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FINAL REPORT REGARDING ASSOCIATION OF DIELDRIN WITH COLLOIDAL PARTICLES
AND AQUIFER MATERIALS IN WELL WATER FROM CORRY STATION WITH
TRANSMITTAL NAS PENSACOLA FL
3/12/1996
UNIVERSITY OF FLORIDA



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Douglas E. Barr
Executive Director

March 12, 1996

Mr. Anthony Robinson, RPM
Southern Division
Naval Facilities Engineering Command
2155 Eagle Drive
Post Office Box 190010
North Charleston, South Carolina 29419-9010

Dear Mr. Robinson:

Additional materials due to the Navy regarding the Corry Station ground water contamination investigation are enclosed. This report on the association of dieldrin with colloidal particles was not received from our subcontractor in time to be included in the original submission to the Navy. Please update your copies of the report 'Dieldrin in Ground Water, Results of Investigation, October 1995' as follows:

- 1) Insert the 'Final Report' into Volume III behind the Appendix H divider.
- 2) Replace page xiii dated 10/01/95 (List of Appendices) with the replacement page dated 03/08/96. This page is found in the front of Volume I.
- 3) Replace pages 137 and 138 dated 10/01/95 with replacement pages dated 03/08/96. These two pages are found in Volume I.

Our records indicate that we forwarded three copies of the report to SOUTHDIV. Accordingly, we are forwarding three sets of additional materials at this time. Please distribute these materials as necessary to update all copies of the Corry Station report in your possession. We will send updated materials directly to the Corry Station Environmental Office for their distribution.

With this submission, the Corry report is complete. Please advise if you have any comments on these additional materials.

Best regards,

Tom Pratt
Chief, Bureau of
Ground Water

TP/me
enclosures

cc: Dr. Chris Howell, Project Director

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FINAL REPORT

**ASSOCIATION OF DIELDRIN WITH COLLOIDAL PARTICLES AND AQUIFER
MATERIALS IN WELL WATER FROM CORRY STATION, FLORIDA**

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Association of Dieldrin with Colloidal Particles and Aquifer Materials in Well Water from Corry Station, Florida

Introduction

The Sand-and-Gravel Aquifer in southern Escambia County is the water source for a variety of uses, including public water supply and industrial demands. Traditionally, the availability of water from the aquifer has been more than adequate to meet the water needs of the area. This is attributable to the excellent water-bearing characteristics of the aquifer and the high rate of local rainfall recharge. Unfortunately, these same characteristics allow for rapid infiltration and transport of surface contaminants into the surficial sands, and ultimately into the underlying Main Producing Zone of the Sand-and-Gravel Aquifer, which serves as the primary source of ground water for the area.

The U.S. Navy operates 10 production wells at Corry Station which supply water to Corry Station and NAS Pensacola. The insecticide dieldrin has been detected in at least 5 of the Corry Station wells. As a result of the dieldrin contamination, the Northwest Florida Water Management District (DISTRICT) is assisting the Navy in performing a Remedial Investigation (RI) at Corry Station. The RI is a detailed hydrogeologic and water quality site assessment in an effort to characterize the extent of the contamination, determine the potential source(s), identify possible future well locations, and develop a remediation plan for the site.

Problem Addressed

One approach to modelling contaminant migration to subsurface environments is to consider the soil and water phases as independent systems, where contaminants partition between the mobile aqueous phase and the immobile solid phase. Models using this approach would predict that contaminants would be relatively immobile given low solubility and high affinity for the solid phase. However, evidence is mounting that contaminant transport to and/or within groundwater can be significantly enhanced via colloidal association, where the colloid phase itself is undergoing transport (Rees, 1987; Buddemeier and Hunt, 1988; McCarthy and Zachara, 1989). Radionuclides, pesticides and industrial organic chemicals, and non-radioactive inorganic contaminants found in groundwater may migrate via colloid-facilitated transport mechanisms. Research has documented the existence and transport of colloid-associated contaminants and microbes to and within groundwater systems (Rees, 1987; McDowell-Boyer et.al., 1986; Buddemeier and Hunt, 1988; Enfield et. al., 1989; Harvey et al., 1989; McCarthy and Zachara, 1989; Kaplan et al., 1993). The colloidal vectors may be inorganic or organic, and in some cases may include micro-organisms (Harvey et al., 1989).

The distinction between organic colloidal- and solution components in soils or aquifers is not discrete. Organic macro-molecules grade upward in size, forming a continuum with organic colloids. "Dissolved" organic carbon (DOC) is commonly defined operationally as $< 0.45 \mu\text{m}$. However, for the purposes of this study we will refer to any particles that can be physically concentrated (e.g., by filtration, coagulation, etc.) as colloidal, even those that are $< 0.40 \mu\text{m}$ in size. Regardless of size, organic components have the potential to facilitate transport

of hydrophobic contaminants (McCarthy and Jimenez, 1985) and to promote the stability of inorganic colloids (Kaplan et al., 1993). The presence of organic colloids may also cause pollution at disposal sites when the suspended particles contain harmful chemical components (U.S. Environmental Protection Agency, 1976).

The present study was conducted to investigate the possibility that dieldrin in water from wells at Corry Station, Pensacola, FL is moving via colloid- and/or DOC-facilitated transport. The low aqueous solubility of dieldrin (0.186 ppm) and its affinity for organic surfaces (Koc of 7600, Briggs, 1981) favor its retention in soils, yet it has moved tens of meters within the aquifer. The sandy, porous, permeable regolith in this area is a potential conduit for particulate organic carbon and inorganic colloids. Furthermore, the rapid percolation of solution would tend to maximize distance travelled by organic particulates relative to degradation rate. Therefore, the DISTRICT was interested in the phase fractionation or partitioning of dieldrin in ground water.

General Objectives

The over-all objective was to determine if colloidal-facilitated transport is a significant factor influencing the fate of dieldrin in ground water. Such a mechanism has implications for the remedial investigation at Corry Station. Specific analytical objectives are presented and explained under materials and methods below.

Materials and Methods

**Objective 1: To concentrate entrained components into particle-size separates.
(Drs. Moye and Harris)**

Explanation

We hypothesized that the dieldrin distribution in the well water should follow that of colloids and/or organic C. Also, physical (non-destructive) removal of a portion of the entrained colloidal particles as by filtration should remove dieldrin as well, reducing its concentration in the filtrate. We intended to determine the abundance of entrained organic carbon in the well water and to relate these data to dieldrin content and sorption. The strategy was to relate dieldrin concentration to abundance of entrained components in 3 particle size separates: $>5 \mu\text{m}$, 5- to $0.40 \mu\text{m}$, and $0.40-$ to $0.03 \mu\text{m}$.

Concentration and fractionation was conducted using tangential flow filtration (TFF). This is a relatively new filtration technology which is reported to minimize clogging and other sampling artifacts (e.g., sorption, changes in size, etc.) which are problems with conventional ("dead-end") filtration (Whitehouse et al., 1986; Koehnken et al., 1988; Ludwig et al., 1989; Michaels, 1989; Kilduff et al., 1992; Harnish et al., 1994). The TFF filter is designed such that the feed flows tangential to the surface of the filter membrane, and a controlled trans-membrane pressure drives a portion of the feed (filtrate) through the filter membrane. Remaining feed (retentate) is recycled back across the filter, continuously sweeping the suspended particles from the membrane surface. This is unlike conventional filtration, in which pressure drives the entire

feed through the membrane.

Task 1.1: Deployment and testing of TFF

A plate-and-frame type TFF system was used because it was considered the most likely to permit sequential fractionation. This type of system accommodates planar sheet-type membrane filters with precisely-sized "track-etch" holes. These filters are superior to the cylindrical type "hollow fiber" membranes which have a micro-fibrous morphology that is more prone than the track-etch membrane to trap particles. A peristaltic pump was used because it was considered the "cleanest", avoiding the seals, gaskets, bushings, etc. that occur in the interior of other types of pumps. The pump was designed to attain a maximum flow rate of 13 L per minute.

Testing of the system was conducted on 100 L of well water from Corry Station. This test will be referred to as "replicate 1", and subsequent fractionations as "replicates" 2 and 3. These 3 fractionations do not constitute replicates in the sense that all conditions were the same, but they were three attempts to concentrate particles in the same 3 size ranges. Conditions for testing were as follows:

1. Tygon tubing was used to connect the system to the filtrate and retentate reservoirs. The peristaltic pump tubing was made of a soft but durable "Norprene" material.
2. 22-L plastic gasoline cans were used to collect and transport 200 L of the raw water. Only 100-L of this water was ultimately used for the filtration process due to the discovery that time limitations for larger volumes were prohibitive. These cans were washed with hexane as a precaution to assure a dieldrin-free status.
3. 100 L of water was transferred from the gasoline cans to a large plastic garbage can which had also been rinsed with hexane. A 4-L beaker which had previously been calibrated precisely using a graduated cylinder was used to measure the water in the transfer. Another hexane-rinsed garbage can served as the filtrate reservoir. As the fractionation proceeded through different filter sizes, the two cans alternated between serving as filtrate and retentate reservoirs.
4. The pump was calibrated to deliver the proper flow rate for the number of filter frames used, in order to assure adequate cross-flow (flow tangential to the membrane). An optimum trans-membrane pressure was determined by measuring the filtrate flow at various differentials between pressure at the inlet and filtrate.
5. A 5- μm filtration was conducted first, producing a retentate consisting of a concentrated suspension of particles presumably $>5 \mu\text{m}$ in size. Water was continuously circulated through the system until sufficient retentate volume was

achieved. The filtrate from this cycle was then fed through the system using a 0.40- μm filter, and a retentate with suspended-particle size presumably ranging from 5- to 0.45 μm was collected. By the same process, a 0.40- to 0.03- μm retentate was collected from the second filtrate, and a final filtrate was obtained.

