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THE EVALUATION OF ORGANIC AND INORGANIC COMPOUNDS IN THE GROUNDWATER SYSTEM FOR HAZARDOUS WASTE DISPOSAL

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ABSTRACT

The increased concerns of the ultimate fate of hazardous waste leachate contamination of the groundwater system has called for the proper evaluation of organic and inorganic compounds existing in the groundwater system. The evaluation requires: 1) site-specific groundwater characterization, 2) laboratory analysis of various organic and inorganic compounds, and 3) recommendation of key parameters for operational groundwater monitoring programs.

INTRODUCTION

The Resource Conservation and Recovery Act of 1976, as amended (RCRA), directs the United States Environmental Protection Agency (USEPA) to promulgate regulations to protect human health and the environment from the improper management of hazardous waste. The goal is to establish a national program to improve solid waste management, including control of hazardous waste, the promotion of resource conservation and recovery and the establishment of environmentally sound solid waste disposal practices. The final rule as adopted on May 19, 1980 has called for detail evaluation of the groundwater system located in the general vicinity of the hazardous waste management site and requirement of long-term monitoring programs.

The purpose of this paper is to discuss the generally acceptable methods of groundwater evaluation and monitoring standards to protect groundwater resources from practices that may threaten to contaminate them. The method of evaluation, establishment of groundwater baseline parameters (physio-chemical, organic and inorganic parameters) and the recommendation of operational monitoring programs are discussed.

SITE SPECIFIC GROUNDWATER CHARACTERIZATION

The characterization of the groundwater system underlying a hazardous waste management site often calls for a well drilling and testing program for the

identification of aquifer, aquitard, aquiclude and the unsaturated zone beneath the land surface. In general, the evaluation includes well inventory of existing wells and abandoned wells for usage and general completion records. The area of coverage ranges from a 1 to 5 mile radius of the site and to a maximum depth of about 1000 feet or to the base of any aquifer containing decent quality water.

The second step of the evaluation is to design and conduct a baseline groundwater monitoring program. Monitoring wells should be constructed to monitor the unsaturated zone, aquifers and sometimes aquitards individually. The location of placement of the wells should stress the downgradient direction. Usually, a ratio of two to three downgradient wells to one upgradient well should suffice for each aquifer. The spatial distribution depends on the site geohydrologic conditions and the size of the hazardous waste management facilities. Frequency of monitoring groundwater should cover seasonal fluctuation over a period of a year or more. In general, quarterly monitoring is acceptable. For the baseline monitoring program, the following list of parameters are generally acceptable to most agencies.

Laboratory Analysis Parameters for Groundwater Samples:

Classical Constituents

pH	Orthophosphates
Temperature	Fluoride
Color	Cyanide
Turbidity	Dissolved organic carbon
Specific conductance	Total chlorinated hydrocarbons
Total dissolved solids	Phenolic compounds
Settleable solids	Oil and grease
Total suspended solids	BOD (by delta COD or long term BOD)
Total volatile solids	COD
Kjeldahl nitrogen	Hardness
Ammonia nitrogen	Alkalinity
Nitrates and nitrites	Dissolved silica
Total phosphorous	Cation/anion balance

Major Cations/Anions

Potassium	Sulfates
Sodium	Bicarbonates, carbonates
Magnesium	Chloride
Calcium	

Selective Trace Metals
Bacteriological Parameters
Radiological Parameters
Trace Organics
GC/MS scanning of volatiles, acid extractable, base/neutral extractable and pesticides/PCB's

The third step of the evaluation generally involves the selection of a competent analytical laboratory. The laboratory to be selected should meet the following criteria:

- o a certified laboratory
- o quality control and assurance program

- o laboratory capacity for handling large number of samples
- o turn-around time of quality analytical results
- o competitive pricing
- o completeness of analytical capability
- o relative distance of laboratory to the project site

The fourth step of the evaluation is to conduct the monitoring, sampling and analytical program in accordance with various standards and procedures on sampling techniques, sample preservation and shipment, laboratory procedures, chain of custody control, and reporting procedures. Most of the standards and procedures are described in detail in references 1 through 8.

