sometimes identified and sometimes not. During water sampling by the State for semi-volatile compounds for United Water-Toms River Water Company in the late 1990s, it was observed that the Department of Health and Senior Services (NJDHSS) laboratory was reporting the presence of Tentatively Identified Compounds (TICs) with their routine analytical results. 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. Many analytical methods can report TICs – they are compounds that the instrumentation can detect but the analysis is not targeting specifically. 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) is clear while the background (i.e., the non-target items), while captured in the picture, is fuzzy.

It became of interest to the state to pursue the investigation into the occurrence of TICs in water samples in general and perhaps to definitively identify and quantify a subset of them. This study was initiated in response to that interest.

According to the 2001 Known Contaminated Site List (KCSL) published by the Site Remediation Program of New Jersey Department of Environmental Protection (NJDEP), there are more than 12,000 contaminated sites in NJ. Many of these are sites containing small leaking underground storage tanks where gasoline or fuel oil is the major contaminant in ground water. The KCSL is broadly defined as “a list of sites affected by hazardous substances.” A very small percentage of these are known to impact water supply wells. In some instances where the source of contamination is not known, a drinking water supply is itself listed as a contaminated site. One of the important reasons for conducting this study was to determine if existing monitoring strategies are adequate for detecting potentially harmful chemicals in water supply systems impacted by contaminated sites.

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 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 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, routine analytical methods were not available to determine the presence or the nature of many non-volatile compounds (e.g., some pharmaceuticals, dyes, and inks) and semi-volatile compounds (e.g., plasticizers, fragrances, and some components of fuel oils), with the exception of certain types of semi-volatiles (i.e., some pesticides and plasticizers). There is a multitude of semi- and non-volatile chemicals being used in industry and commercially, but current routine analytical methods detect only a fraction of them. 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, 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 and responsible steps can be taken to protect public health.

Water monitoring is a complex science involving multiple analytical methodologies. Each method is tailored to look for specific compounds and, while that method may be able to detect other compounds, it will not be able to definitively identify nor quantify them without further manipulation of the whole or parts of the system. A nonconventional method is a research method, or an adaptation of a conventional method, that is known to be useful in the identification of certain classes of compounds or certain specific chemicals. By definition, the U.S. Environmental Protection Agency (USEPA) has not developed formal protocols or laboratory certification procedures for nonconventional methods. Sometimes the same analytical instrument as in a conventional analysis is used but under different conditions. One set of conditions may be considered a conventional method while another would be considered nonconventional. It is important to understand the differences between conventional and nonconventional methods and among the different types of analytical methods within these broad categorizations in that it explains why only certain classes of compounds are reported when a water system samples its water for potential contamination.

Objectives

Current conventional analytical methods for analyzing water samples for contamination may not be adequate to detect and quantify all possible synthetic organic chemicals present in a water sample. This can be important when a water source impacted by a contaminated site is being used for drinking water. Ground water that has been contaminated by a waste site can be used for drinking purposes when it is treated to remove contaminants from the water. Most often, the contamination has been believed to be primarily by volatile organic compounds. Water is analyzed before and after water treatment to ensure that all volatile organic chemical contamination has been removed or brought to levels below the maximum contaminant levels (MCLs) prior to distributing the water to consumers. For the most part, the treatment present for removal of volatile organic compounds for public water systems in NJ is air-stripping, which basically works on the premise that, by aerating the water, the contaminants volatilize (or evaporate) from the water to air. Some systems also have carbon filters, where contaminants are absorbed onto the carbon surface, or a combination of air and carbon. However, typically only the volatile organic contamination is monitored with frequency, because these are the types of compounds that can be detected using current conventional methods. One of the primary objectives of the study described here was to screen selected, worst-case water samples for the presence of unregulated, semi-volatile and non-volatile organic compounds. There is presently little information on the prevalence of these types of compounds in NJ’s public drinking water supplies. Once an initial screening is done, additional steps can be taken, such as: identification and quantification of selected organic compounds; more detailed investigation of unregulated compounds including potential sources state-wide; and preliminary human-health

evaluations of selected compounds. In the study described here, nonconventional analytical procedures were used to screen impacted waters for the presence of non- and semi-volatile organic substances.

There were three related objectives to this multi-year project, each of which is described in more detail below.

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.

1. Tentatively identify and possibly quantify chemicals present in raw and treated water samples collected from water supply systems impacted by hazardous waste sites.

NJDEP staff scientists have been aware of the presence and reporting of TICs in analytical methods for a while. Due to the uncertainty in identification and lack of systematic occurrence information, it has been difficult to know how to interpret TIC information when submitted by an analytical laboratory. Over the years and throughout many programs in NJDEP, it has become of interest to better characterize the presence of these potential contaminants in order to develop strategies to make decisions regarding their presence in drinking water samples. The first step of the study described here was to develop analytical techniques that maximize the detection of those types of chemicals that are not normally targeted in conventional analytical methods. Given the nature of TICs (tentative identification of compounds in an analytical method), it is impossible to develop a formal “method” for their detection. The emphasis here was rather to reconnoiter vulnerable areas to determine if contamination by currently unregulated chemicals is occurring in the state.

2. In instances where chemicals are present in the raw water, determine if existing water treatment is effective at removing them.

All the water systems selected for this study had historical organic contamination, according to Bureau of Safe Drinking Water (BSDW) records (except for the control system, which was selected because it had never had any instance of organic contamination other than trace levels of disinfection by-products). As part of this study, all water samples were analyzed using conventional analytical methods in addition to the non-conventional methods to confirm the historical contamination. Further, all the systems selected had some type of treatment designed to remove the contamination (either air strippers or carbon filters or both). It was an important objective of this study to evaluate the effectiveness of these treatment technologies on the removal of TICs. BSDW records indicated that the treatment was effective at removing the volatile organic contamination, and this study sought to investigate the treatments’ efficacy of semi- and non-volatile organic chemical removal.

3. Characterize the types of unregulated compounds present in water samples due to sampling and laboratory contamination.

To determine if chemicals (that are not ordinarily targeted for analysis) are actually present in a water sample, it is necessary to characterize the types of chemicals present in sample bottles, reagent chemicals used for analysis, preservatives, lab water and chemicals introduced during separation and analysis (e.g., chemicals formed by reaction of internal standards with other

chemicals in the water sample). When conducting conventional analysis, laboratories run such tests to ensure that target analytes are not present in analysis reagents. Field and trip blanks are collected and analyzed for the target analytes. When target analytes appear in the blank samples, then blank correction is performed on the environmental samples. Because TICs are by definition tentatively identified compounds, it is not possible for laboratories to institute specific steps to eliminate these unknowns from the analytical procedure. Therefore, it was important that this quality assurance measure be a fundamental part of the overall investigation in order to account for any potential occurrence of TICs due to sampling, handling and analysis of the water samples.

Methods

SELECTION OF WATER SYSTEMS FOR SAMPLING

In 2001, there were 606 community water systems, 936 nontransient, noncommunity water systems, and 2707 transient water systems in the state. A Public Water System (PWS) is defined as a system that provides water for human consumption to at least 15 service connections or serves an average of at least 25 people for at least 60 days each year. There are three types of PWS's: community (such as towns), nontransient noncommunity (such as schools or factories with their own drinking water systems), or transient noncommunity systems (such as rest stops or parks with their own drinking water systems). Of particular interest for this study were the community water systems and nontransient, noncommunity water systems, because these are systems from which people are routinely drinking on a daily basis at home, school or work. Overall, systems were selected based on potential or known impacts to the raw ground water supplying them. Many of the water systems selected for the study are included on the Known Contaminated Sites list as actual contaminated sites. A "site" is broadly defined as a "site affected by hazardous substances."

In addition, five bottled waters from grocery stores in areas near the public water systems sampled were purchased and analyzed as part of this study.

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 BSDW. Review of this data showed which systems had historical organic contamination above appropriate MCLs and what 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 points-of-entries 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. Other factors that were considered in the selection process included: proximity to a hazardous waste site; actual identification of the site(s) that caused the water contamination; presence of additional treatment to remove organic contamination (i.e., with both activated carbon and air stripping present); and geographic representation for the state. Using this candidate list, the investigators selected appropriate water systems to sample as part of this study.

During the first year only of this study (1997), USEPA was conducting a similar study in USEPA-Region 2 (New York, New Jersey and Puerto Rico) to look for TICs in drinking waters using two conventional USEPA analytical methods (Methods 524.2 and 625). These methods are capable of detecting volatile and semi-volatile compounds but not non-volatile compounds. Because the NJDEP project involved the use of methods that are capable of detecting many more classes of contaminants than USEPA, NJDEP sampled the same four sites in NJ as USEPA as well as additional NJ sites. Sampling at the sites-in-common occurred on the same days to minimize any

sampling errors. The four water systems in common were sampled during the first week of December, 1997.

USEPA was interested in testing drinking water before and after water treatment at community water supply systems where the water treatment was included as part of the Record of Decision (ROD) at a hazardous waste site. That is, the source(s) of the contamination to the drinking water wells had been identified and the responsible party is paying for the operation and maintenance of the contaminant removal technology at the drinking water system. NJ's candidate selection criteria was simply that wells were contaminated with volatile organic compounds and the water treated for organic chemical removal.