6. The retentate was concentrated to approximately one to two L for the 5.0- and 0.4- μm filtrations. A small retentate volume was not possible for the 0.03- μm filtration even after several days of continuous cycling and an intermediate cleaning of the filter (see "problems" below).
7. Retentates and samples of filtrates were stored in amber-L bottles for dieldrin analyses. Smaller aliquots for determination of solids and C content were stored in acid-washed nalgene containers.
8. Membranes were cleaned using a stainless-steel ultrasonic bath and repeated rinsing with distilled water. Solids from the filtrates were not added to retentate but were determined separately. There were sufficient solids on the 0.40- μm to conduct mineralogical analysis.

A number of problems became evident in the testing phase regarding various aspects of the filtration and analyses. The most serious of these involved materials that promoted adsorption or contamination. We tried to alleviate these problems in subsequent filtrations. The following is a summary of these problems:

1. The containers selected for convenient transport of water adsorbed dieldrin significantly. This demonstrated that if dieldrin were sorbed onto particles, it readily desorbed in favor of the container walls. Dieldrin was still present in high enough concentration for the monitoring of its behavior in the system, but a marked reduction in concentration prior to fractionation is unfavorable. **Solution:** Use thoroughly clean 20-L glass containers. We had initially proposed to use stainless steel containers, but the cost was prohibitive and we considered glass a comparably nonreactive material. Glass containers are routinely used for water sampling.
2. The retentate loop of the system adsorbed the remaining dieldrin in solution, though some dieldrin could be detected even in the 0.03- μm filtrate. Only the first (5.0- μm) retentate had a detectable level of dieldrin, and this level was well below that of the filtrate. We observed that with time the interior of the Norprene tubing used for the peristaltic pump was intricately and deeply cracked. The extent of cracking increased as more and more of the tubing was moved to the pump clamp to avoid over-stress and rupture for any one section of the tube. We concluded that the tubing was adsorbing the bulk of the remaining dieldrin preferentially for the retentate, which never "escaped" the system but repeatedly cycled through it. **Solution:** Use a different pump or a minimally-adsorptive peristaltic tubing. The

latter is difficult, because the synthetic components that impart the flexibility and durability pose the greatest risk of sorption.

3. The 0.03- μm filtration was prohibitively slow. We maintained pump operation on a nearly continuous basis (day and night) for a week, including a weekend, but were unable to reach a small retentate volume. The filtrate flow rate continued to decrease as the volume reduced. We concluded that the 0.03- μm filtration was not feasible for large volumes with the system on hand. **Solution:** Either eliminate this filter, or work with smaller volumes of water.

Task 1.2: TFF fractionation

Two additional fractionations (one more than contracted for) were conducted subsequent to the test fractionation of task 1.1. The procedure was essentially the same as described for that task, with the following exceptions, which are adjustments to accommodate the problems encountered in the test:

1. 20-L glass containers were used to transport and store the water, and to serve as reservoirs in the fractionation. They were thoroughly cleaned to remove any potentially adsorbing contaminant. The cleaning sequence was as follows: (i) soap and scrub brush, (ii) tap water rinse, (iii) laboratory deionized-water rinse; (iv) 20% hydrochloric acid rinse, (v) 10% hydrogen peroxide rinse, (vi) ultra-pure reagent deionized-water rinse, and (vii) hexane rinse. The bottles were covered with aluminum foil to prevent light entry.
2. Immediately upon sampling the bottles were placed in tubs and packed in ice. This was an additional precaution taken to prevent significant microbial fixation of C. This precaution was inspired by the very low C levels found in the water (see Task 2.2 results), and the consequent potential for even minor C fixation over time to confound the results.
3. Bottles were transported, on the day sampled, to a cold room at the University of Florida. Additional ice was used to maintain cold conditions during the fractionation.
4. Tygon tubing in the system was replaced by teflon. We were uncertain as to the extent of possible dieldrin adsorption by tygon, but decided to eliminate tygon as a precaution (a small length of tygon was used in replicate 3; see below).
5. Different pumping systems were used for the second and third fractionation. The second fractionation (replicate 2) was conducted using a gear pump with chemically-resistant (presumably nonadsorptive) gears and interior. The gear pump was thoroughly cleaned of oily residue by washing with several L of alcohol, hexane, alcohol, de-ionized water, and raw water, respectively. The third

fractionation made use of a short tygon tube in the peristaltic pump, connected to teflon on both ends of the pump.

6. The problem of very slow filtration flow rate for the 0.03- μm filter was avoided by reducing the volume used for the filtration (100-L to 20-L).

Objective 2: To determine total-, organic, and inorganic mass of entrained components in the retentates. (Dr. Harris)

Explanation

It was necessary to determine the concentration of components in the retentate suspensions for several reasons:

1. To assess dieldrin/component relationships.
2. To assess particle-size distribution.
3. To check mass balances for the system and raw water.
4. To verify sufficient solid yield for subsequent mineralogical assessment.

Task 2.1: Determination of total entrained mass in retentates and filtrates via gravimetry

Precise aliquots were withdrawn in triplicate at constant depth from retentate suspensions by pipette, deposited in tared weighing pans, and placed in an oven to dry at 90° C. Pans for replicate 1 were removed from the oven when residues were dry, and placed in a desiccator for equilibration at 56% relative humidity as controlled by a $\text{Mg}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ slurry. We discovered, however, that we could obtain better precision simply by allowing the pans to equilibrate to the laboratory temperature and atmosphere. Therefore we abandoned the desiccator precaution in subsequent fractionations. Residue weight was determined on a 5-place electronic microbalance. From this weight and the aliquot volume, total entrained concentration (e.g., mg/L) could be calculated.

An attempt was made on the first replication to determine residue weights before and after oxidation of organic matter with hydrogen peroxide (H_2O_2) (Lavkulich and Wiens, 1970). We initially suspected organic C would make up a greater proportion of the entrained solids than proved to be the case. The very small amount of C made the gravimetric estimation futile, and this part of the task was abandoned on subsequent fractionations.

Task 2.2: Determination of total-, organic-, and inorganic entrained carbon mass in retentates and filtrates via chemical methods

Total-, organic-, and inorganic C (Nelson and Sommers, 1982) in retentate suspensions and filtrates were determined in triplicate using a carbon analyzer (Dohrman model DC 190), which was available in the Soil and Water Science Department through the courtesy of Dr. Ramesh Reddy. The instrument measures organic C using infrared absorption of the CO_2 evolved

from a sample following ignition in a hot (680° C) pyrolysis tube. Total C is obtained from a second aliquot (injected through a different port) after phosphoric acid digestion to release any inorganic C present. Inorganic C is calculated as the difference between total and organic C.

Quality Control

Analyses for total C, organic C, inorganic C, inorganic colloids, and dieldrin were conducted in triplicate. Only acid-washed containers or other materials contacting the samples in the analyses were used.

Objective 3: To determine mineralogy of inorganic components in the retentates and aquifer materials. (Dr. Harris)

Explanation

Knowledge of the entrained minerals in the water provides information about the nature of inorganic surfaces available for interaction with dieldrin. The mineral components proved to be more important than we had originally suspected, given the low levels of organic components. We determined the mineralogy of retentate solids using x-ray diffraction (Whittig and Allardice, 1986) and thermal analysis (Karathanasis and Harris, 1994).

Task 3.1: Isolating inorganic material for mineralogical analysis

The concentration of solids in the retentates of various fractions was too low to obtain enough mass for mineralogical analysis. However, there was enough material washed from the 0.40- μm filter of replicate 1 for x-ray diffraction and differential scanning calorimetry (DSC). These solids were suspended in a small volume of deionized water and collected on a 0.45- μm filter under suction.

The clay fraction from two aquifer samples was obtained using standard centrifugation procedures (Whittig and Allardice, 1986). A particle-size distribution was calculated by weighing the gravel and sand removed by sieving, and the silt fraction removed by centrifugation. The clay weight fraction was obtained by difference.

Task 3.2: X-ray-diffraction analysis

Retentate clay was saturated (while still on the 0.45- μm filter, see above task)) with Mg by washing with N MgCl_2 followed by deionized water (to remove free salt). The purpose of saturation was to establish a standard condition for identification of expansible phyllosilicates (Whittig and Allardice, 1986). Glycerol solvation of the Mg-saturated material was also performed for diagnostic purposes. Filters were removed from the filtration housing and inverted over a glass slide. The filter cake was transferred to the slide using a bevel-and-peel technique (Drever, 1973). The mounted sample was scanned with $\text{CuK}\alpha$ radiation from 2 to 60° 2θ using a computer-controlled x-ray diffractometer. Minerals were identified from X-ray diffraction peak positions, making use of differentiating responses to saturation (Whittig and Allardice, 1986).

Clay mineralogy of the aquifer clay was determined in a similar manner to that of the 0.40- μm retentate. However, potassium saturation was performed in addition to the Mg/glycerol treatment as an extra diagnostic check for the aquifer samples, since there was sufficient clay for multiple mounts.