LABORATORY ANALYSIS OF ORGANIC/INORGANIC CONSTITUENTS

The laboratory analysis of groundwater samples can be classified under the following categories:

- o Classical Constituents
- o Major Cations/Anions
- o Trace Metals
- o Bacteriological Parameters
- o Radiological Parameters
- o Trace Organics

Most of the above categories can be analyzed by methods established in references 2 through 8. The analysis of trace organics has been a major challenge to geohydrologists because state-of-the-art knowledge has been established only in recent years. For the analysis of trace organics constituents in groundwater samples, the analytical technique should meet the following criteria:

- o Fast analysis of a multi-component mixture
- o Identifications with little possibility of false positives
- o Precise quantitation (+ 10%)
- o Computer assisted data handling
- o Use generally available instrumentation

The techniques employed in the mid-1960's used relatively inexpensive equipment (GC, IR, UV, etc.) and followed detailed, labor-intensive chemical procedures. These approaches had several drawbacks. Unless the analyst had prior knowledge of the compounds that were likely to be present in a sample, they probably could not be identified in the analyzed sample. Also, in order to include all significant compounds of interest, hundreds of procedures would have to be developed and tested. Scientists realized that more general methods of analysis with high information content were required if large-scale environmental assessment and monitoring programs were to be conducted. The combination of gas chromatography and mass spectrometry (GC/MS) developed in the mid-1960's, combined with the introduction of the mini-computer-based data systems with the ability to utilize the high volume output of data from a GC/MS system, quickly revolutionized the field of trace organic analysis. The utilization of GC/MS for environmental analysis substantially increased the capacity of a laboratory to handle large numbers of samples, and to identify organic compounds reliably.

The analysis of the organic constituents in a water sample involves 4 steps:

1) Extraction and concentration
2) Chromatography to separate individual compounds
3) Mass spectral analysis
4) Data interpretation

One of two extraction techniques are used depending on the sample constituents being analyzed. Volatile non-water soluble compounds are purged from the sample with an inert gas and concentrated on a polymer trap. Higher boiling (>200°C) compounds are extracted by methylene chloride and concentrated by solvent distillation.

The state-of-the-art in GC analysis employs a 30 meter SE-54 fused silica column for the separation of solvent extractable compounds. Over 80 compounds on the USEPA priority pollutant (ref. 7) list can be separated in less than 45 minutes. Due to the inertness of fused silica and the high resolution columns available, acidic, basic and neutral compounds can be analyzed in a single injection. A 2 meter x 2 mm i.d. 0.2% SP1000 or Carbowax 1500 on Carbopak C column is used to separate the volatile compounds. Volatile compounds routinely analyzed range from chloromethane to dichlorobenzene in volatility and are usually chlorinated hydrocarbons.

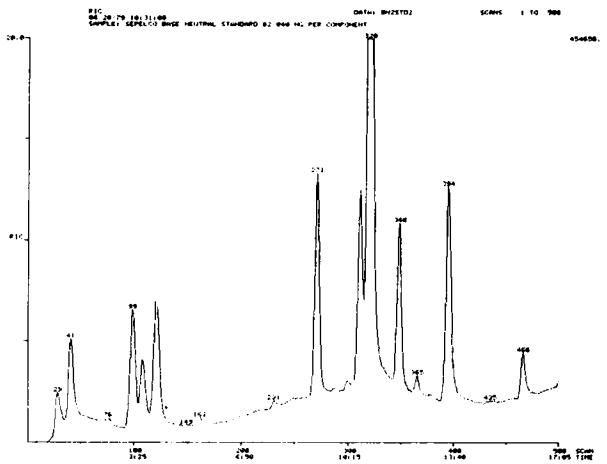
Electron impact mass spectrometry is used for over 90% of all GC/MS analysis in environmental monitoring. In addition, the vast majority of MS systems are low resolution quadrupole instruments with a mass range of 4-1000. High resolution capillary columns produce GC peak widths of less than 4 seconds and MS scan speeds of up to 1500 amu/second are required to obtain at least 8-10 scans across the peak. For precise quantitation, at least 10 scans across a peak is usually required.

Typical detection limits for volatile organics are 200 parts-per-trillion to 1 part-per-billion (ppb) depending on the compound. Detection limits for solvent extractable compounds are 1-5 ppb. Sample matrix has a great effect on the detection limit and can raise limits by several orders of magnitude.

The Finnigan OWA® (Sunnyvale, California, USA) is an example of a computerized GC/MS designed with hardware and software features optimized for organics-in-water analysis. This system is equipped with a Bellar-Lechtenberg (ref. 8) liquid sample concentrator (LSC) developed for the Environmental Monitoring and Support Laboratory of the U.S. Environmental Protection Agency (EPA). This LSC device automates purging and analysis of volatile organics in water. Software that automates the process of compound identification and quantitation using a multi-point response curve makes this the preferred system for GC/MS environmental monitoring.

The analysis of a single water sample may require only 45 minutes to collect the data, but many hours will be spent performing the data reduction. The reduction of mass spectral data generally takes two forms: searching for a preselected list of compounds and surveying the sample to identify all or part of the compounds present. Searching for selected compounds is referred to as target compound analysis with the selected compounds the targets.

a.



b.