As stated, four of the 21 water systems sampled in this study had water treatment that fulfilled part of the remedial requirements stipulated in the ROD for the hazardous waste site known or suspected to be causing the contamination. There were several exceptions to the criteria for selection of water systems for the study. Two of the water systems were very small (one is a church and the other is a school) with no water treatment and were included as part of the study because historical organic results showed the presence of unusual organic contamination, according to BSDW records. One surface water system was selected in order to compare the raw surface water quality of a system with known organic chemical contamination to that of contaminated ground water, and to investigate on a preliminary basis the efficacy of water treatment from a surface water system. As a control, a water system using ground water from a relatively shallow well but with no known impacts and no treatment to remove organic contamination was sampled. This system reported no historical volatile contamination during the life of the system except for trace levels of disinfection by-products and was therefore considered the "control" site. That is, results from this pristine water system were compared to those from the contaminated systems to help characterize potential naturally occurring contaminants that may be present in water samples. Two of the systems sampled had multiple points-of-entries (POEs) with only one POE having treatment to remove organic contamination. All POEs were sampled in these cases for comparison purposes. Ultimately, 21 water systems were sampled as part of this study and are listed in Table 1. Their geographical distribution is shown in the map in Figure 1. 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.

TABLE 1. WATER SYSTEMS SAMPLED AS PART OF NJDEP'S TIC STUDY.

Water System Name	County	Public Water system Identification (PWSID)	# of POE with treatment	Type of VOC treatment
1997/98 SAMPLING				
Fairlawn Water Dept.	Bergen	0217001	2	packed aeration
Garfield Water Dept.	Bergen	0221001	1	packed aeration
Rahway Water Dept.	Union	2013001	1	packed aeration & GAC
Merchantville Pennsauken*	Camden	0424001	3	packed aeration
Rockaway Borough Water Co.*	Morris	1434001	1	packed aeration
			2	packed aeration & GAC
Rockaway Township Water. Co*	Morris	1435002	1	packed aeration & GAC
Perth Amboy-Old Bridge Water* Dept.	Middlesex	1216001	1	packed aeration
Rosemont Water Dept.**	Hunterdon	1007002	0	none
1999 SAMPLING				
NJ American Water Co - Atlantic City***	Atlantic	0119002	2	packed aeration
Park Ridge Water Dept.	Bergen	0247001	4	GAC
			1	diffused aeration
			3	packed aeration
Flemington Water Dept.	Hunterdon	1009001	3	no treatment for organic removal
			1	aeration
Waldwick Water Dept.	Bergen	0264001	3	packed aeration
Rocky Hill Water Dept.	Mercer	1817001	1	packed aeration
Sea Girt Water Dept.	Monmouth	1344001	2	1 tray aeration
			1	no treatment for organic removal
Elizabethtown Water Co.	Various	2004002	5	aeration
2000 SAMPLING				
Salem Water Dept.	Salem	1712001	1	air and carbon injection
Ridgewood Water Dept.	Bergen	0251001	5	packed aeration
			5	diffused aeration
			1	slat tray aeration
Newton Water & Sewer Utilities	Sussex	1915001	1	packed aeration
Christ Care United Missionary	Camden	0436462	0	none
East Amwell Elementary School	Hunterdon	1008301	0	none
United Water, Toms River	Ocean	1507005	1	Carbon and packed aeration

GAC = granular activated carbon

* Also sampled in the first year by USEPA.

**Control water system.

***Bottles were broken, so these water samples were not analyzed.

New Jersey ranks 11th in consumption of bottled water nationally. It was of interest to the investigators to use the same conventional and nonconventional analyses on representative bottled waters in the state as were used on the water system samples. Consequently, five brands of bottled water purchased in stores where customers of these systems may frequent were sampled as part of the project as well. The bottled water was purchased in grocery stores in areas near several of the waters supply systems sampled as part of the study.

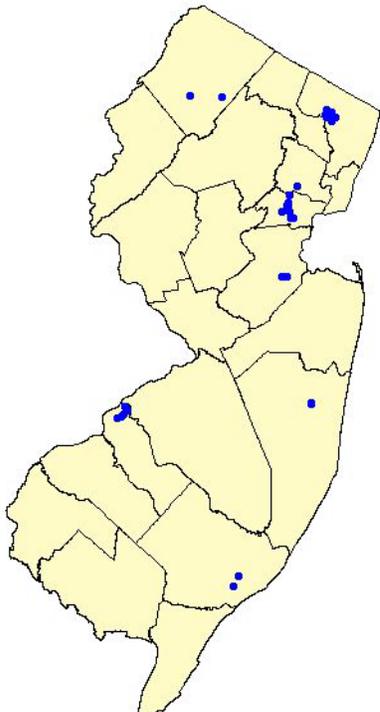


FIGURE 1. LOCATIONS OF THE WELLS SAMPLED DURING THE STUDY.

SAMPLE COLLECTION

For conventional analysis, samples were collected in accordance with standard methods with one exception. Additional field and trip blanks were collected as part of this study. A field trip sample consists of empty sample bottles that are filled with laboratory water at the same time and place as the environmental sample. Laboratory water is transported to the water system specifically for this purpose. A trip blank consists of sample bottles filled at the laboratory with laboratory water. The bottles are not opened but are transported with the sample bottles.

For nonconventional analysis, the standard methods of sample collection for USEPA Method 525.2 (conventional method for semi-volatile analysis) were followed. Again, more blank samples were collected as part of this study than is required by the method. Also, every sample was collected in duplicate to be used by the laboratory in the event that further concentration of the water samples was needed, as well as for quality control purposes.

Water samples were stored in a cooler on ice and maintained at 4 degrees centigrade until delivered to the laboratories, where they were immediately refrigerated. Chain-of-custody forms were generated and accompanied the samples from sample collection through final analysis.

Coordination with USEPA

During the first year of this multi-year study, NJDEP coordinated sampling with a concurrent USEPA study that was being conducted in Region 2 (New York, New Jersey and Puerto Rico). USEPA sampled four community water systems in NJ, and these water systems were also selected for the NJ study. In the USEPA study, the focus was on drinking water systems known to be impacted by identified hazardous waste sites. In fact, USEPA selected systems where the water treatment on the well was part of the remediation strategy for the site. As these water systems fit the criteria for the NJDEP study, they were included automatically. By sampling these systems simultaneously with USEPA, it was possible to generate additional data for inter-laboratory and inter-method comparison. The two agencies coordinated sampling efforts so that water samples were collected within minutes of each other. The only difference in sampling was that NJDEP sampled every well individually as well as blended raw water and finished water, whereas USEPA collected one blended raw water sample and one finished water sample. For some of the systems, the raw water collected by USEPA was obtained from a number of wells, while, for others, one well supplied the raw water for a particular facility. In instances where many wells supplied the water, NJDEP sampled each one individually as well as collecting a blended sample, while USEPA

collected one blended water sample to reflect raw water quality overall. USEPA used two conventional analytical methods (Method 524.2 for volatile organic chemicals and Method 625 for semi-volatile organic chemicals) to analyze the water samples and investigated the TICs that were reported with these methods. They then acquired analytical standards to confirm the presence of the TICs, at which time the TICs became target analytes.

After the first year, NJDEP selected candidate water systems using the database made available from the BSDW. Criteria for selection included historical volatile organic contamination with water treatment to remove the contamination. Raw and finished water samples were collected at each selected system and analyzed using conventional methods



Well house at one of the water supply systems sampled as part of this study.

524.2 and 525.2 (for volatile and semi-volatile organic contaminants) and nonconventional methods. Conventional analyses were performed by the NJ Department of Health and Senior Services (NJDHSS), and nonconventional analyses were performed by the research laboratories at the Environmental & Occupational Health Sciences Institute (EOHSI) (GC method) and at the Rutgers Center for Advanced Food Technology (CAFT) (LC method). From 1997 through 2000, 199 water samples were collected from both untreated ground water and finished water from 21 water systems throughout NJ: 19 ground water suppliers (one water system used both ground and surface water sources – both raw waters were sampled for this study); and one surface water supplier. Bottled water samples were also provided for analysis and comparison.

CHEMICAL ANALYSIS

Tentatively Identified Compound

A TIC (Tentatively Identified Compound) is a compound that can be seen by the testing method but its identity and concentration cannot be confirmed without further investigation. TICs can be reported for both conventional and nonconventional methods. Many analytical methods can report TICs – they are compounds that the instrumentation can detect but the analysis is not targeting specifically. 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) is clear while the background (i.e., the non-target items), while captured in the picture, is fuzzy.

One of the primary objectives of this research was to begin to characterize and quantify these types of chemicals. A TIC is not a part of the targeted analyte list for a method, so it is only tentatively identified by the method. The tentative identification is based on a match between the TIC characteristics (retention time and mass spectral characteristics) and those characteristics for compounds incorporated in a mass spectral computer library database attached to the analytical

detector of the analytical instrumentation. This computer library is used to tentatively identify the compound by comparing the analytical characteristics of the detected compound with characteristics of known compounds. The computer generates a “best match” and reports the compound as a TIC. The library database used in this study was the most extensive available at the time, containing chromatograms for thousands of chemicals. In this study, matches were further evaluated by the analytical chemist, thereby strengthening the possible compound identification. A big difference between computer-generated TICs and TICs reported in this study is this extra but vital step. Whenever possible, the analyst reported the estimated concentration of the TIC. The concentration is estimated based on the known concentration of the internal standard used in the analysis peaking closest to the TIC. For more detailed explanation of the methods used and the details of TIC identification, see the final technical report, which is available from the NJDEP project manager.