X-ray diffraction analysis was also conducted on material collected by the DISTRICT using "dead-end" 0.45- μm filtration of the Corry Station well water. Amount of this material was so low that a special low background quartz mount was used. The material was removed from the filter using an ultrasonic bath and deionized water. It was deposited on the mount as a suspension and air-dried prior to scanning by x-ray.

Task 3.3: . Differential Scanning Calorimetry (DSC)

This is an analytical technique which exploits differences in thermal reactivity among minerals (Karathanasis and Harris, 1994). It monitors relative heat capacity with increasing temperature, using a thermally inert material as a standard. Reactions or phase changes which alter heat capacity produce a peak on a heat-flow vs. temperature plot, the area of which is proportional to the heat of reaction. We used DSC to corroborate mineral identification by x-ray diffraction; it can also be quantitative for some minerals. Small aliquot (about 2 mg) of the samples used for x-ray diffraction were used for DSC analyses, which were conducted at a temperature range of 25 to 600° C and heating rate of 20° C per minute.

Objective 4: Adsorption of dieldrin on aquifer material. (Dr. Nkedi-Kizza)

Explanation

If dieldrin transport is facilitated by the mobile particles, then sorption of dieldrin must be occurring on particle surfaces. This objective was intended to establish the level of surface affinity for dieldrin. Unfortunately, the determination of sorption of sparingly soluble neutral organics like dieldrin on soil materials, is very difficult to carry out in aqueous systems, because strongly hydrophobic organics can sorb on any container walls (Nkedi-Kizza et al., 1985). To minimize sorption of such sorbates on container walls the use of mixed solvents has been proposed in batch slurry sorption experiments (Nkedi-Kizza et al., 1985). This is achieved by employing the solvophobic theory to calculate sorption coefficient of a sorbate in aqueous systems using the cosolvency model (Rao et al., 1985; Nkedi-Kizza et al., 1985). With this approach it is possible to increase the solubility in cosolvent of a sparingly soluble sorbate in water, while reducing the potential for sorption of the sorbate on container walls. The approach used for this task was therefore to determine dieldrin sorption on aquifer materials in mixed solvents and to calculate sorption coefficients in aqueous systems using the cosolvency model.

Task 4.0: Determination of dieldrin sorption characteristics for aquifer material

Two aquifer samples taken from the Sand-and-Gravel Aquifer of Escambia County were provided by the Northwest Florida Water Management District. The samples were taken at depths of 47-48m and 57-58m. The samples were air-dried and sieved with a 2 mm sieve to

separate gravel from the fine materials. The fine materials (< 2 mm) were later used for the sorption experiments. Dieldrin of 98% purity, was purchased from Chem Service, Inc., West Chester, PA. HPLC-grade methanol and water purchased from Fisher Scientific, were used to prepare water + methanol mixed solvents. The supporting electrolyte was 0.01M CaCl₂ prepared in HPLC-grade water.

Dieldrin Analysis by HPLC with UV-detection.

The first task was to develop an analytical method for dieldrin detection in solution using UV-absorbance. Since analysis with GC was too expensive, and no method for HPLC-UV detection of dieldrin was available in the literature an analytical method was developed for Task 4.0. A solution of 0.5 ppm of dieldrin was prepared in methanol and was scanned on a Beckman DU-40 spectrophotometer to find the wavelength of maximum dieldrin absorbance within the range of 200 - 300 nm. Maximum UV absorbance was found at 220 nm. Stock solutions of 1, 5, and 10 ppm of dieldrin were prepared in methanol. The samples were analyzed using a Spectra Physics HPLC system equipped with an SP8800 ternary pump, SP4290 computing integrator and an SP8780 autosampler. The detector used was a Waters Programmable Multiwavelength detector set at 0.04 AUFS. The system was run under the following conditions:

Column: Supercosil LC-18 reversed-phase
Mobile Phase: 80% methanol in HPLC water
Flow Rate: 1 ml/minute
Detection: UV at 220 nm
Retention Time: 9 minutes

This method was used to analyze all dieldrin solution samples during the sorption experiments.

Sorption of Dieldrin on Container Walls.

Since dieldrin was suspected to sorb on container walls (plastic centrifuge tubes, and glass HPLC autosampler vials), a sorption experiment for dieldrin on these containers was conducted as a function of volume fraction methanol. 20 ml of a known concentration of dieldrin were added to five separate centrifuge tubes and shaken on a rotating shaker for 24 hours. Half a ml of the solution was then added to 0.5 ml of methanol in an HPLC vial and dieldrin concentration was measured according to the method outlined earlier. The experimental set up and data obtained are presented in Table 1.

Table 1. Dieldrin Sorption on Centrifuge Tubes

Tube #	Fraction of Methanol (fc)	Initial Conc. dieldrin ($\mu\text{g/ml}$)	Final Conc. dieldrin ($\mu\text{g/ml}$)	Sorbed on centrifuge tube %
1	0.35	9.4	8.8	6.8
2	0.35	9.4	8.8	6.2
3	0.35	9.4	8.9	5.1
4	0.35	9.4	8.9	5.3
5	0.35	9.4	8.5	9.4
6	0.40	14.1	13.2	6.4
7	0.40	14.1	13.0	7.8
8	0.40	14.1	13.3	5.7
9	0.40	14.1	13.1	7.1
10	0.40	14.1	13.1	7.1
11	0.45	23.5	23.8	-1.3
12	0.45	23.5	24.0	-2.1
13	0.45	23.5	24.6	-4.7
14	0.45	23.5	24.4	-3.8
15	0.45	23.5	24.3	-3.4
16	0.50	42.3	43.1	-1.9
17	0.50	42.3	44.5	-5.2
18	0.50	42.3	43.2	-2.1
19	0.50	42.3	44.5	-5.2
20	0.50	42.3	43.2	-2.1

From these results it was concluded that dieldrin is not sorbed on centrifuge tubes in volume fractions of methanol greater than 0.40. However for volume fractions of methanol greater than 0.45, dieldrin would not possibly sorb on the aquifer materials.

Cosolvency Model.

The cosolvency model was developed by Rao et al., 1985 and data were presented by Nkedi-Kizza et al., 1985, for sorption of neutral organic chemicals on soils in mixed solvent systems. The model for sorption of a given sorbate in volume fraction of methanol is given by:

$$\ln (K^m/K^w) = -a\alpha^c\sigma^c f^c \quad (1)$$

where K^w = equilibrium sorption coefficient from water, mL/g; a = empirical constant accounting for water-cosolvent interactions. Note that for water-methanol $a = 1$, implying the absence of water-cosolvency interactions; α^c = the empirical constant accounting for solvent/sorbent interactions; σ^c = the cosolvency power of a solvency for a solute accounting for solvent/solute interactions, and f^c is volume fraction cosolvent. A plot of $\ln(K^m)$ vs f^c would

yield a line with an intercept equal to $\ln(K^w)$, from which K^w in aqueous systems can be calculated.

Sorption Experiments of Dieldrin on Aquifer Materials.

The batch slurry method of Nkedi-Kizza et al., 1985 was used to determine sorption coefficients of dieldrin in mixed solvent systems. Twenty ml of appropriate concentrations of dieldrin at each fraction cosolvent (0.35, 0.40 and 0.45, Table 1) were added to 50 ml centrifuge tubes. The centrifuge tubes were rotated on a shaker for 24 hours. The amount of dieldrin in solution was then determined. The solution concentration in each tube was taken as the initial dieldrin concentration and then 10 gm of aquifer materials were added. Two centrifuge tubes were used for each aquifer material at a given f^c . The soil in the tubes was also shaken for 24 hours and then centrifuged at 10,000 RPM for 15 minutes. Half a ml of clear solution was then added to 0.5 ml of methanol in an HPLC vial and dieldrin in solution was determined. The amount of dieldrin sorbed on aquifer material was calculated by difference from the initial dieldrin concentration according to the equation below:

$$S_e = V/M (C_o - C_e) \quad (2a)$$

$$K^m = S_e/C_e \quad (2b)$$

Where S_e is the amount of dieldrin sorbed ($\mu\text{g/gm}$); V is the volume of the mixed solvents (ml); M is the mass of aquifer material (gm); C_o is the initial dieldrin solution concentration in the centrifuge tube ($\mu\text{g/ml}$) after 24 hours before adding the aquifer material; C_e ($\mu\text{g/ml}$) is the dieldrin concentration in solution after equilibration with aquifer material; and K^m is the sorption coefficient (ml/gm). The K^m values for each f^c and aquifer material are presented in Table 2.

Table 2. K^m values as a function of f^c

f^c	aquifer material (47-48 m)	aquifer material (57-58 m)
	----- K^m (ml/gm) -----	
0.35	0.80	1.15
	0.82	0.66
0.40	0.24	0.33
	0.22	0.30
0.45	0.16	0.20
	0.19	0.15

Use of the Cosolvency Model:

The K^m values at each fraction cosolvent were plotted against f^c for each aquifer material, then the sorption coefficient in aqueous systems was calculated according to Equation 1.

Objective 5: To determine dieldrin concentrations as related to entrained component mass. (Dr. Moye)

Explanation

The need for this objective is straightforward. Dieldrin concentrations of various retentates and filtrates must be known to relate the influence of entrained components on dieldrin distribution. An association between dieldrin and mobile particulates should result in such an influence.