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FINNIGAN TARGET COMPOUND ANALYSIS
QUANTITATION REPORT    FILE  BN2BTD2

DATA  BN2BTD2 TI
08/28/79 10 31 08
SAMPLE  SEPELCO BASE NEUTRAL STANDARD @2 @40 NG PER COMPONENT
SUBMITTED BY  HEAD /PF       ANALYST  PH

AMOUNT=AREA(HGHT) * REF AMNT/(REF AREA(HGHT)* RESP FACT)
RESP  FAC  FROM LINEAR FIT TO THE   3 CLOSEST DATA POINTS IN  RL

 NO  NAME
  1  D10-ANTHRACENE(INTERNAL STANDARD)
  2  1,3-DICHLOROBENZENE
  3  1,4-DICHLOROBENZENE
  4  HEXACHLOROBUTADIENE
  5  NAPHTHALENE
  6  BIS(2-CHLOROETHOXY)METHANE
  7  ACENAPHTHENE
  8  FLUORENE
  9  HEXACHLOROBENZENE
 10  ANTHRACENE
 11  DIETHYLPHTHALATE

NO  M/E  SCAN   TIME  REF   RRT  METH     AREA(HGHT)  AMOUNT        %TOT
 1  188   393  13 26   1  1 000  A BB      147912    20 000 NG     4 65
 2  144    29   0 59   1  0 074  A BV       86763    36 285 NG     8 43
 3  146    41   1 24   1  0 104  A VB      178244    39 468 NG     9 17
 4  225    99   3 23   1  0 252  A BB       90284    45 600 NG    10 60
 5  128   121   4 08   1  0 308  A BB      474993    40 038 NG     9 30
 6   93   108   3 41   1  0 275  A BB      181682    37 520 NG     8 72
 7  154   271   9 16   1  0 690  A BB      297257    41 787 NG     9 69
 8  166   311  10 30   1  0 791  A BB      320175    40 411 NG     9 39
 9  284   348  11 53   1  0 885  A BB       86637    46 332 NG    10 77
10  178   395  13 30   1  1 005  A BB      375348    40 192 NG     9 34
11  149   320  10 56   1  0 814  A BB     3446358    42 769 NG     9 94
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c.

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UNKNOWN SAMPLE QUANTITATION        OWA REVERSE SEARCH STATUS REPORT

THE INTERNAL STANDARD AREA IS:     3 PERCENT OF THE LAST STANDARD RUN
          INTERNAL STANDARD FOUND FOR LIBRARY: LIBRARYUB

COMPOUNDS QUANTITATED BY INTERNAL STANDARD USING PARAMETERS IN LIBRARYUB
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REPORT ENTRY NO.	EXPECTED SCAN	BEST SCAN	FIT	PURITY	LIBRARY ENTRY NO.	PEAKS FOUND	PEAKS QUANT	SATURATED PEAKS
1	393	393	943	151	1	1	1	0
2	28	29	989	522	2	1	1	0
3	40	41	998	536	3	1	1	0
4	96	99	998	222	4	1	1	0
5	118	121	997	539	5	1	1	0
6	104	108	997	426	6	1	1	0
7	271	271	997	538	7	1	1	0
8	311	311	993	461	8	1	1	0
9	348	348	998	282	9	1	1	0
10	395	395	999	333	10	1	1	0
11	320	320	998	417	11	1	1	1

```
NUMBER OF COMPOUNDS IDENTIFIED  11
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Figure 1 *Target compound analysis report, a) A reconstructed ion chromatogram of a 40 ng per component base/neutral standard, b) the quantitation section of the report, and c) the quality control portion of the report.*

A target compound analysis report produced by the Finnigan OWA GC/MS has three parts (Figures 1a, 1b, and 1c). Part A (Figure 1a) is a reconstructed ion chromatogram. This gives the analyst a picture of the total data file and is normally included in the laboratory's storage files.

Part B contains the names of all the target compounds in the quantification library with their entry numbers and the quantification report. If a target compound is not detected, a NOT FOUND is printed in the report.

Part C is the reverse search status report. This report provides the analyst with all of the data needed to evaluate the chromatography (expected scan) spectral match quality (fit and purity) and the quantitative analysis (number of peaks saturated). Based on the information contained in this report, the analyst can determine if any manual confirmation is needed.

A report of this type requires less than 15 minutes to generate. The data system automatically identifies the target compounds (listed in fig. 1b) and performs the quantitation without operator interaction. A laboratory operating on an 8 hour shift and using the Finnigan developed software could analyze 8-10 samples for 80 compounds.

RECOMMENDATION OF OPERATIONAL MONITORING PROGRAM

The final compilation of chemical parameters for the baseline groundwater monitoring program will show spatial distribution with time and variations of concentrations. With the knowledge of the anticipated leachate chemical composition (derived from waste composition and transport media), a key list of organic and inorganic compounds and sampling frequency can then be recommended for the operational groundwater monitoring program for maximum protection of the groundwater system involved.

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