Conventional Analytical Methods

All water samples were sent to the 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. The list of target analytes detected using these methods is shown in Table 2. Both USEPA methods are designed specifically for the analysis of drinking water samples. The NJDHSS laboratory also had available and used for this study a sensitive analytical adaptation of Method 525.2 for the detection of styrene-acrylonitrile trimer (a compound, which is actually the sum of four isomers, that had been detected in the United Water – Toms River water supply in November 1996). A separate analytical run was made using a more sensitive adaptation of 525.2 to detect acrylonitrile. The total number of compounds detected by conventional analysis was 130 targeted analytes. TICs reported using the conventional analysis were compared to those reported in the screening methods. Results were reported to NJDEP and were sent to the EOHSI and CAFT investigators. Conventional analyses were dropped during the final year of the study in order to better focus efforts (both economic and academic) on the TIC analysis.

Nonconventional Analytical Methods

General nonconventional methods

Nonconventional analytical methods were developed at EOHSI and CAFT. The EOHSI method utilized gas chromatography to analyze for semi-volatile and a small subset of volatile compounds. The CAFT method utilized high pressure liquid chromatography to analyze for non-volatile compounds. All water samples were analyzed by these methods at least once to screen for types of chemical compounds. In order to evaluate the characteristics of the chemicals that were present, multiple analyses of the samples were performed as the instrumentation was

Table 2. Target analytes for conventional analytical methods used in the study.

Volatile Organic Chemicals

USEPA Method 524.2

1,1,2-trichloroethane	acrylonitrile	methacrylonitrile
1,1-dichloroethane	allyl chloride	methyl acrylate
1,1-dichloroethene	benzene	methyl iodide
1,1-dichloropropanone	bromobenzene	methyl tert-butyl ether
1,1-dichloropropene	bromochloromethane	methylene chloride
1,2,3-trichlorobenzene	bromodichloroethane	methylmethacrylate
1,2,3-trichloropropane	bromoform	naphthalene
1,2,4-trichlorobenzene	bromomethane	n-butylbenzene
1,2,4-trimethylbenzene	carbon disulfide	nitrobenzene
1,2-dibromo-3-chloropropane	carbon tetrachloride	n-propylbenzene
1,2-dibromoethane	chloroacetonitrile	o-xylene
1,2-dichlorobenzene	chlorobenzene	pentachloroethene
1,2-dichloroethane	chloroethane	p-isopropyltoluene
1,2-dichloropropane	chloroform	propionitrile
1,3,5-trimethylbenzene	chloromethane	richlorofluoromethane
1,3-dichlorobenzene	cis-1,2-dichloroethene	sec-butylbenzene
1,3-dichloropropane	cis-1,3-dichloropropene	styrene
1,4-dichlorobenzene	dibromochloromethane	tert-butyl alcohol
1-chlorobutane	dibromomethane	tert-butylbenzene
2,2-dichloropropane	dichlorodifluoromethane	tetrachloroethene
2-butanone	diethyl ether	tetrahydrofuran
2-chlorotoluene	ethyl methacrylate	toluene
2-hexanone	ethylbenzene	trans-1,2-dichloroethene
2-nitropropane	hexachlorobutadiene	trans-1,3-dichloropropene
4-chlorotoluene	hexachloroethane	trans-1,4-dichloro-2-butene
4-methyl-2-pentanone	isopropylbenzene	trichloroethene
acetone	m,p-xylenes	vinyl chloride

Semivolatile Organic Chemicals

USEPA Method 525.2

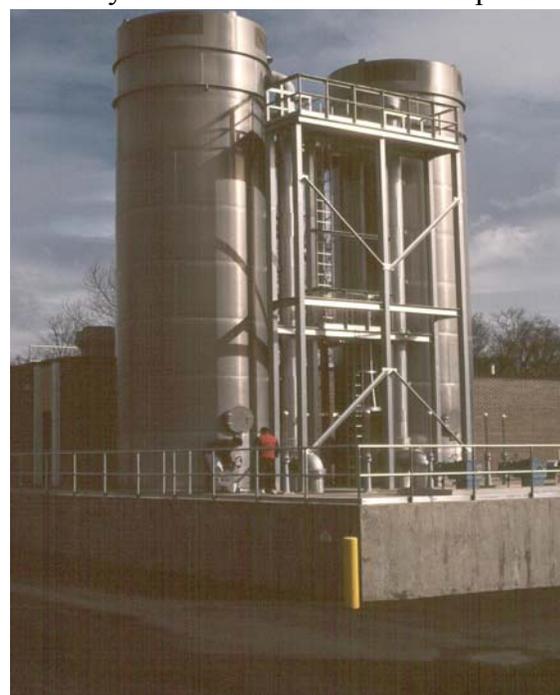
2,2',3,3',4,5,6,6'-octachlorobiphenyl	benzo[b]fluoranthene	gamma-chlordane
2,4,5-trichlorobiphenyl	benzo[g,h,l]perylene	heptachlor
2,2',4,4'-tetrachlorobiphenyl	benzo[k]fluoranthene	heptachlor epoxide
2,2',4,4',5,6-hexachlorobiphenyl	benz[a]anthracene	hexachlorobenzene
2,2',3,4,6-pentachlorobiphenyl	butylbenzylphthalate	hexachloropentadiene
2,3-dichlorobiphenyl	chrysene	indeno[1,2,3,c,d]pyrene
2-chlorobiphenyl	di(2-ethylhexy)adipate	lindane
acenaphthylene	di(2-ethylhexy)phthalate	methoxychlor
alachlor	di-n-butylphthalate	pentachlorophenol
aldrin	dibenz[a,h]anthracene	phenanthrene
alpha-chlordane	diethylphthalate	pyrene
anthracene	dimethylphthalate	simazine
atrazine	endrin	THNA trimers
benzo[a]pyrene	fluorene	Trans-nonachlor

developed and optimized. A detailed technical report on the analysis component of this study is available under separate cover. The EOHSI investigators provided several reports detailing the development of their analytical methods and the results of their analyses and of the CAFT analyses. This report interprets the analyses performed by the two laboratories and does not go into great detail on the analytical procedures, which are described fully elsewhere.

During the first two years of the study, water samples were analyzed using all analytical methods. The liquid chromatographic technique was dropped after two years because no contaminants were detected using this method, even when samples were concentrated.

Gas Chromatography with Ion Trap Mass Spectrometry (GC/ITMS)

Modified versions of USEPA Methods 525, 625 and 8270 were used on a Varian 2000 system for the analysis of the semi-volatile compounds such as pesticides, polycyclic aromatic hydrocarbons (PAHs) and polychlorinated biphenyls (PCBs). The total ionic counts were used for retention time assignment and the mass spectral data was used for compound identification or confirmation.



Air stripping system at the Rahway Water Dept, the surface water system sampled during this study.

Experiments coupling two mass spectrometers in series were possible using this equipment and were used to help identify a specific compound or to clean up a complicated mass spectrum by isolating only a few mass units at a time. This became especially important when there was a question of peak overlap between unknown compounds. Ion trap mass spectrometry uses a unique configuration of the lenses to “trap” ions of interest until they are released as desired from the trap. This enables the MS/MS or even MS/MS/MS experiments to be carried out both to improve sensitivity and to gain more information about compound structure. Ion trap mass spectrometry is a relatively new technique and may eventually replace many of the conventional quadrupole MS techniques currently used in USEPA methods. This spectrometer was used to screen for the semi-volatile compounds.

While a gas chromatography system with flame ionization detection and electron capture detection was available for compound specific confirmation by a secondary technique, it was not necessary to use this. Semi-volatile compounds were preconcentrated on solid phase cartridges and subsequently extracted with organic solvents and analyzed using gas chromatography coupled to an ion trap mass spectrometer (GC/ITMS).

Samples were introduced both by injection and by purge and trap. This instrument also has a feature that allows for samples of up to 40 liters to be used on the column. Larger sample volumes allow for potentially greater sensitivity in the detection of these semi-volatiles. This instrument has both the chemical ionization and electron impact ionization, described above, for greater flexibility in compound detection.

The current optimized method used a relatively long elution time (roughly 60 minutes) to separate all of the substituents used in the quantification scheme. Using selected compounds as target analytes, the detection limits were determined to be in the tens of picograms for six PCBs, six PAHs and six pesticides.



Well house at the Garfield Water Department, sampled as part of this study.



Well house and air stripper at the Flemington Water Department, sampled as part of this study.

High Pressure Liquid Chromatography

Water samples were concentrated under low heat and rotovapping (evaporation) then analyzed using HPLC with diode array detection. Subsequently, a VGI Fisons (micromass) mass spectrometer was used with positive ion electrospray mode of ionization. Atmospheric pressure chemical ionization mass spectrometry was also used but with less success.