Task 5.0: Dieldrin analyses of retentates, filtrates, aquifer materials, and raw water

The method used was adapted from the National Pesticide Survey Method number 2 for analysis of chlorinated pesticides in drinking water. This method is based upon the extraction of sampled water with methylene chloride, concentration by Kuderna-Danish device or rotary evaporation, solvent exchange to methyl-butyl ether, and analysis by gas chromatography with electron capture detection.

Samples were extracted by placing 1 liter quantities in 2 liter separatory funnels, adding 60 mL of methylene chloride, shaking, draining, and repeating the procedure with a fresh portion of methylene chloride. Methylene chloride fractions were evaporated away in a 500mL Kuderna-Danish device equipped with Snyder column, with subsequent portions of ethyl-butyl ether added, to give a final volume of 5 mL. Methanol extracts was concentrated to 50 mL by rotary evaporation under reduced pressure at room temperature.

Gas chromatographic analysis were conducted on a Hewlett-Packard 5890 gas chromatograph equipped with a 30 m long x 0.25 mm ID DB-5 bonded silica column of 0.25um film thickness, programmed from 60°C to 300°C at 4°C/min. A 63NI film electron capture detector was used. Injection was 2 μ L volume in splitless mode. Quantities of dieldrin were read from a previously established analytical curve, done on a daily basis. All analyses were in triplicate. Residue concentrations were determined, along with standard deviations of laboratory triplicates. Correlation coefficients for analytical curves were determined.

Results and Discussion

Tasks 1.1, 1.2, 2.1, and 2.2.

These tasks are combined for presentation of results and discussion because they are closely inter-related. They comprise the collection and assessment of various size fractions of

entrained components using TFF.

The problems encountered in the testing phase of the TFF system and the adjustments made to overcome them were presented under materials and methods (Tasks 1.1 and 1.2). Water budgets (Table 3) show some water loss in the test fractionation, but negligible loss in the two subsequent ones. The large volume and duration for the test greatly increased the risk of hose rupture and failure, which was the major cause of loss. Fortunately, someone was always in attendance when hose problems occurred. Also, losses occurred in all cases early in the filtration cycle before significant concentration had occurred. Enough information was recorded to estimate entrained solids lost, but corrections for loss were of dubious value given other cumulative errors in measuring large volumes.

Table 3. Water budget data for fractionation replications.

	Rep 1	Rep 2	Rep 3
Original volume (mL)	100000	19000	18883
5-um Retentate (mL)	2807	565	783
5-um Filtrate (mL)	1120	850	850
0.40-um Retentate (mL)	1830	777	1021
0.40-um Filtrate (mL)	1120	850	700
0.03-um Retentate (mL)	25881	1031	1113
0.03-um Filtrate Sampled (mL)	1430	1000	700
Final 0.03- μ m Filtrate Volume (mL)	91031	13855	13660
Calculated Final Volume (mL)	92813	13927	13716
Percent Lost	1.782	0.379	0.296

The budget for solids (Table 4) showed some disparities between "no-loss" calculated predictions based on raw water solid concentrations and actual measurements for replicates 2 and 3. The disparities are not great, and are probably attributable to the cumulative error in repeatedly measuring large volumes of water. The budget for the first replication was very close, however, despite the fact that it involved the greatest volume of water. The solids content of the raw water was very consistent from sample to sample, averaging about 85 mg/L. A summary of the nature and abundance of colloidal particles in subsurface systems presented by Buffle and van Leeuwen (1993) indicates a wide range in solids concentration, from <1 mg/L to values exceeding 100 mg/L. However, the concentration of solids in the Corry Station water was higher than the majority of the values reported in the summary.

Table 4. Summary of fractionation data for Corry Station well water.

Fraction	Replicate 1		Replicate 2		Replicate 3	
	Solid Conc., mg/mL	Total Solids, mg	Solid Conc., mg/mL	Total Solids, mg	Solid Conc., mg/mL	Total Solids, mg
0.03 μ m F	0.0647	4215	0.0662	983	0.0932	1338
0.03 μ m R	0.1338	3464	0.107	110	0.0967	108
0.40 F			0.068	58	0.0935	65
0.40 R	0.1233	226	0.0978	80	0.1088	111
5.00 F			0.0815	69	0.0805	68
5.00 R	0.0952	267	0.106	60	0.089	70
Sum		8172		1366		1760
Raw Water	0.0827	8267	0.085	1615	0.0818	1545

Concentration of solids in retentates were greater than for raw water, but not markedly so (Fig. 1). The fractionation data presented as "weight fraction" (Fig. 2) reveals an important characteristic of the solids: they are predominantly very small, smaller than for the majority of samples summarized by Buffle and van Leeuwen (1993). Most of the particles are less than 0.03 μ m in size. This attribute makes true particle-size fractionation a moot consideration, since the bulk of solids are within a size range too small for practical fractionation. We probably would not have learned of the very small size range without the use of TFF, because even relatively coarse dead-end filters would have retained the finer particles by clogging. The finer particles passed through all the filters used in the sequence because the cross-flow effect prevented significant clogging.

The TFF procedure could not accomplish a true particle fractionation for the Corry Station water because of the very small size of entrained solids. The paucity of larger particles means that the finer particles made up a high proportion of all retentates. In effect, not all of the finer particles have the opportunity to pass through the filter. This imparts a volume dependency to the budgeting of solids. For example, the 0.03- μ m retentate of replicate 1 ostensibly indicates a higher proportion of the 0.03- to 0.40- μ m fraction than in the case of replicates 2 and 3 (Fig. 2). This difference is not real, but is a consequence of the much greater volume of 0.03- μ m retentate "suspension" of replicate 1 which arose from the inability to reduce the volume further.

Carbon content of the Corry Station water samples was very low (Table 5), barely above that of ultra-pure reagent grade de-ionized water. Carbon comprises only a small fraction of the total entrained solids: roughly 1 to 2 percent. The organic matter content would be nearly

double this, since it contains other elements. However, analyses indicated that inorganic C was present in about the same order of magnitude as organic C. Carbon content was barely above the precision limits of the instrument used for analyses, thus the discriminating value of the data is questionable. Nevertheless, retentates consistently had higher levels of C than filtrates, which is what was expected. Carbon data for the second replication are not reported because of C contamination from the gear pump; apparently a lubricant leaked from the gear axle at high-speed operation.

Table 5. Summary of carbon data for filtrates and retentates of replicates 1 and 3. Carbon data for replicate 2 was confounded by pump contamination.

Fraction	Replicate 1			Replicate 3		
	Total C	Inorg. C (mg/L)	Org. C	Total C	Inorg. C (mg/L)	Org. C
0.03 F	1.03	0.92	0.11	2.56	1.47	1.09
0.03 R	2.85	1.31	1.54	2.93	1.33	1.61
0.40 F				1.98	1.42	0.56
0.40 R	1.43	1.25	0.18	3.18	1.53	1.60
5.00 F	1.24	1.09	0.15	3.00	1.92	1.08
5.00 R	1.30	0.66	0.64	3.61	1.59	2.02
Raw Water				1.3	0.91	0.39
Blank 1 ¹				1.28	0.00	1.28
Blank 2				0.37	0.01	0.36

¹Blanks were ultra-pure reagent deionized water.

The aquifer samples contained very small amounts of C (Table 6), but the levels were well within the detection limits for the method used. Samples were dominated by sand- and gravel-sized particles. Even if the C content is expressed as a percentage of the clay (which was actually used in the C determinations), the amount is only about 0.3 %. This is an order of magnitude lower than the C content for materials entrained in the ground water. The higher proportion of C entrained in water is not surprising since C derived from such depths is likely to be of very small size or truly "dissolved". Each of the latter conditions would favor mobility. No definite conclusions can be drawn about the relation between aquifer C and the C entrained in the well water, because of limited sampling, etc. However, the data available to date "make sense." Future research tracking C and groundwater contaminants should probably encompass a solid-state analysis for C (as was done for the aquifer clays) in order to attain adequate

sensitivity. However, this would require the collection of an appreciable mass of material via filtration, centrifugation, etc.

Table 6. Particle-size, total C (TC), and total N (TN) data for aquifer sample CRY-1-14D.

Depth (cm)	Sand ——	Silt (% < 2mm)	Clay ——	Whole Material						TC (%)	TN (%)
				Gravel (> 2mm) (%)	Fines (< 2mm) (%)	Sand (%)	Silt (%)	Clay (%)			
4770	94.1	2.7	3.2	13.3	86.7	81.7	2.3	2.7	0.0092	0.0011	
5670	92.9	3.4	3.7	32.8	67.2	62.4	2.3	2.5	0.0072	0.0009	

Tasks 3.1, 3.2, and 3.3

These tasks encompass the mineralogical assessment of the TFF retentate solids from the Corry Station well water and aquifer clay material collected at two depths in the vicinity of the well.

