Implementation of the National Pesticide Survey, and Recommendations for Conducting Future Occurrence Surveys[1]

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Background

In 1984, a joint project between the USEPA's Office of Ground Water and Drinking Water (OGWDW) and the Office of Pesticide Programs (OPP) was initiated to conduct a statistically based survey of pesticide contamination of drinking water wells. The National Pesticide Survey (NPS) had two primary objectives. The first objective was to provide statistically valid data which could be extrapolated to represent both rural domestic and community drinking water wells nationally. The second objective was to attempt to evaluate possible associations between pesticide contamination of drinking water wells and pesticide use and hydrogeological vulnerability.

A discussion of the results obtained in this Survey is beyond the scope of this article. However, a Phase I report detailing the results of the first objective was released in the fall of 1990. Copies of the "National Pesticide Survey of Pesticides in Drinking Water Wells, Phase I Report" (Order # PB9l-125765) are available from the National Technology Information Service, 5285 Port Royal Road, Springfield, Virginia 22161. A report concerning the results obtained from the evaluations based on the second objective is currently being prepared.

The data obtained in this Survey are being used by the OGWDW to identify compounds for future regulation and will allow better assessments of drinking water treatment methods for the removal of these compounds. The OPP may use these data in setting labeling and use restrictions for pesticides, and to assist in defining monitoring requirements of pesticide registrants.

Presented in this article are brief descriptions of the design and implementation of the National Pesticide Survey, and the analytical methods that were used. Also presented are a series of recommendations for the conduct of occurrence surveys.

Pilot Study

A pilot study was conducted in March and April of 1987 to test many aspects of the planned Survey implementation. Eight rural domestic and eight community sites were sampled in each of three states; California, Minnesota, and Mississippi Duplicate samples from each site was analyzed at both an EPA, and a contract laboratory.

Full Survey

The key elements of the final design of the Survey included: 1) a statistically based sampling design using hydrogeologic vulnerability and pesticide usage as stratification variables to select approximately 600 community system and 800 rural domestic wells used as a source of drinking water; 2) analytical methods capable of accurately quantifying 127 pesticides, pesticide degradation products, and related compounds; 3) health advisories for 61 pesticides of primary interest to the Agency; 4) a collection of information concerning well construction and pesticide use patterns, specific to each sample collection site; and 5) a quality assurance program that encompassed all components of the Survey. In April of 1988, sampling began for the full Survey. Sampling of community water systems was completed in December, 1989, and the rural domestic systems in February, 1990.

Analytical Methods

The following eight analytical methods were used to analyze each sample collected in the NPS. Six of these analytical methods were developed specifically for the NPS. Samples were also analyzed using 2 previously developed EPA methods.

NPS Method #1: Determination of Nitrogen Phosphorous Containing Pesticides in Ground Water by Gas Chromatography with a Nitrogen Phosphorous Detector (39 analytes).

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A measured volume of sample of approximately 1 L is solvent extracted with methylene chloride by mechanical or manual shaking. The methylene chloride extract is isolated, dried, and concentrated to a volume of 5 mL after solvent substitution with methyl tertiary butyl ether (MTBE). Chromatographic conditions are identified for the separation of the analytes using both primary (30 m. x 0.25 mm. I.D. DB-5) and confirmational (30 m. x 0.25 mm. I.D. DB-1701) fused silica capillary gas chromatography columns.

NPS Method #2: Determination of Chlorinated Pesticides in Ground Water by Gas Chromatography with an Electron Capture Detector (25 analytes).

A measured volume of sample of approximately 1 L is solvent extracted with methylene chloride by mechanical or manual shaking. The methylene chloride extract is isolated, dried, and concentrated to a volume of 5 mL after solvent substitution with MTBE. Chromatographic conditions are identified for the separation of the analytes using both primary (30 m. x 0.25 mm. I.D. DB-5) and confirmational (30 m. x 0.25 mm. I.D. DB-1701) fused silica capillary gas chromatography columns.