Quality Assurance/Quality Control

National Institute of Standards and Technology (NIST) reference materials were used whenever possible as primary check standards both for retention time and mass spectral characteristics. There are no NIST standards available that contain all of the compounds of interest in one solution. Several were selected for use as internal quality control spikes and checks throughout the run. NIST traceable standards were used in all sample runs. These samples were used both to calibrate the retention times and mass spectral fragmentation patterns as well as to verify the accuracy of the quantitation methods employed. Approximately 10% of all of the analytes was a quality control sample.

Results

CONVENTIONAL ANALYSIS

USEPA Method 524.2: As shown in Table 3, VOC results obtained from the two laboratories (NJDHSS and USEPA), using the same methods were similar, indicating good agreement for inter-lab study (good precision). Results like this indicate that the concentration of contaminants detected are probably within the narrow range reported by the method. The volatile organic compounds most frequently detected above maximum contaminant levels in the raw waters were trichloroethylene, tetrachloroethylene, and 1,1,1-trichloroethane. Results for all the conventional analyses, including the volatiles, are presented in Table 4. Water samples collected after the air treatment systems indicated that these compounds were removed to levels below the MCLs, mostly below method detection levels, although in 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.

Trichloroethylene, tetrachloroethylene and trichloroethane are common groundwater contaminants in many areas of NJ and other parts of the U.S. In the mid-1980's, when mandatory monitoring for volatile organics began in NJ, approximately 15 to 20% of community water systems contained these solvents at levels between 1 and 100 µg/L, according to NJDEP reports. Due to the imposition of state and federal standards in the late 1980s, the number of systems with solvent violations has decreased dramatically.

Chloroform, bromodichloromethane, dibromochloromethane and bromoform are known collectively as trihalomethanes (THMs). These compounds are formed as an unintentional result of chlorine disinfection of drinking water to destroy potential disease-causing (pathogenic) microorganisms. The low levels detected in the distribution systems (approximately 1 to 5 µg/L combined) are typical of groundwater disinfected with chlorine. In many parts of NJ where surface water is chlorinated for disinfection, THM levels are typically 25 to 75 µg/L. Chloroform was also detected at low levels (generally less than 1 or 2 µg/L) with some consistency in some wells, prior to chlorination, indicating that this chemical is present in the raw samples. According to studies conducted by NJDEP and USGS, this chemical has previously been detected at low levels elsewhere in the shallow Cohansey aquifer of NJ. Although the source or sources of the chloroform are not known with certainty, chloroform in untreated well water may be present due to the discharge of bleach from septic tanks or waste sites.

Table 3. Comparison results of conventional analysis by NJDHSS and USEPA labs, including the reporting of TICs from the various methods used by the two laboratories.

Location	Analyses	Conventional Contaminants Detected by NJDHSS: concentration (µg/L or ppb)	Conventional Contaminants Detected by USEPA : concentration (µg/L or ppb)	NJDHSS TICs: TICs at Q=> 50	USEPA TICs: Nontarget Contaminants estimated concentration (µg/L)
WEEK OF DECEMBER 5, 1997 SAMPLING EVENT WITH USEPA					
Rockaway Boro : Facility #01 Raw, wells 1,5,6	USEPA: 524.2, 625 NJDHSS: 524.2, 525.2	cis-1,2-dichloroethylene: 1 trichloroethylene: 4 tetrachloroethylene: 44	cis-1,2-dichloroethylene: 1.2 trichloroethylene: 4.5 tetrachloroethylene: 49 1,1,2-trichloroethane: 1.9	phthalic anhydride	none
Rockaway Boro : Facility #01, Treated	USEPA: 524.2, 625 NJDHSS: 524.2, 525.2	chloromethane: 3	chloromethane: <1		Oleic acid: 35
Rockaway Township Water. Co.: Fac 01, Raw blended	USEPA: 524.2, 625 NJDHSS: 524.2, 525.2	1,1-dichloroethylene: 0.8 MTBE: 1 1,1-dichloroethane: 1 cis-1,2-dichloroethylene: 0.8 1,1,1-trichloroethane: 5 trichloroethylene: 32	1,1-dichloroethylene: 1.05* MTBE: not anal. 1,1-dichloroethane: <1 cis-1,2-dichloroethylene: <1 1,1,1-trichloroethane: 4.5* trichloroethylene: 27*		
Rockaway Township Water. Co.: Fac 01, Treated	USEPA: 524.2, 625 NJDHSS: 524.2, 525.2	none	tetrachloroethylene: 1*	1-methyl-4-(1-methylbenzene) (1195-32-0)	
Merchantville Pennsauken: Fac. National, Raw, blended	USEPA: 524.2, 625 NJDHSS: 524.2, 525.2	1,1-dichloroethylene: 1 1,1-dichloroethane: 4 cis-1,2-dichloroethylene: 8 chloroform: 1	1,1-dichloroethylene: 1.6 1,1-dichloroethane: 4.2 cis-1,2-dichloroethylene: 8.6		Oleic acid: 7.15*

Location	Analyses	Conventional Contaminants Detected by NJDHSS: concentration (µg/L or ppb)	Conventional Contaminants Detected by USEPA : concentration (µg/L or ppb)	NJDHSS TICs: TICs at Q=> 50	USEPA TICs: Nontarget Contaminants estimated concentration (µg/L)
		1,1,1-trichloroethane: 2 1,2-dichloroethane: 0.7 trichloroethylene: 3 1,2-dichloropropane: 2 tetrachloroethylene: 2	chloroform: 1.4 1,1,1-trichloroethane: 2.6 1,2-dichloroethane: <1 trichloroethylene: 2.9 1,2-dichloropropane: 1.9 tetrachloroethylene: 1.9		
Merchantville Pennsauken: Fac National, treated	USEPA: 524.2, 625 NJDHSS: 524.2, 525.2	dibromochloromethane: 4 bromoform: 0.6	dibromochloromethane: <1 bromoform: <1	5,9,13-pentadecatrien- 2-one (1117-52-8)	
Perth Amboy-Old Bridge Water Dept.: Fac. 01, Raw well 6A	USEPA: 524.2, 625 NJDHSS: 524.2, 525.2	chlorobenzene: 0.3	chlorobenzene: <1	indolo(2,3- b)quinolizine, 1 (13233-45-9)	

* Average of two analytical runs on the same sample.

** Compound found in only one of two duplicate samples collected. Oleic acid was detected in a trip blank at 3.5 ppb.

Note: MCLs for the conventional contaminants listed in the table are: cis-1,2-dichloroethylene, 70 µg/L; trichloroethylene, 1 µg/L; tetrachloroethylene, 1 µg/L; 1,1,2-trichloroethane, 3 µg/L; 1,1-dichloroethylene, 2 µg/L; 1,1-dichloroethane, 50 µg/L; MTBE, 70 µg/L; 1,1-dichloroethane, 50 µg/L; cis-1,2-dichloroethylene, 70 µg/L; 1,1,1-trichloroethane, 30 µg/L; trichloroethylene, 1 µg/L. **Trihalomethanes:** Dichlorobromomethane, Chlorodibromomethane, Bromoform and Chloroform: : 80 µg/l running annual average of total of these 4.

Table 4. Results of conventional analysis by NJDHSS lab (units are ug/L). Blank cells are non-detects.

Water Supply		Arsenic	Mercury	chloroform	Total THMs	Trichloroethylene	Tetrachloroethylene	1,1,1-Trichloroethane	cis-1,2-dichloroethylene	1,1-dichloroethane	1,1-dichloroethylene	MTBE
MCL, ug/L		10	2	Total	Total	1	1	30				70
Bottled Water												
Trip blank	blank	1.2	0.06									
Field blank	blank		0.08	0.4 - 60	0.5							0.6
Dept.	Raw											
Dept.	Finished				0.3-1.0							
Fair Lawn Water Dept.	Raw			0.5 - 13	0.5-6	2 - 51	1 - 320	0.5 - 28	1 - 54	0.6 - 4	1 - 13	1 - 270
Fair Lawn Water Dept.	Finished		0.08		0.3-5				1			0.7
Flemington Water Dept.	Raw	5 - 12		0.5		28 - 35	2		5			
Flemington Water Dept.	Finished	12.2			0.4							
Garfield Water Dept.	Raw			0.6 - 1	0.2-0.5	0.6 - 100	2 - 15	7	0.6 - 110	1	3	1
Garfield Water Dept.	Finished											
Pennsauken	Raw			1	0.6-4	1 - 81	0.8 - 5	2 - 23	0.5 - 8	4	1 - 16	0.5
Pennsauken	Finished											
Newton Water Dept.	Raw			0.95	1.2			1.5				
Newton Water Dept.	Finished			0.76								
Park Ridge Water Dept.	Raw			0.3 - 2		0.6 - 22	0.8 - 52	0.6 - 3	0.5 - 10		0.4 - 0.7	0.9 - 1
Park Ridge Water Dept.	Finished			0.3 - 1		0.8	0.8					0.8
Perth Amboy-Old Bridge	Raw				0.4-1.2						0.1	
Perth Amboy-Old Bridge	Finished			6								
Rahway Water Dept.	Raw				3.9-4	0.33 - 3	4					0.63 - 2
Rahway Water Dept.	Finished			11 - 34								
Ridgewood Water Dept.	Raw			0.98			0.67 - 2.9					
Ridgewood Water Dept.	Finished											
Raw	Raw					4	44		1			
Finished	Finished											
Rockaway Township	Raw			0.8		1 - 76	13	2 - 10	0.8 - 2	1-1	0.8 - 2	0.5 - 1
Rockaway Township	Finished	3.1										
Rocky Hill Water Dept.	Raw	3.2										
Rocky Hill Water Dept.	Finished											
Rosemont Water Dept.	Raw				0.5-2							
Rosemont Water Dept.	Finished	2.2	0.08									
Salem Water Dept.	Raw	1.9	0.05 - 0.08	0.13								
Salem Water Dept.	Finished											
Sea Girt Water Dept.	Raw				0.9							
Sea Girt Water Dept.	Finished	1.2	0.06	1								
UWTR- Dover Township	Raw											
UWTR- Dover Township	Finished	2.8, 1.2										
Waldwick Water Dept.	Raw	1.3 - 2.8		0.3	0.5-2	1 - 9	3 - 20	0.7 - 0.8	8		0.3	0.5
Waldwick Water Dept.	Finished			2								

Table 4 cont'd.