Mineralogical compositions of the aquifer clay, the 0.40- μm retentate solids, and a sample collected on a dead-end 0.45- μm filter by the DISTRICT were quite similar (Figs. 4, 5, and 6). The dominant mineral present in all samples is kaolinite, as indicated by x-ray diffraction peaks at 7.2 Å and 3.5 Å. An endothermic peak between 450- and 550 C was substantiating evidence provided by DSC analysis. The latter peak is attributable to the dehydroxylation reaction undergone by kaolinite in this temperature range. Other minerals present in the aquifer clays were mica (illite) and smectite. Mica is also present in the water-entrained clay, and there is evidence for smectite or a smectite-like (expanding, hydrated interlayers) mineral. The peak in the smectite region is too diffuse for the retentate for definite identification. However, the behavior of the peak in response to K and Mg saturation is characteristic of smectite for the aquifer clays (Fig. 4). There is possibly a small amount of quartz in the aquifer clay, but this identification is also tenuous because the major peak for quartz corresponds with one of the strong peaks for illite. The less intense peaks for quartz are not evident.

The peak width at half height, an index of particle-size and crystallinity in x-ray diffraction, is much greater for the water-entrained clay than for the aquifer clay. This is consistent with the very fine size of the entrained clay. The finest particles would have the greatest probability of being mobilized and making the passage through the pores of the aquifer matrix.

Smectite is a mineral with permanent negative charge due to structural cation substitutions (McBride, 1989). Electro-neutrality is maintained by exchangeable cations which would be hydrated in an aqueous medium or in the presence of water vapor. Also, the smectite surface would be hydrated as well due to dipole interactions with water and surface oxygen

atoms. Thickness of the positively-charge diffuse layer of hydrated exchangeable cations surrounding smectite is maximized at low ionic strength. Repulsion between diffuse cation layers minimizes particle interactions and promotes a stable colloidal suspension. Kaolinite also has a charged surface that is to some degree influenced by pH. At the pH of the water (about 5.5) it would be negatively charged, but magnitude of charge would be less than that of smectite. Dilute suspensions of each of these mineral should be quite stable at low ionic strength and in the absence (or near absence) of aggregating agents such as Fe, carbonates, or organic matter.

The charged, hydrophilic surfaces of kaolinite and smectite would not be as favorable for adsorption of a non-ionic contaminant such as dieldrin as would organic matter. However, in cases where organic solids are very low, inorganic surfaces can become a dominant retentive sink even for hydrophobic contaminants (Schwartzbach and Westall, 1981; Banerjee et al., 1985). One reason for this is that the mineral surface is still a lower energy environment for the organic contaminant than the aqueous phase. Another mechanism that could promote organic-contaminant association with mineral surfaces would be the presence of natural organic matter coatings on suspended mineral particles which would increase surface affinity. A smectite group mineral (montmorillonite) has been implicated in the facilitated transport of DDT. Another factor favoring sorption to mineral surfaces, even if dieldrin coverage per unit surface area is low, is the very large specific surface of the entrained particles. Expansible layer silicates (such as smectite) have a specific surface of 700 to 800 m²/g (McBride, 1989). The specific surface of kaolinite is much lower, but increases with decreasing particle size. In the particle-size range of the entrained particles kaolinite could have a specific surface exceeding 30 m²/g.

Substantiating the apparent link between the mineralogy of the retentate and aquifer clay would require spatial replication.

Task 4

The sorption coefficients (K^m) in cosolvent are plotted as a function of volume fraction of methanol in Figure 7. All data for both aquifer materials are pooled together (Figure 1A) and individually (Figure 7B). The data are well described by the cosolvency model even if K^m values could not be obtained in f^c values less than 0.30 due to low solubility of dieldrin or at f^c above 0.45 due to low sorption on aquifer materials. K^w values obtained in water for both aquifer materials were not significantly different. Therefore the K^w value of 181 (ml/gm) is used (Figure 7A) for the calculation of K_{OC} . Based on organic carbon content of 0.01% for the fine fraction of the aquifer material, K_{OC} is calculated as 1,810,000. This value of K_{OC} is 238 times larger than the literature value. We believe that in addition to organic matter, the inorganic components of the clay fraction contributed to the sorption of dieldrin. Normalizing K^w to clay content (3.41%) of the fine fraction yields K_{clay} of 5171 which is close to K_{OC} of 7600. This leads to conclusion that the clay fraction as a whole is responsible for dieldrin sorption on aquifer materials studied. Therefore, facilitated transport of dieldrin into well water found at the Corry Station, is most likely due to the clay fraction of materials above and within the aquifer.

Task 5

The dieldrin analyses for raw water, retentates, and filtrates (Table 5) of the testing

phase (replicate 1) revealed problematic aspects of the TFF system. The water for this replication was collected in containers (see materials and methods) which reduced dieldrin concentration 6-fold from that which was determined in amber liter bottles. Despite this reduction, there would probably still have been sufficient dieldrin concentration to monitor differences between retentates and raw water had there not been further profound loss of dieldrin within the system itself. The filtrates had higher dieldrin concentrations than retentates, though even they were markedly reduced. We deduced from the data and physical inspection that the component most responsible for dieldrin adsorption by the system was the peristaltic tubing (see materials and methods). The retentate continuously cycled through the tubing until the fractionation was complete, whereas the filtrate "escaped" this loop. Over time, the interior of the tubing became progressively more cracked, increasing its surface area.

The glass containers used to store the raw water and serve as fractionation vessels in the second and third replication did not reduce dieldrin concentrations below levels normally reported for the well (Table 7). Use of different pumping systems and tubing materials (see materials and methods) greatly reduced, but did not eliminate, dieldrin adsorption within the system. Budget calculations show that approximately 1/2 (replicate 3) to 3/4 (replicate 2) of the dieldrin determined for the raw water was lost to the system during filtration. Loss to the system could probably be further reduced, perhaps to negligible amounts, if (i) the 0.03- μm filtration were eliminated and (ii) only one filtration were conducted. The 0.03- μm filtration within a sequential scheme required a long residence time in the system and thus extended the opportunity for adsorption.

Table 7. Summary of dieldrin concentrations ($\mu\text{g/L}$) for filtrates (F) retentates (R) and raw water samples.

Fraction	Replicate		
	1	2	3
0.03 F	0.002	0.06	0.14
0.03 R	BDL ¹	0.11	0.20
0.40 F	0.004	0.09	0.31
0.40 R	BDL	0.38	0.33
5.00 F	0.009	0.56	0.26
5.00 R	0.0004	0.12	0.21
Raw Water	0.28 ²	0.45	0.32

¹ BDL - below detection limits

² Mean determined for 2 amber liter bottles.

Comparison between dieldrin concentrations in retentates and filtrates showed similar trends for replications 2 and 3 (Fig. 3). Retentates of 0.40- and 0.03- μm filtration had higher dieldrin concentrations than did filtrates. However, the reverse was the case for the 5.0- μm filtration. TFF results are therefore inconclusive regarding a dieldrin-colloid association, despite results (Task 4) showing that dieldrin sorbed readily to the aquifer material with clay mineralogy (Task 5) quite similar to that of the entrained solids. The major confounding factor was the extremely small size of the solids, which meant that only a minimal concentration was achieved for the filters used in this study. In effect, solid concentration of retentates was barely above that of filtrates, particularly for the 20-L filtrations. The dieldrin-colloid association would best be assessed where substantial increases in solids concentration were obtained for retentates over that of raw water. This differential would be increased if all the particles above a fine filter size were collected without previous fractionation. The filter size would have to be a compromise, in that it should be fine enough to collect sufficiently but not so fine as to be prohibitively slow.

Summary and Conclusions

The particles entrained in well water from Corry Station are very small, dominantly less than 0.03 μm in size. This is a smaller size range than is commonly reported, though there is a wide variation in size of particles in groundwater. The total solids content for the water as measured for different samples was quite consistent, averaging about 0.085 mg/mL. This is on the higher end of the range for reported data, though there is also considerable variation for this measure. The dominance of particles smaller in size than the smallest filter precluded a true particle size fractionation by TFF. Retentates had only modestly elevated solid concentrations with respect to filtrates and raw water. A volume dependency in allocating solids to size fractions indicates that a high proportion of particles in retentates are actually smaller than the filter pore size, and would have passed were the filtration carried out to completion. Carbon content of the water was barely above that of ultra-pure de-ionized water, barely above detection limits for aqueous determination, and only a little over one percent of the solids. The C concentration was consistently higher in the retentates than filtrates, however, supporting the presence of some particulate C. The aquifer clay contained an order of magnitude less C than did the entrained solids, suggesting that C is preferentially mobilized in groundwater flow. The paucity of C places greater significance to the prospect of facilitated transport via inorganic particulates. The mineralogy of the clay from entrained solids, of solids filtered by the DISTRICT, and of aquifer clay were quite similar. The dominant mineral was kaolinite, with lesser amounts of illite and smectite. These are phyllosilicates with hydrated surfaces, but these surfaces still constitute a lower energy environment for a hydrophobic contaminant than the aqueous phase. Phyllosilicates have been implicated in the transport of pesticides, particularly where organic C is very low. Dieldrin analyses of filtrates and retentates failed to show a consistent relation between dieldrin concentration and solids concentration. Confounding factors were (i) the small differentials between solids concentrations of filtrates, raw water, and retentates; and (ii) the tendency for dieldrin to sorb on system components. Any future attempt to establish a link between dieldrin and colloid concentrations should be designed to maximize that potential while minimizing residence time within the system during filtration. Fractionation

is counter to these goals and should not be conducted. The sorption coefficient (K^w) of dieldrin on both aquifer materials in water was 181 ml/g. This implies that if 1 gram of the aquifer material is contained in 1 ml of water, the aquifer material will contain 181 times more dieldrin than in solution. Sorption coefficients of aquifer materials in water were not significantly different. Based on the amount of organic C in the fine material (0.01%) and the literature K_{OC} of dieldrin of 7,600, K^w should be about 0.76 ml/g, which is almost 238 times less than was found in the sorption experiments. Thus inorganic materials in the clay fraction also sorbed dieldrin. Normalizing the sorption coefficient to clay content (3.5%) yields K_{clay} of 5171, which is close to K_{OC} of 7,600. These data clearly indicate that the aquifer materials can adsorb dieldrin even if they contain very little organic C. This is expected since dieldrin is very hydrophobic and can essentially adsorb on any material.