NPS Method #3: Determination of Chlorinated Acids in Ground Water by Gas Chromatography with an Electron Capture Detector (13 analytes)

A measured volume of sample of approximately 1 L is adjusted to pH 12 with 6 N sodium hydroxide and shaken for one hour to hydrolyze acid derivatives. Extraneous organic material is removed by a methylene chloride wash. The sample is acidified, and the chlorinated acids are extracted with ethyl ether by mechanical or manual shaking. The acids are converted to their methyl esters using diazomethane. The ethyl ether extract is concentrated to a volume of 10 mL after solvent substitution with MTBE. Chromatographic conditions are identified for the separation of the analytes using both primary (30 m. x 0.25 mm. I.D. DB-5) and confirmational (30 m. x 0.25 mm. I.D. DB-1701) fused silica capillary gas chromatography columns. The method provides a Florisil cleanup procedure to aid in the elimination of matrix interferences that may be encountered.

NPS Method #4: Determination of Pesticides in Ground Water by High Performance Liquid Chromatography with an Ultraviolet Detector (16 analytes).

A measured volume of sample of approximately 1 L is solvent extracted with methylene chloride by mechanical or manual shaking. The methylene chloride extract is isolated, dried, and concentrated to a volume of 5 mL after solvent substitution with methanol. Chromatographic conditions are identified for the separation of the analytes using both primary (250 mm. x 4.6 mm. I.D. DuPont Zorbax ODS) and confirmational (250 mm. x 4.6 mm. I.D. J+W Cyano) HPLC columns.

NPS Method #5: Measurement of N-methyl Carbamoyloximes and N-methyl Carbamates in Ground Water by Direct Aqueous Injection HPLC with Post-Column Derivatization (10 analytes).

The water sample is filtered, and a 400 uL aliquot is injected onto a reverse phase HPLC column. Separation of the analytes is achieved using gradient elution chromatography. After elution from the HPLC column, the analytes are hydrolyzed with 0.05 N sodium hydroxide at 95°C. The methyl amine formed during hydrolysis is reacted with o-phthalaldehyde and 2-mercaptoethanol to form a highly fluorescent derivative which is detected using a fluorescence detector. Chromatographic conditions are identified for the separation of the analytes using both primary (150 mm. x 3.9 mm. I.D. Waters Novapak C18) and confirmational (250 mm. x 4.6 mm. I.D. Supelco LC-1) HPLC columns.

NPS Method #6: Determination of Ethylene Thiourea (ETU) in Ground Water by Gas Chromatography with a Nitrogen-Phosphorous Detector (1 analyte)

The ionic strength and pH of a measured 50 mL aliquot of sample are adjusted by the addition of ammonium chloride and potassium fluoride. The sample is poured onto an Extrelut brand column. ETU is eluted from the column with 400 mL of methylene chloride. The extract is solvent exchanged to ethyl acetate and concentrated to a volume of 5 mL. Conditions are identified for the

chromatography of ETU using both primary (10 m. x 0.25 mm. I.D. DB-Wax) and confirmational (5 m. x 0.25 mm. I.D. DB-1701) fused silica capillary gas chromatography columns.

EPA Method 504: 1,2-Dibromoethane and 1, 2-Dibromo-3-Chloropropane in Water by Microextraction and Gas Chromatography

Thirty five mL of sample are extracted with 2 mL of hexane. Chromatographic conditions are identified for the separation of the analytes using both a primary (30 m x 0.32 mm I.D. Durawax-DX3) and confirmational (30 m x 0.32 mm I.D. DB-l) fused silica capillary GC columns. Three additional analytes (l,2-dichloropropane, and cis and trans-l, 3-dichloropropene) were added to the scope of Method 504.