Water Supply		Other (ug/L)	MCL (ug/L)
Trip blank	blank	chlorobenzene - 0.3	50
		o-xylene - 0.7	1000 (total)
		methylene chloride - 2	3
Field blank	blank	methylene chloride - 0.4-2	3
		chlorobenzene - 0.4-0.5	50
Bottled Water		toluene - 0.23-0.38	1000
Elizabethtown Water Dept.	Raw		
Elizabethtown Water Dept.	Finished		
Fair Lawn Water Dept.	Raw	carbon tetrachloride - 0.5-4	2
		chlorobenzene - 1	50
		1,3-dichlorobenzene - 0.7	600
		1,4-dichlorobenzene - 3	75
		1,2-dichlorobenzene - 2-15	600
		1,2,4-trichlorobenzene - 0.5	9
Fair Lawn Water Dept.	Finished		
Flemington Water Dept.	Raw	carbon tetrachloride - 5	2
Flemington Water Dept.	Finished	chlorobenzene - 0.3	50
Garfield Water Dept.	Raw	dichlorodifluoromethane - 2.0	none
		trans-1,2-dichloroethylene - 0.6	100
			2
Garfield Water Dept.	Finished		
Merchantville-Pennsauken	Raw	1,2-dichloropropane - 2	5
		1,1,2-trichloroethane - 0.3	3
		atrazine - 0.73	3
		1,2-dichloroethane - 0.7-0.8	2
		methylene chloride - 1, 1, 2, 8	3
Merchantville-Pennsauken	Finished		
Newton Water Dept.	Raw		
Newton Water Dept.	Finished		
Park Ridge Water Dept.	Raw		
Park Ridge Water Dept.	Finished		
Perth Amboy-Old Bridge	Raw	chlorobenzene - 0.3	50
Perth Amboy-Old Bridge	Finished		
Rahway Water Dept.	Raw		
Rahway Water Dept.	Finished	1,1-dichloropropanone - 1.3	none
Ridgewood Water Dept.	Raw	dieldrin - 0.06-0.56	none
		heptachlor epoxide - 0.062	0.2
Ridgewood Water Dept.	Finished		
Rockaway Borough: Raw	Raw	1,1-dichloroethylene - 2	2
Rockaway Borough: Finished	Finished	methylene chloride - 3	3
Rockaway Township	Raw	trichlorofluoromethane -2	none
Rockaway Township	Finished		
Rocky Hill Water Dept.	Raw		
Rocky Hill Water Dept.	Finished		
Rosemont Water Dept.	Raw		
Rosemont Water Dept.	Finished		
Salem Water Dept.	Raw		
Salem Water Dept.	Finished		
Sea Girt Water Dept.	Raw		
Sea Girt Water Dept.	Finished		
UWTR- Dover Township	Raw		
UWTR- Dover Township	Finished		
Waldwick Water Dept.	Raw		
Waldwick Water Dept.	Finished		

USEPA Method 525.2: This method revealed the presence of targeted compounds. Of the targets, phthalates were reported frequently, in both samples and in field, trip and laboratory reagent blanks, at levels generally less than 1 µg/L. The highest reported phthalate level for conventional contaminants was di(2-ethylhexyl)phthalate at 2.89 µg/L in a trip blank. Phthalates are common components of plastic materials, and the low levels detected are likely to be the result of trace contamination of the laboratory or sampling environment from ubiquitous plastics. For this reason, the NJDHSS Laboratory suggests that phthalates at levels below 2 or 3 µg/L probably reflect contamination during sampling, sample handling, and analysis. Even if present in environmental samples, the levels of phthalates are well below health-based guidance levels. Reference guidance for di-n-butyl phthalate, butylbenzyl phthalate and diethyl phthalate in drinking water are 1000, 2000 and 5000 µg/L, respectively. The MCL for di(2-ethylhexyl) phthalate is 6 µg/L.

Atrazine was detected in a raw water sample in the Merchantville-Pennsauken water system at a level below the current MCL for this herbicide of 3 µg/L.

SCREENING ANALYSIS

High Pressure Liquid Chromatography

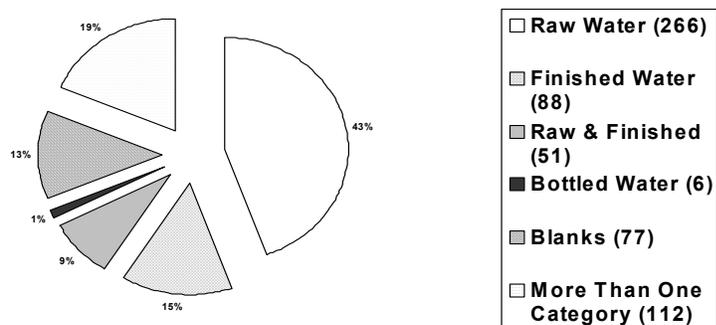
During the first two years of the study, no non-volatile compounds were detected using HPLC. During the third year of the study larger sample sizes were analyzed. Two liters of sample were used instead of one to improve the overall method detection limit. Even with larger sample size, almost all of the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

Gas Chromatography

Water Systems:

Over the course of the 4 year study, approximately 600 tentatively identified organic compounds 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 this one compound is included under “more than one category”. The remaining 488 were detected in the distribution shown in Figure 2 and Table 5, which delineate TIC distribution in raw, finished, raw & finished, bottled and blank samples. All chemicals detected are TICs. A follow-up to this study is seeking to confirm the identities of several of the TICs (such as atrazine) by running the method with corresponding analytical standards (for instance, to confirm the presence of atrazine in a water sample, a standard containing atrazine at known concentrations would be analyzed in

Figure 2. Distribution of TICs (unique to the group) by type of water sample.



the same series as the water samples). By so doing, concentrations for the chemicals will be generated as well.

One of the interesting patterns observed in the data was that unique TICs appeared in almost all of the water systems (see Figure 3 and 4 for TIC distribution by water system) and in the bottled waters. That is, there were TICs in one water system that did not appear again in the study. There were no unique TICs in the water samples collected from the control water system. This indicates that the water systems sampled impacted by hazardous waste sites have unique chemicals affecting them. Bottled and blank water samples contained unique TICs in their respective groups as well.

Table 5. Numbers of TICs found in 20 water systems.

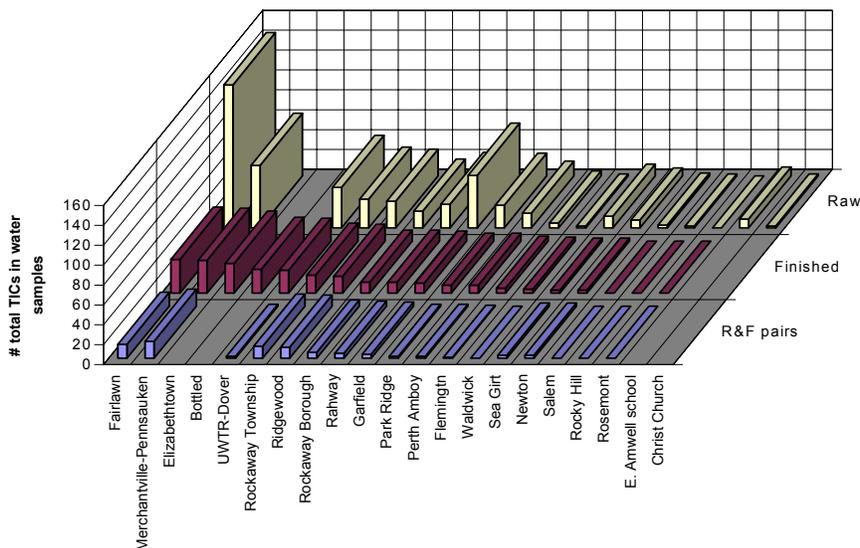
Sample Type (N)	Number of TICs detected total in the group	Number of TICs detected in the group but not in corresponding blanks	Number of TICs in the group and not in other groups
Raw water samples* (108)	399	338	266
Finished water samples* (51)	195	154	88
Both Raw and Finished water samples**	84	58	51
Bottled waters (5)	32	24	6
Field & Trip Blanks (35)	164	95	77
TOTAL NUMBER OF TICs	600	600	600***

*Does not include TICs that were detected in both raw and finished samples from the same system.