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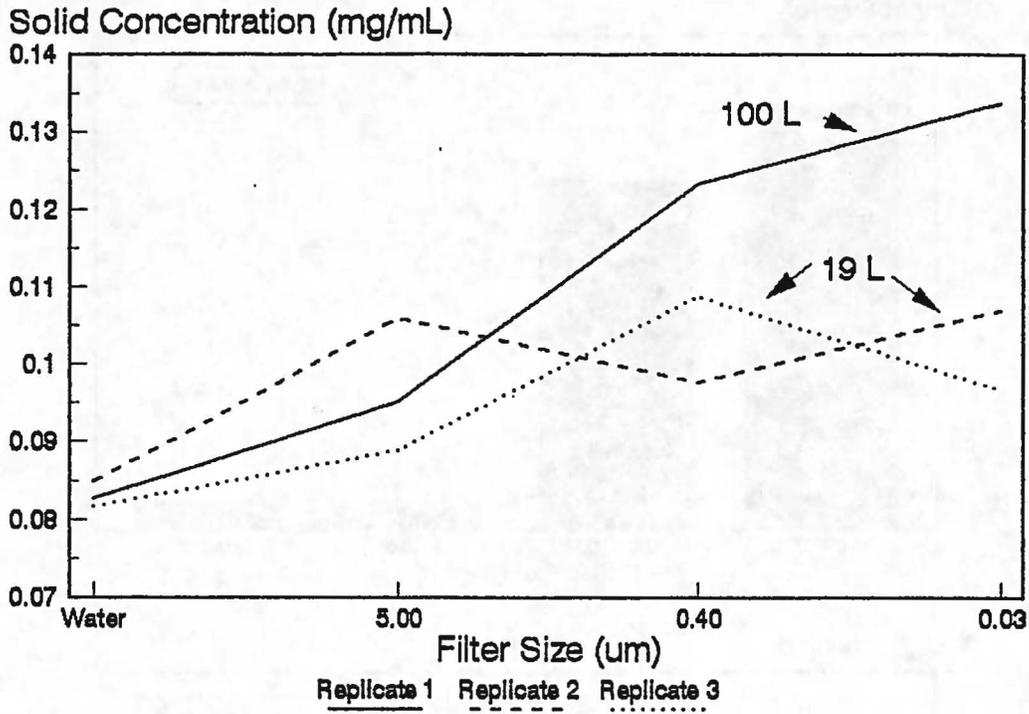


Figure 1. Concentration of solids in raw water and designated retentate fractions collected by tangential flow filtration.

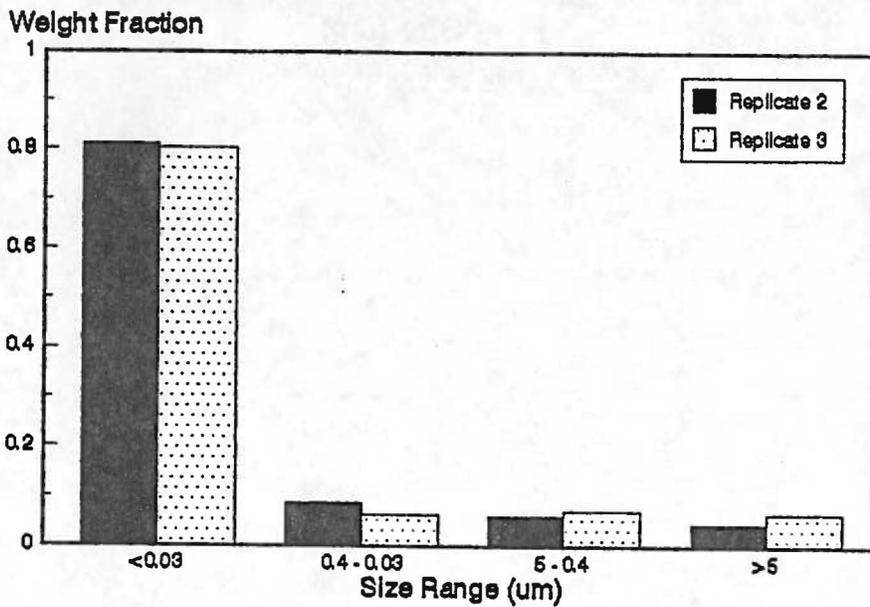
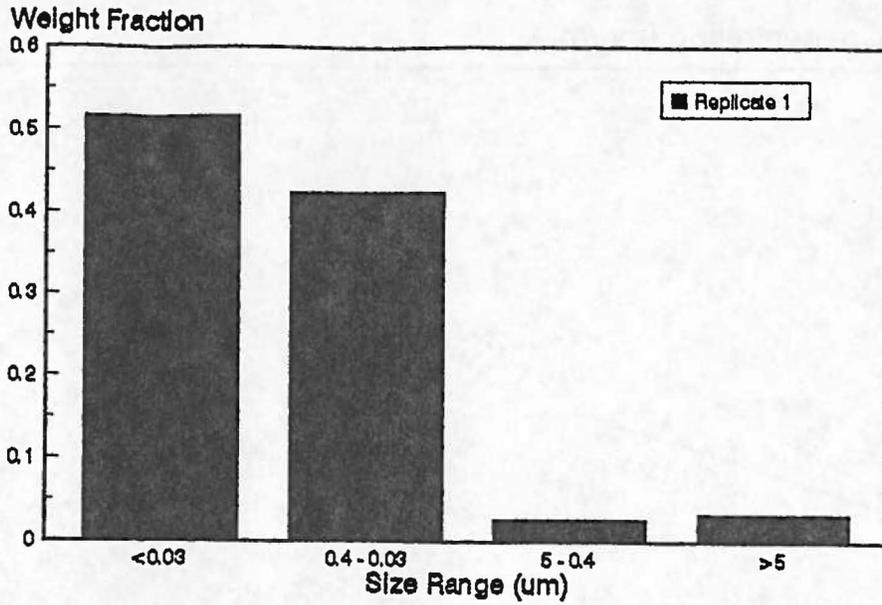


Figure 2. Weight fraction of total solids partitioned by apparent particle-size range as determined by tangential flow filtration. The data are a not true indicator of particle size because the majority of particles are below size range for practical filtration (see text).

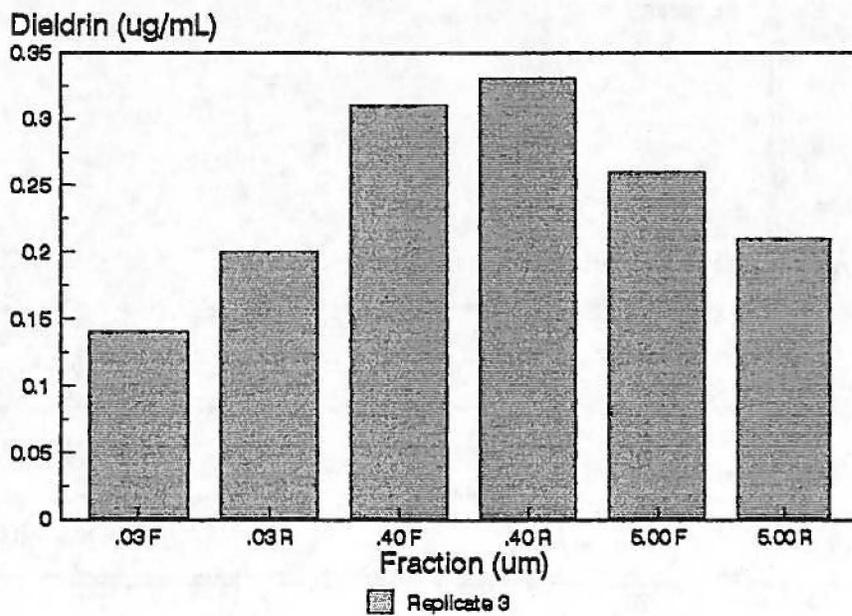
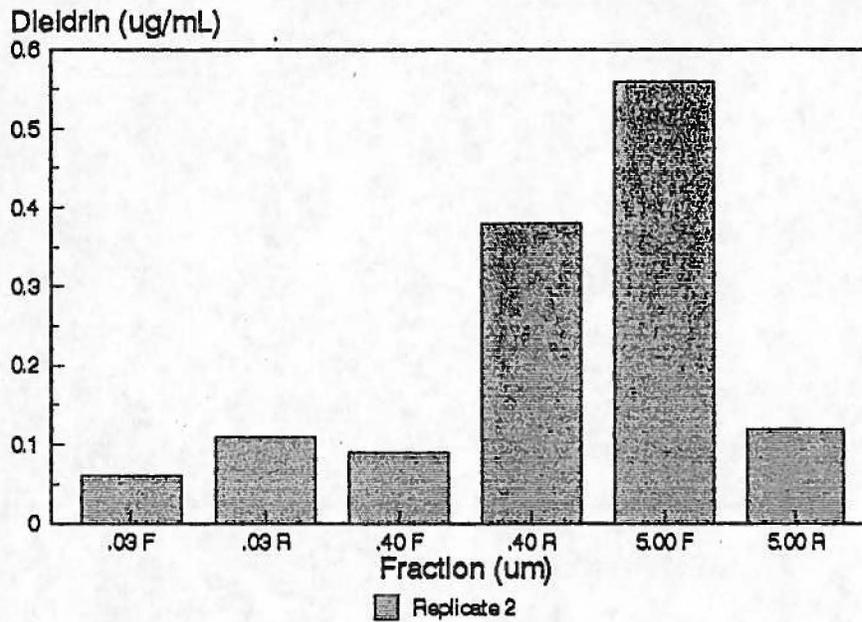


Figure 3. Graphical representation of dieldrin concentration for retentates and filtrates of replications 2 and 3.