EPA Method 353.2 Nitrogen, Nitrate-Nitrite, Colorimetric, Automated, Cadmium Reduction

A filtered sample is passed through a column filled with granular copper-cadmium to reduce any nitrate present to nitrite. The concentration of nitrite is determined by diazotizing with sulfanilamide and coupling with N-(1-naphthyl)-ethylenediamine dihydrochloride to form a highly colored azo dye, which is measured colorimetrically.

Four of the methods developed for the NPS have been issued as EPA drinking water compliance monitoring methods; NPS 1 (EPA 507), NPS 2 (EPA 508), NPS 3 (EPA 515.1), NPS 5 (EPA 531.1). These 4 methods and EPA 504, as well as other methods proposed for use in conjunction with the Safe Drinking Water Act, are contained in a manual titled "Determination of Organic Compounds in Drinking Water", order number PB-89-220461/AS. This manual is available through the National Technical Information Service, 5285 Port Royal Road, Springfield Virginia 22161.

The identification of all pesticide and pesticide related analytes were both qualitatively and quantitatively confirmed. Confirmations were conducted by reanalyses of all sample extracts using a second capillary gas chromatographic (GC) or high performance liquid chromatographic (HPLC) column. These analyses provided both a preliminary qualitative confirmation for all GC determinations, and the final confirmation for HPLC analyses. The analytes detected using a GC based method were also qualitatively confirmed using gas chromatography/mass spectrometry (GC/MS). These confirmation procedures proved to be essential due to the large percentage of false positives observed when using only one chromatographic column.

Due to the problems encountered with the comparability of calibration standards used in the pilot study, all laboratories were provided with calibration standards from a common source. The purity of all compounds used as calibration standards was certified through the EPA Pesticide and Industrial Chemicals Repository. Using these certified materials, The Bionetics Corporation produced stock (1-2 mg/mL) standards, sealed in glass ampules, of each analyte, internal standard, and surrogate compound. These standards were verified by the appropriate EPA laboratory each time that a new set of ampules was prepared. Following verification by the EPA laboratories, these ampules were supplied to each NPS laboratory.

<u>Recommendations for Conducting Occurrence Surveys</u>

1. **Develop written data quality objectives.** These describe the minimum quality acceptable to meet the needs of the data users. They should be developed in cooperation with all parties associated with the survey including sample collectors, analytical personnel, and the final data users.

2. **Appoint a survey leader.** A director or project manager should be appointed to serve as the main focus for all survey related activities.

3. **Appoint a quality assurance officer**. Even for extremely modestly sized surveys a quality assurance officer cam be very helpful. This person should be responsible for determining that everyone involved in the survey understands the work they are to perform, and then throughout the progress of the survey, monitors that all operations are being conducted as planned. It is best if this person is not responsible for any of the management functions of the survey, and that they report directly to the survey director or a more senior official.

4. **Additional *QA/QC* procedures**. QA/QC procedures, such as a program of analyzing duplicate samples at a second laboratory, analyses of performance evaluation samples, etc., are very beneficial for maintaining acceptable levels of data quality. Also, if analyses are being performed by more than one person or laboratory, each should be provided with the same calibration materials. This will greatly increase the validity of comparisons made between data obtained from 2 or more sources.

5. **Centralized data storage**. All data should be submitted to a central person or organization. All data should be submitted in a format specified prior to beginning the survey.

6. **Health and treatment information**. Heath and treatment information should accompany any findings that are released to interested parties or the general public. Without this information, people receiving the data will not be able to make informed judgments of the true impact of the findings, and therefore will almost always assume the worst.

7. **Consider analyte degradation products**. When designing the survey, consider not only the parent compound of interest but also any possible degradation products of that compound. Frequently chemicals released into the environment are chemically altered by exposure to air, water, sunlight, etc., and the true impact of the chemical on the environment will be underestimated if analyses are performed for only the original chemical.

For additional information about the National Pesticide Survey please call the Safe Drinking Water Hotline at 1-800-426-4791.