**TIC was found in both the raw and the finished water samples from the particular system.

*** Includes TICs found in multiple categories.

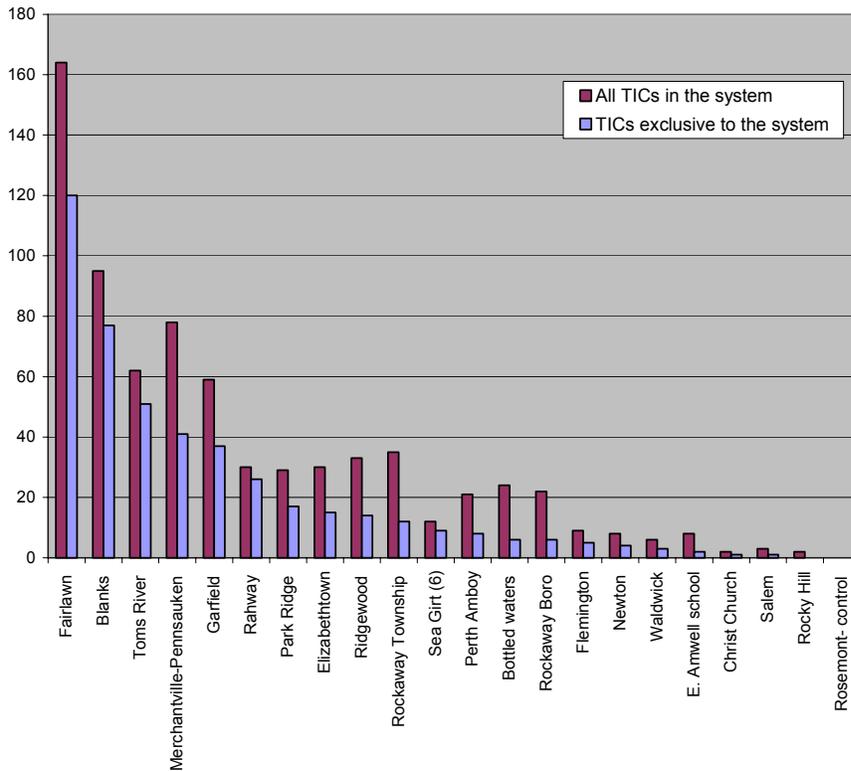
Figure 3. TICs in Water Samples (not including TICs that were detected in blanks)



Raw & Treated Sample Pairs

The most frequently detected TIC in raw & finished water samples (and that did not appear in corresponding blank samples) was 2,4-(3H,5H)furandione, 3-methyl. Some of the commonly detected TICs are shown in Table 6. While atrazine (a commonly used herbicide) was detected

Figure 4. Number of TICs Found by System



once in corresponding raw and finished water samples, it appeared in six additional raw water samples in two of the 20 systems sampled. In the instance where atrazine was detected in both raw and finished water, carbon treatment was not present. 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. Incidentally, the conventional analytical method 525.2 also detected atrazine in one of the same raw water samples where it appeared as a TIC. The EOHSI method was able to detect this pesticide in the finished water at that same system as well as in the raw water of an additional water system.

The study results show that some semi-volatile organic chemicals appearing in raw water are not removed by existing air treatment technology, though carbon treatment was very effective at removing both the volatile and semi-volatile compounds present.

Table 6. Some examples of TICs detected in raw & treated pairs of samples.

Tentatively Identified Compound in raw and treated samples collected from the same water system	Number in corresponding blanks	Number in sample pairs, and not in corresponding blank	Use, toxicity and health information available
diethyl phthalate	10	4	It is used as a solvent, a wetting agent and a plasticizer. Classified as practically non-toxic, based on oral LD50. Mutagen.
phenol, 2,4-bis(1,1-dimethylethyl)	4	4	Alkylphenols are a class of environmentally pervasive compounds, found both in natural (e.g., crude oils) and in anthropogenic (e.g., wood tar, coal gasification waste) materials. Alkyl phenols can inhibit the enzyme cyclooxygenase).
hexadecanoic acid	1	3	It is used in the manufacture of metallic palmitates, soaps, lube oils, waterproofing, and food-grade additives. Mild irritant to human skin. Classified as practically non-toxic, based on oral LD50. Wells in the Besos basin, Northeast Spain were found to contain palmitic acid concns ranging from 40 to 430 ng/l (hsdb). Found in Cincinnati, OH on October 17, 1978; Cincinnati, OH on January 14, 1980; Miami, FL on February 3, 1976; New Orleans, LA on January 14, 1976; Philadelphia, PA on February 10, 1976; Ottumwa, IA on September 10, 1976 and Seattle, WA on November 5, 1976. (hsdb)
2,4-(3H,5H)furanedione, 3-methyl	0	3	There is no available information in the literature on this chemical.
butylated hydroxytoluene	10	2	Food additive, antioxidant for synthetic rubbers, plastics, soaps, animal and vegetable oils; antiskinning agent in paints and ink. Positive animal carcinogen; mutagenic, tumor promoter; eyes, skin and upper respiratory irritant. Classified as slightly toxic, based on oral LD50.
di-n-octyl phthalate	2	2	Reproductive Effector, Primary Irritant, Practically Non-Toxic to Relatively Harmless An experimental teratogen. Low via intraperitoneal route. A skin and eye irritant. Oral, Rat, 47 g/kg (Relatively Harmless), Intraperitoneal, Rat, >50 ml/kg; Oral, Mouse, 6513 mg/kg (Practically Non-toxic).
nonanoic acid	2	2	Organic synthesis, lacquers, plastics, production of hydrotropic salts, pharmaceuticals, synthetic flavors and odors, flotation agent, esters for turbojet lubricants, vinyl plasticizer, gasoline additive.
benzene,1,1'(1,1,2,2-tetramethyl-1,2-ethanediyl)bis	1	2	Vulcanizing agent for natural & synthetic rubber; crosslinking agent for polyethylene; synergist for flame retardants in polystyrene foams; curing agent for silicone rubber
octadecanoic acid	0	2	Additive in industrial preparations. Used in the manufacture of stearates of aluminum, zinc and other metals, used in soap, candles, phono- graph records, insulators, modeling compounds, impregnating plaster of Paris, vanishing creams and other cosmetics, stearate driers, lubricants, soaps,

			pharmaceuticals, shoe and metal polishes and food packaging. Considered nontoxic. Negative animal carcinogenic study.
phenol,4,4'--(1,2-diethyl-1,2-ethanediyl)bis-,(R*,S*)-	0	2	Tumorigen, Drug, Mutagen, Reproductive Effector, Hormone Slightly Toxic
benzenesulfonamide,N-butyl	6	1	Classified as slightly toxic, based on oral LD50.
bis(2-ethylhexyl) phthalate	6	1	Plasticizer, used in vacuum pumps, pesticides. relatively harmless, primary irritant, tumorigen, mutagen, reproductive effector
2,5-heptadien-4-one, 2,6-dimethyl	1	1	LD 50: Subcutaneous, Rabbit, 700 mg/kg
1,2-benzenedicarboxylic acid, 3-nitro	0	1	Phthalate esters Used as Industrial Plasticizers; readily leached and volatilized from various formulated products; potentially hazardous to several organisms; readily biodegradable)
1,3-dichlorobenzene	0	1	Tumorigen, Mutagen. MCL is 600 ppb. LD50 Intraperitoneal, Mouse, 1062 mg/kg
1H-indene,2,3-dihydro-1,1,3-trimethyl	0	1	Volatile hydrocarbon compound found in some air samples at contaminated areas
1H-indine,1-ethylidene-	0	1	Volatile hydrocarbon compound found in some air samples at contaminated areas.
2-mercaptobenzothiazole	0	1	Fungicide, rubber vulcanization, canine & bovine ointment Contact dermatitis, positive animal carcinogen
atrazine	0	1	Herbicide. Positive animal carcinogen; heart, lung and kidney congestion, hypotension, muscle spasms.

* Unknowns with numbers were named according to their retention time in the analytical run.

Finished Drinking Water Samples

One of the most significant objectives of the study was the characterization of TICs in finished water, representing water delivered to the general public. There are two categories of interest in this group: 1) TICs in finished water that were also present in raw water and therefore not removed by existing treatment, and 2) TICs unique to finished water, indicating that treatment techniques or reagents themselves are introducing TICs into the water.

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

Table 7. Selected TICs found more than once in treated water samples only.