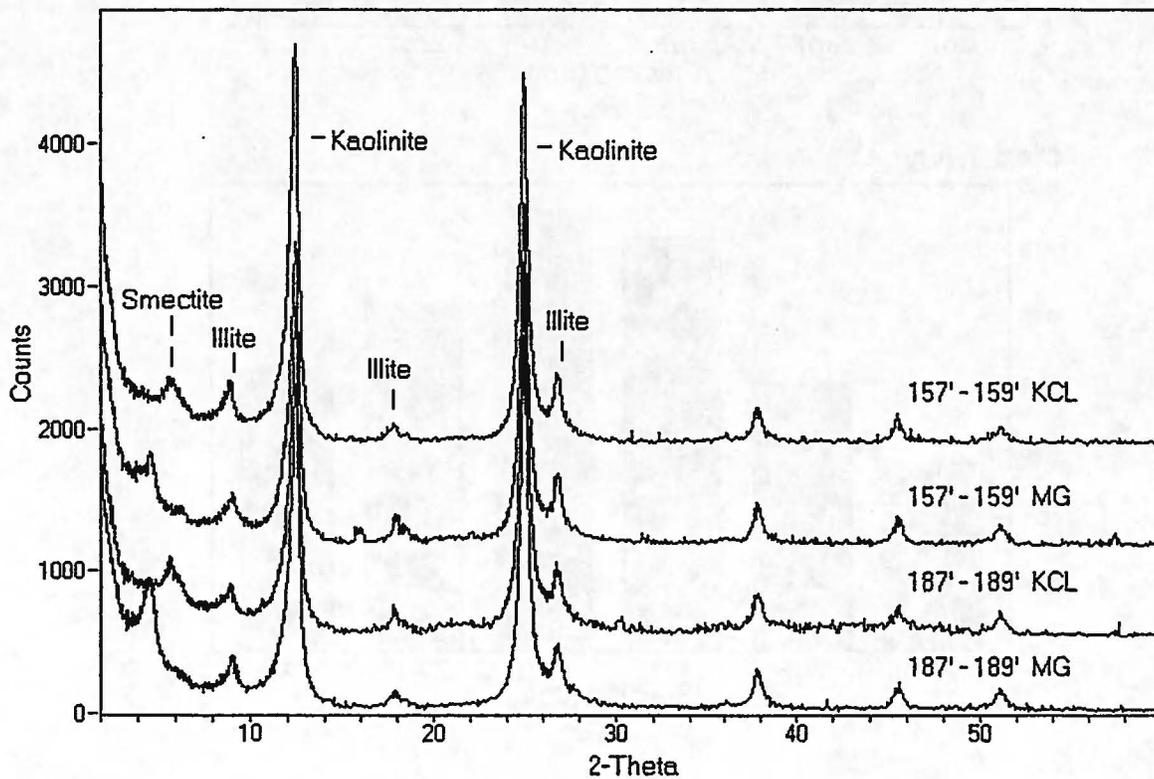


Figure 4. X-ray diffraction patterns for two aquifer sample clays (designated by depth), showing peaks for minerals and diagnostic behavior under K and Mg saturation.

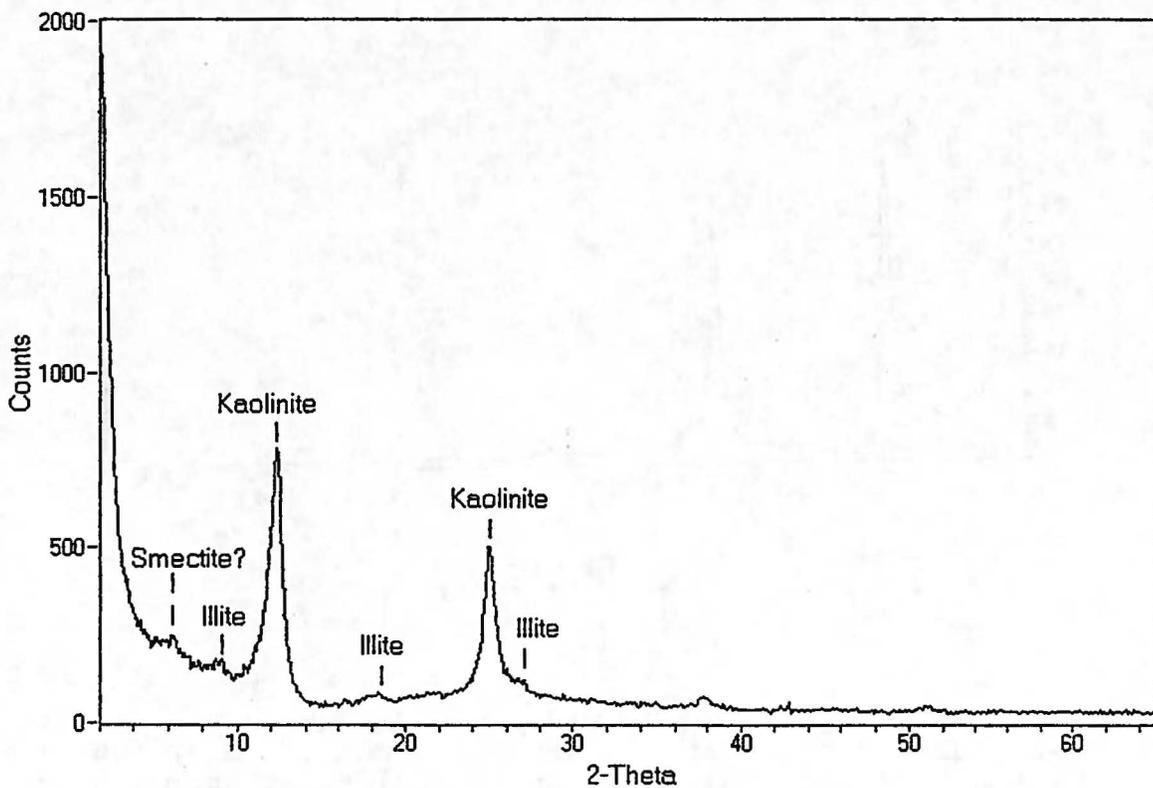


Figure 5. X-ray diffraction pattern of solids collected on 0.40- μm filter during 100-L tangential flow filtration (replicate 1), with peaks labelled by mineral. This pattern is indistinguishable from that for clay collected on filter by the DISTRICT (see Fig. 6).

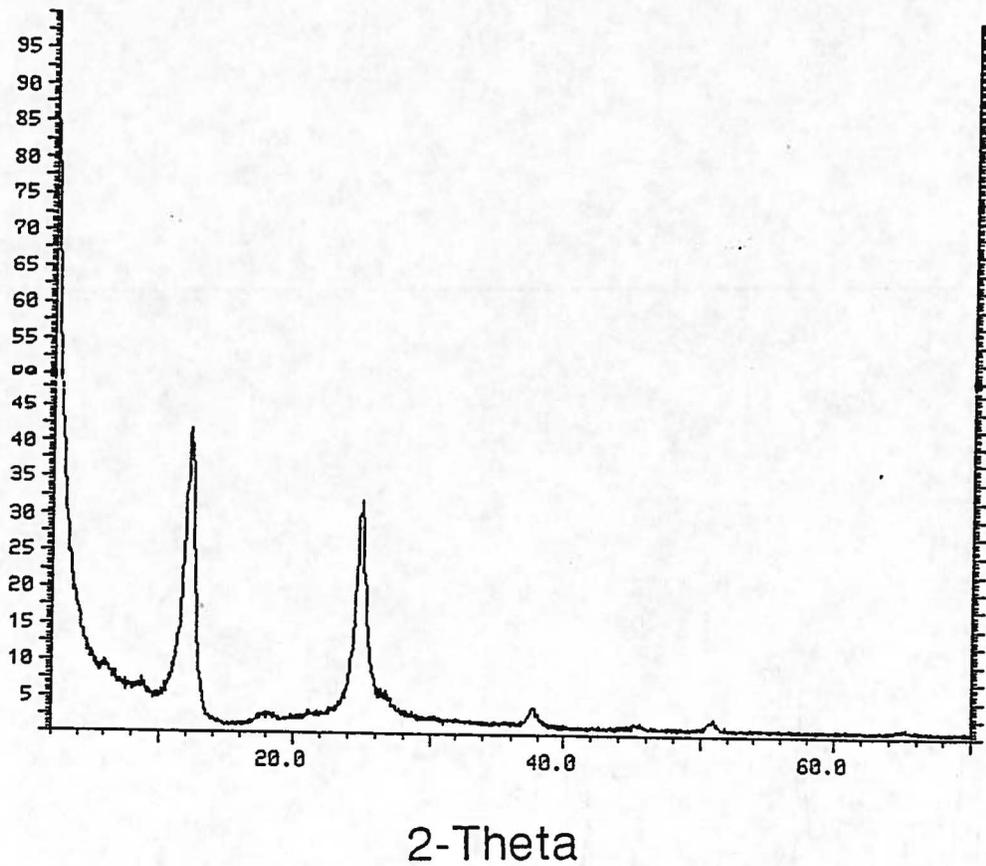


Figure 6. X-ray diffraction pattern of solids collected on filter by the DISTRICT. This pattern is indistinguishable from that collected by tangential flow filtration (see Fig. 5).