TIC	# detects	Use, toxicity and health information available
quinoline, 8-methyl	3	Mutagen
butane, 1,2-dibromo-	2	Undergoing review
4,4'-dichlorodiphenylsulphide	2	LD oral, rodent-rat > 500 mg/kg.
1-H-pyrrole-2,5-dione, 3,4-dichloro-1-phenyl-	2	Undergoing review
thiourea,N'-phenyl-N,N-dipropyl	2	Undergoing review
2,3,4-tribromothiophene	2	Undergoing review

While 88 unique TICs were detected in finished water samples, only 8 of these appeared in more than one finished water sample (shown in Table 7). 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. This is not surprising, as the addition of disinfection chemicals leads to the formation of by-products. 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, 266 were detected only in raw water samples, 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 water 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.

Table 8. Number of times TICs found in raw water samples only

bromacil	11	Isothiazole,4-methyl	2
1-eicosanol	6	Mepivacaine	2
1,2,5,6-tetramethylacenaphthylene	6	Methanone,phenyl(5,6,7,8-tetrahydro-2-naphthalenyl)-	2
benzene,(1,1-dimethylnonyl)-	5	Metolachlor	2
hexadecanoic acid, octadecyl ester	5	1-naphthalenamine	2
acridine,9,10-dihydro-9,9,10-trimethyl-	4	2-naphthalenamide	2
cyclotetradecane,1,7,11-trimethyl-4-(1-methylethyl)	4	1,3,2-oxazaborolidine,3,4-dimethyl-2,5-diphenyl	2
2-propenal,3-(2,2,6-trimethyl-7-oxabicyclo[4.1.0]hept-1-yl)	4	pentadecane, 4-methyl-	2
unknown 21.8	4	phenanthrene	2
2-propenoic acid, 3-(4-methoxyphenyl)-2-ethylhexyl ester	4	2-phenyl-4,6-di(2-hydroxyphenyl)pyrimidine	2
cyclodecanol	3	6H-purine-6-thione,1,7-dihydro-1-methyl	2
Cyclododecanemethanol	3	triindenol[2,3:3',3',2'',3''']benzene	2
7-hydroxy-7,8,9,10-tetramethyl-7-8-dihydrocyclohepta[d,e]naphthalene	3	2,3,4-trimethyl hexane	2
3-methoxy-2-methyl-cyclohex-2-enone	3	undecanone,2-methyl oxime	2
2H-pyran,tetrahydro-2-(12pentadecyloxy)-	3	bis (2-methoxyethyl)phthalate	2
Toluene,3-(2-cyano-2-phenylethenyl)	3	benzamide, N-(4-hydroxyphenyl)-2-methyl	2
Benzene, 1-isocyanato-2-methyl-	3	Benzene, (1,1-dimethylbutyl)-	2
1,2-benzenedicarboxylic acid, 3-nitro	3	Benzene (1-methyldecyl)-	2
Phenol, 3-(1,1-dimethylethyl)-4-methoxy-	3	Benzene, 1,3,5-tri-tert-butyl	2
Hexanoic acid, 3,5,5-trimethyl-,1,2,3-propanetriyl ester	3	Benzene,1-ethyl-3-methyl	2

Ethanone, 1-(5,6,7,8-tetrahydro-2,8,8)	2	5-hexadecenoic acid, 2-methoxy-, methyl ester	2
1H-indene, 2,3-dihydro-4,5,7-trimethyl	2	9,12-octadecadienoic acid (Z,Z)-	2
2-isopropenyl-3,6-dimethylpyrazine	2	Unknown 12	2
		Unknown 21.6	2
		Unknown 24.38	2
		Unknown 25.1	2

The most frequently detected TICs in raw water samples overall include: bromacil, 1-eicosanol, a naphthalene derivative and a benzene derivative. These and other TICs detected in raw water samples and not in blanks (or detected infrequently in blanks) are listed in Table 8. Table 8 shows those compounds where a particular TIC appeared in more than one raw water sample and did not occur in the corresponding blank samples (or occurred infrequently, as compared to its occurrence in raw water samples).

In some water systems, the TICs occurred in the raw water sample and not in corresponding blank samples, but at other water systems, the TICs were detected in both the raw water samples as well as the blanks. The detection of a TIC in the blank water sample does not necessarily mean that it is not present in the environmental sample, but it does raise suspicion. This issue is discussed further in the blanks section of the report.

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 and these are listed in Table 9. Only one of the eight TICs unique to bottled waters was detected in more than one bottled water and not detected in the blanks: 3,5-di-tert-butyl-4-hydroxybenzyl alcohol. NJDHSS has reported in their review of bottled waters sold in NJ that none had detectable levels of semi-volatile organics, using Method 525.1. Several volatile compounds were detected at trace levels using USEPA Method 524.2. The report does not describe TIC occurrence, so it is not known what types of TICs may have appeared in the method.



Sample bottles for conventional analytical methods are washed and reused. Residual contaminants may be present in the bottles themselves and be detected in the analytical method as TICs.

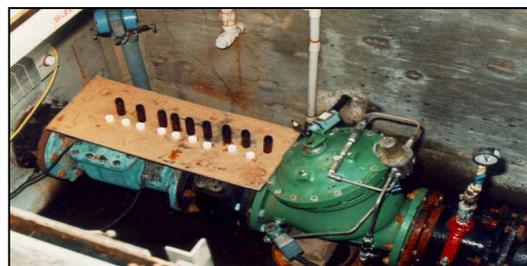
Table 9 . Some of the TICs found in bottled water samples and their properties.

TIC	Use, toxicity and health information available
3,5-di-tert-butyl-4-hydroxybenzyl alcohol	Mutagen. Oral, Rat, 7 g/kg; Oral, Mouse, 7 g/kg
L-alanine,N-[phenylmethoxy]carbonyl]-	There is no available information in the literature on this chemical
coumarin-6-ol,3,4-dihydro-4,4,5,7-tetramethyl-,methylsulfate(ester)	LD50, Oral, Rodent-rat, 1500 mg/kg
pyrimidine,6-oxo-5-acetyl-4-hydroxy-1,6-dihydro-	There is no available information in the literature on this chemical
diisooctylphthalate	There is no available information in the literature on this chemical

benzene,1-methyl-4-(1-methylpropyl)	There is no available information in the literature on this chemical
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Blank Samples

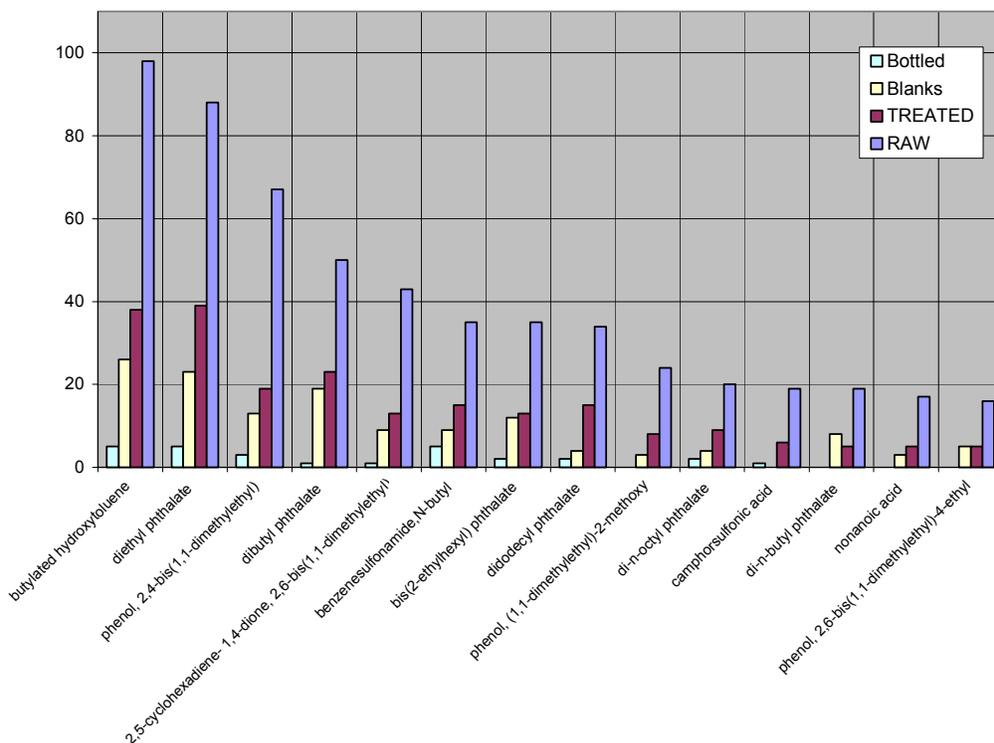
Because of the prevalence of TICs in blank water samples, it is difficult to interpret their presence in environmental water samples. However, several patterns emerge when investigating the data of TICs in blank water samples: there is a population of TICs that occur only in blanks; there are TICs that occur frequently in blanks and environmental samples; and there are TICs that sometimes appear in a blank and



Collection of sample, duplicates and field blanks at one of the Fairlawn well sites.

sometimes appear in an unrelated environmental sample. For instance, in raw & finished pairs, there were 51 TICs unique to this group and where these TICs were not detected in the corresponding blanks. If we eliminate TICs that ever appeared in any blank sample during the course of the entire study from this population of 51, the number of TICs is reduced to 36. Some examples of TICs and their occurrence in the study are shown in Figure 5.