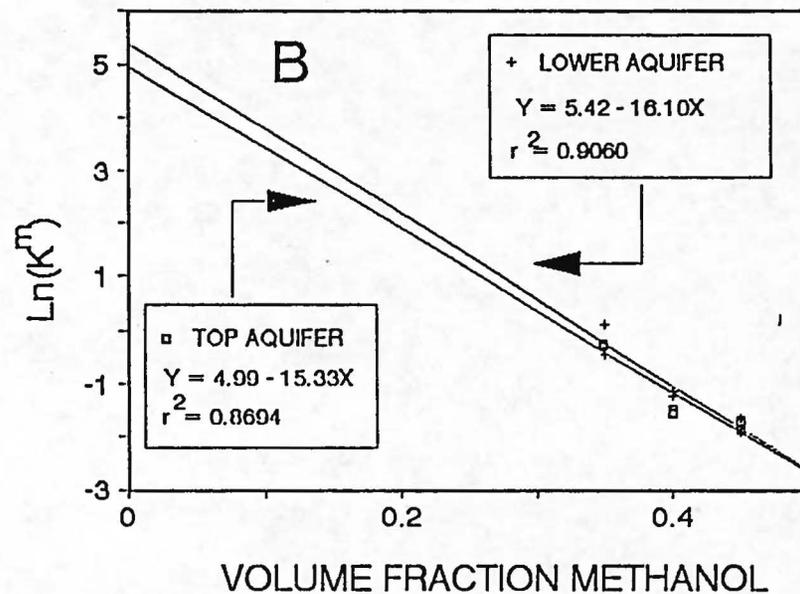
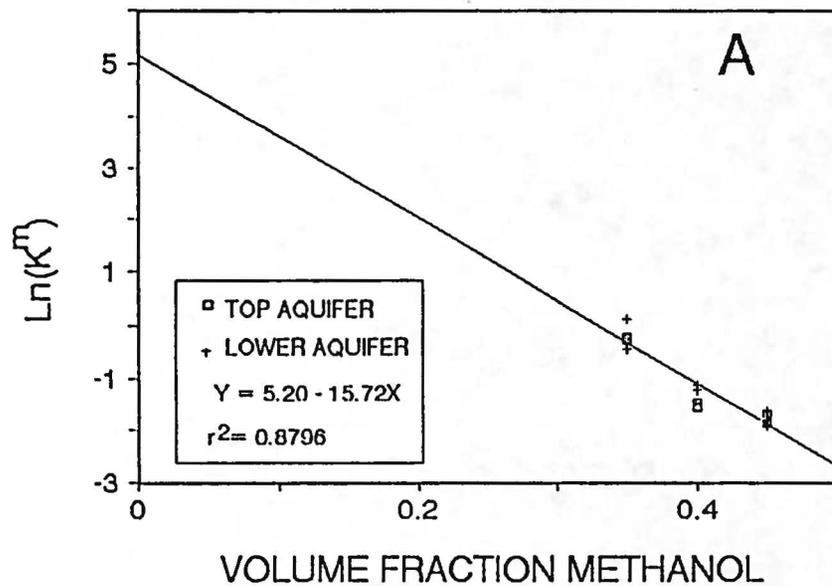


Figure 7. Sorption coefficients of dieldrin as a function of volume fraction methanol. A) Data for both aquifer materials. B) Data for each aquifer material. Top Aquifer = 47-48 m; Lower Aquifer = 57-58 m.

LIST OF APPENDICES
(continued)

Appendix G -- Well Schedules for Existing Project Wells

- Appendix G-1. Well Schedules for Corry Station Production Wells
- Appendix G-2. Well Schedules for Corry Station UST Monitor Wells
- Appendix G-3. Well Schedules for Private, Off-base Wells
- Appendix G-4. Well Schedules for DEP Warrington Village PCE Wells
- Appendix G-5. Well Schedules for Peoples Water Service Production Wells
- Appendix G-6. Well Schedules for Abandoned Corry Station Wells.

**Appendix H -- Association of Dieldrin with Colloidal Particles and Aquifer
Materials in Well Water from Corry Station, Florida**

backwashed and discharged to the environment in order to restore the hydraulic efficiency of the vessel. As a result of this information, it was originally planned to sample the solids accumulating in the vessels. It has since been determined that the waste material generated during the backwash process of the most contaminated wells is contained and properly disposed of off-site. The practice of discharging this material to the environment has been discontinued for the most heavily contaminated wells (personal communication; PWC staff). Accordingly, this aspect of the public supply assessment was not performed.

Currently, prior to pumping GAC treated ground water into the distribution system, the water contained in the GAC vessel is purged into the environment. For the sake of completeness, this environmental pathway was sampled and analyzed.

10.8.3 Summary of Results

Sub-assessment 1 -- Analysis of raw water samples collected provided dieldrin concentration data consistent with historical concentrations. Dieldrin was detected in three of the nine supply wells sampled, Corry #7, #8 and #11. Chlordane and heptachlor epoxide were each detected in two of the Corry supply wells. Chlordane was present in Corry #7 and #8, while heptachlor epoxide was detected in Corry #8 and #13 (Plate 7).

Analytical results show current dieldrin concentrations in the public supply wells are of the same order-of-magnitude as previously observed data. Dieldrin exhibited the highest concentrations, followed by chlordane and heptachlor epoxide. Corry #8 showed the highest levels of contamination and was the only supply well to show the presence of all three contaminants.

Other organic contaminants (benzene and PCE) were detected in Corry #12. The presence of these contaminants is consistent with previous findings. The most likely source for these contaminants is the commercial corridor immediately east of Corry Station. Numerous potential sources are located in this area.

Lindane was also detected in Corry #12. Like dieldrin, lindane is a persistent chlorinated pesticide used against insects. It has been used in a wide range of applications, including soil treatment, timber and wood protection, foliage application, treatment of animals for ectoparasites and treatment of water for mosquitoes. Lindane was not detected in any other wells. The source of the lindane was not determined.

Sub-assessment 2 -- The total solids content of the raw water from Corry #8 was very consistent from sample to sample, averaging 85 mg/L. The tangential-flow filtration (TFF) of raw water samples (particle size fractionation) was performed utilizing 5 micron, 0.4 micron and 0.03 micron membranes. Results showed most of

the particles to be less than 0.03 microns. Thus, the use of membranes noted above, did not effectively partition the solids known to be present in the raw water. Virtually all of the colloids present passed through the 0.03 micron membrane. Fractionation of particles with membrane finer than 0.03 micron was not practical given the volume of sample processed and the type of equipment used.

The retentate solids were analyzed for mineral content where a sufficient mass of solids was retained. In addition, clay present in two split spoon samples collected from the MPZ of the aquifer were analyzed. The mineralogical composition of all samples analyzed was quite similar, consisting predominantly of kaolinite with mica (illite) and smectite, indicating that the source for the water-entrained solids is the aquifer matrix clay fraction. Analysis of x-ray diffraction peak width indicates very fine particle size of the colloidal clay entrained in the water, as compared to the particle size of clay collected from the aquifer matrix.

Dieldrin adsorption experiments on aquifer matrix material clearly indicated that the aquifer materials can sorb dieldrin despite their very low organic carbon content. The sorption coefficient (K^w) of dieldrin on aquifer materials in water was 181 ml/g. This implies that if 1 gram of the aquifer material is contained in 1 ml of water, the aquifer material will contain 181 times more dieldrin than the water.

Lack of effective size partitioning of colloids and several problematic aspects of TFF techniques used to prepare samples for organic analysis precluded direct association of colloidal size fractions and the presence of sorbed dieldrin. However, the sorption experiments demonstrated a strong preference for dieldrin to sorb onto aquifer materials. Therefore, colloid-facilitated transport of dieldrin into the water wells at Corry Station, while not clearly demonstrated to be occurring, cannot be ruled out. The adsorptive capacity of the aquifer material also shows a capacity for the aquifer to retard the movement of dieldrin. A complete discussion of the techniques used and results of these experiments is found in **Appendix H**.

Sub-assessment 3 -- During 1994, the process of purging Corry #7, #8, and #11 was observed. For procedures and well discharge rates in effect at that time, no purge water left the vicinity of these wells. Purge waters infiltrated into the ground around these wells.

No chlorinated pesticides were detected in the soils collected near the splash pads of Corry #7, #8 and #11. In addition, no pesticides were detected in the purge water collected from the GAC vessels at these wells. Current operational procedures of discharging limited amounts of purge waters at the well is not resulting in noticeable spread of contaminants.