Figure 5. Examples and numbers of TICs in sample types



These patterns are actually not unique to TICs. When first investigating volatile organic chemicals, researchers needed to address the issue of blank occurrence of these compounds. 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. 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 on the actual occurrence of a contaminant in an environmental sample.

Due to the complexity of interpreting TIC data in general and in blanks in particular, the data in Table 10 show the most frequently detected TICs in the study, showing their distribution in raw, finished and bottled water samples alongside their occurrence in the blank water. Further complicating the interpretation of the TIC data is the lack of information in the literature on the occurrence of these compounds in drinking water. Recently, the USGS published the results of a study showing the occurrence of trace levels of pharmaceutical chemicals (target analytes) in surface raw waters downstream of sewage treatment plants. But the USGS study did not investigate the presence of compounds in raw waters used for drinking water nor in finished drinking water itself. Nor did they report TICs.

Butylated hydroxytoluene (BHT) was the TIC most frequently detected in the study overall. This compound is ubiquitous in the environment, as it is used widely commercially as an overall preservative and food additive. BHT was detected in blank samples as well as the bottled and water supply system samples. Its presence in the blanks raises suspicion about its actual occurrence in the environmental samples but does not eliminate it as a potential environmental contaminant.

The TICs detected most frequently in blank samples and that also appeared in environmental samples are shown in Table 10. In general, the TICs listed in this table were considered suspect when detected in an environmental samples, due to their detection frequency in blank samples. However, further work is needed to estimate concentrations of the TICs in blank samples in order to more fully understand the presence of these particular TICs in environmental samples.

Table 10. Number of samples where a TIC was detected.

TIC	Blanks (35*)	Raw (108*)	Finished (51*)	Bottled (5*)
butylated hydroxytoluene	26	98	38	5
diethyl phthalate	23	88	39	5
dibutyl phthalate	19	50	23	1
phenol, 2,4-bis(1,1-dimethylethyl)	13	67	19	3
bis(2-ethylhexyl) phthalate	12	35	13	2
2,5-cyclohexadiene-1,4-dione, 2,6-bis(1,1-dimethylethyl)	9	43	13	1
benzenesulfonamide,N-butyl	9	35	15	5
di-n-butyl phthalate	8	19	5	0
phenol, 2,6-bis(1,1-dimethylethyl)-4-ethyl	5	16	5	0
unknown 25.6	5	11	5	0
benzaldehyde, 4-nitro-,	5	11	4	0

oxime				
unknown 42.3	5	8	9	0
unknown 31.9	5	8	5	0
didodecyl phthalate	4	34	15	2
di-n-octyl phthalate	4	20	9	2
unknown 21.7	4	13	11	0
3,5-di-tert-butyl-4-hydroxybenzaldehyde	4	9	4	0
caffeine	4	3	2	0
phenol, (1,1-dimethylethyl)-2-methoxy	3	24	8	0
nonanoic acid	3	17	5	0
1,2-benzisothiazole	3	3		0
benzyl butyl phthalate	3	1	3	0
hexadecanoic acid	2	13	5	0
benzene,1,1'(1,1,2,2-tetramethyl-1,2-ethanediyl)bis	2	12	7	0
1,2,3,3a,4,5,6,10b-octahydrofluoranthene	2	12	3	0
butylated hydroxyanisole	2	11	3	1
2,5-heptadien-4-one, 2,6-dimethyl	2	11	3	0
octadecanoic acid, 2-methylpropyl ester	2	10	0	0
1H-indene, 2,3-dihydro-1,4,7-trimethyl	2	6	0	0
phenol,4,4'--(1,2-diethyl-1,2-ethanediyl)bis-(R*,S*)-	2	5	3	0
7,9-di-tert-butyl-1-oxaspiro(4,5)deca-6,9-diene-2,8-dione	2	4	3	0
phenyl, nonyl	2	3	1	0
thiophene, 2,5-bis(1,1-dimethylpropyl)-, or thiophene, 2,5-bis(2-methylpropyl)	2	3	0	0
1,3-dichlorobenzene	2	3	0	0
phenol,o-(4,6-diamino-s-triazin-2-yl)	2	2	1	1
benzoic acid	2	2	0	0
H-1-benzopyran-2-carboxylic acid, 60amino-4-oxo-, ethyl ester	2	2	0	0
phenol,4,4'-(1-methylethylidene)bis-butylbenzylphthalate	2	2	0	0
ITD ionol	2	1	1	4
tridecane,2-methyl-2-phenyl-	2	1	1	1

* Number of samples collected and analyzed in this category.

Toxicity Assessment

A component of this study included a review of available literature on the manufacture, use in industry, fate & transport in the environment, chemical characteristics, toxicity in animals, and human health effects of the TICs found in the study. This information was available in varying amounts. For some of the compounds, particularly some of the pesticides, food additives, pharmaceuticals and pharmaceutical by-products, there was a great deal of information available. For most of the TICs, however, very little information was available for review. A separate study is currently in progress investigating the available toxicity and health information of these TICs. It is being conducted by toxicologists and public health experts at the College of Public Health at the University of Medicine and Dentistry, NJ (UMDNJ). A report on this work is expected by the summer 2003.

Information on some of the TICs present in finished drinking water and in bottled water is presented in Tables 6, 7 and 9 . It is anticipated that much more information on potential human health impacts will be available upon completion of the UMDNJ report.

Discussion

IMPACT OF HAZARDOUS WASTE SITES ON CONTAMINANT OCCURRENCE IN GROUND WATERS

For the past several years (beginning around the same time as this study), the NJDEP has been delineating Source Water Assessment areas around all wells and surface water intakes used by public water systems throughout the state as part of the Source Water Assessment Program (SWAP). A public water system is defined as "a system for the provision to the public of water for human consumption through pipes or other constructed conveyances, if such system has at least fifteen service connections or regularly serves at least twenty-five individuals. NJDEP Source Water Assessment Plan can be found at www.state.nj.us/dep/swap.

The purpose of the SWAP is to provide for the protection and benefit of public water systems and to increase public awareness and involvement in protecting these sources. In addition, the SWAP will allow the State to determine if current monitoring should be revised based on individual assessments. For each ground water source, three tiers are calculated and labeled as Tier 1, a 2 year time of travel; Tier 2, a 5 year time of travel; and Tier 3, a 12 year time of travel. Within these tiers, all contaminated sites and land uses are identified to assist in determining the water source's susceptibility to contamination.

These SWAP assessment areas have been delineated and are available for several of the water systems sampled as part of this study. They are shown in Figures 6-9. Hazardous waste sites exist in all three tiers of the protection areas (distinguished by color on the figures). Tier 1 indicates a two year travel time for water to travel from a contaminated site in this zone to the well; Tier 2 indicates a five year travel time; and Tier 3 indicates a 12 year travel time. In other words, for a site located in the Tier 3 delineation of a water supply well, it may take water (and presumably a contaminant, though contaminants generally travel slower than water) from that site 12 years to reach the well.

When looking at the maps, it is clear that there are potential sources of contamination near some of the community supply wells sampled as part of the study. The Department 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. The Department is initiating a complementary study in the next year to actually track contaminants emanating from hazardous waste sites to wells used for drinking water. By evaluating the data on what types of wastes were disposed of at the sites and analyzing water samples from both site monitoring wells as well as potentially impacted drinking water wells, it may be possible to definitively link a specific site as the source of contamination to a well. GC and more sensitive LC analytical methods are

expected to be used in the tracking. The SWAP delineations will be very helpful in the follow-up study where tracking of chemicals from waste sites to public wells will be attempted.

RISK ASSESSMENTS FOR MIXTURES

Both the federal USEPA and state NJDEP regulate individual contaminants in drinking water by establishing maximum contaminant levels (MCLs) for them. These MCLs have been developed for organic chemicals with a history of occurrence in the waters of the country and in the state. For instance, trichloroethylene is detected frequently in groundwater in NJ at various concentrations and often at levels of human health significance. It was therefore prudent for the state to develop an individual health-based water standard for this compound. Adversely, it is difficult to recommend the development of chemical-specific MCLs for the compounds (detected as TICs) described in this study for a number of reasons: the identifications are tentative rather than definitive; the concentrations are estimates; there is sparse information available on human health effects; and many were detected in only one water system. New York is considering the possibility of developing action levels or guidelines for chemical classes. That is, numerical limits or guidelines are set on classes of compounds having a similar chemical structure and thought to behave similarly in the human body. This is a difficult and somewhat subjective exercise but represents an important step toward further protecting human health.

USEPA has developed guidelines for the health risk assessment of chemical mixtures. The assessment assumes the availability of toxicological information for each individual chemical in the mixture. In the cases described in this study, not all components in the water samples are definitively known, exposure data are uncertain, and toxicological data on the tentatively identified components of the mixtures are severely limited. Therefore, it is impossible to conduct actual risk assessments on TIC mixtures in water. Assessment of risk on waters having a mixture of chemicals present and having a number of TICs included in the mixture would need to be done on a case-by-case basis. The issue of how or even if to regulate individual unusual compounds in drinking water is complex. It is further complicated when one considers that there may be more than one such compound in a water sample.

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.

The study described herein focused on the occurrence of TICs in water samples from water supply systems using ground water as their water source. 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 UMDNJ have scanned 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.

