

## ORGANIC POLLUTANTS IN GROUND-RECHARGED WATER

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### INTRODUCTION

Withdrawal of water from potable aquifers is rapidly approaching the recoverable streamflow and ground water supply in the United States (Eliassen, 1968). This trend is painfully evident in the southwestern states. Many proposals for multiple re-use of waste waters have been suggested to save the precious water supply. Tertiary treatment of effluent has been used in some municipalities, but it is expensive. Another process which has shown promise is filtration of secondary effluent through soil: the ground recharging system. (Bower, 1968, 1970; Lance, 1972, 1976; Thomas, 1969; Schmidt, 1978).

A pioneering study (Bower, 1974) of ground recharging was initiated at Flushing Meadow, Phoenix, Arizona by the U.S.D.A. Water Conservation Laboratory in 1967. In this project, secondary sewage effluent was spread onto rapid infiltration basins. Wells at various depths were used to pump up the renovated water for analysis. The results of this renovation are shown below:

1. Essentially complete removal of suspended solid, biological oxygen demand and fecal coliform bacteria was effected.
2. Phosphate removal was at least 50%.
3. Boron was not removed and reached levels of about 0.8 mg/liter.
4. Copper and zinc concentrations were reduced by about 80%, while cadmium and lead remained the same.
5. Mercury levels were reduced from about 2 to 1.3 micrograms/liter.
6. Total dissolved salt content was less than 1,200 mg/liter. (This was 2% higher than the effluent due to evaporation. The pH was 7.)
7. Nitrogen removal was about 30%; however, this removal could be nearly tripled.
8. The renovated water still contained about 5 mg/l of total organic carbon.

The cost of renovating the secondary effluent was estimated at \$4.30/1,000 m<sup>3</sup>, much less than the tertiary treatment.

Despite the impressive reclamation statistics, the water was still classified for use only in restricted irrigation and recreation (Bower, 1974, 1979) although it has been approved for cooling tower purposes for the Palo Verde Nuclear Plant (Bower, 1979). Part of the cautious attitude towards its unrestricted use is based on the presence of 5 ppm of organic carbon. In recent years, numerous reports of the toxicity of halogenated and other organic compounds in water supplies have been published. These reports have caused municipal water managers to scrutinize the organic content of potential drinking water supplies. (Water Pollutants, 1981)

Our interest was attracted to the organic fraction of the ground recharged water, which had not yet been characterized. A number of questions confronted us. Were

there any toxic compounds in the water? Where did they come from? What types of compounds were removed by the soil? Were any compounds added to the recharged water by the soil? To answer these questions at least in part, we decided to sample the water supply which entered the Flushing Meadow basin, from its source at the Salt and Verde Rivers, through the treatment plants and the sewage plant. Limitations of time and resources required us to limit our analysis to certain specific substances and to develop the analytical procedures for their detection.

The EPA lists 114 priority pollutants (Van Hall, 1979) that it routinely monitors in drinking water. There are additional organic compounds that enter secondary effluents, besides non-toxic substances which are converted to toxic compounds upon chlorination. An analysis of all these substances would be a monumental job. Therefore, we restricted our scope to certain target organic compounds.

#### THE OBJECTIVES OF THIS STUDY ARE LISTED BELOW:

1. To determine the haloform concentrations: i.e., chloroform, bromoform, dichlorobromomethane, carbon tetrachloride and others.
2. To determine the haloform concentration after treatment with chlorine. This gives an estimate of the trihalomethane precursor (THMP) which still remains in the water sample.
3. To determine the phenol content of the water samples. Phenols may be toxic; they form odorous chlorinated phenols and some of them may form haloforms.
4. To determine the humic acid content. Humic acid is the major organic constituent of most natural waters and is a known haloform producer (THMP).
5. To develop analytical procedures for the above.

#### ANALYTICAL PROCEDURES

##### 1. Determination of Haloforms in Water Samples

###### a. Instrumentation

For the purpose of this analysis, we purchased an Electron Capture Detector (ECD) gas chromatograph (Varian 3700). This instrument was capable of detecting 1 part per billion (ppb) of less of chloroform and other haloforms. The most frequently reported haloforms in drinking water are chloroform, bromodichloromethane, chlorodibromomethane, bromoform and carbon tetrachloride.

###### b. Head space analysis

The method developed by our Laboratory is somewhat simpler than the published analytical technique (Oliver, 1976). The water sample (100 ml) was placed in a 125 ml. Erlenmeyer flask and capped with a rubber septum. It was then placed in a gyrating water bath at 74°C and allowed to equilibrate for 20 minutes. Ten microliters of the headspace was withdrawn from the sample with a gas tight syringe, compressed to 1 microliter and injected into the gas chromatograph. The gas chromatograph conditions were established as follows: Column 6' x 1/8" 0.2% Carbowax 1500 on 80/100 Carbowax C.

Injector port temperature: 220°C

Detector " : 300°C

Column " : 50°C

Gas flow: 30 ml min.

The concentration of haloform was determined by comparison of the integrated area under the curve to a standard curve, which was constructed from standard haloform solutions prepared in an identical manner to the test samples. Although this technique was a significant improvement over the Oliver method, it was still time-consuming. Furthermore, it was destructive to the expensive gas syringes.

###### c. Direct Aqueous Injection (DAI)

This method (Hammerstrand, 1976; Nicholson, 1977) is by far the simplest of all

the methods used for the detection of trihalomethanes. A sample of 5-10 microliters can be withdrawn from a water solution and directly injected into the port of a GLC instrument. No other preliminary treatment is necessary, although certain precautions may be necessary (Stevens, 1978). To carry out this analysis, we used the following conditions:

Column: Chromosorb 101 80/100 Mesh 4.5' x 1/4"

Injector port temperature: 250°C

Detector: 300°C

Column: 150°C

Gas flow: 60 ml/minute

#### d. Chlorination of Water Samples

The concentration of residual trihalomethane precursor (THMP) in aquatic samples can be estimated by chlorinating the sample and then measuring the amount of chloroform generated. For this analysis, the following procedure was used: to 10 ml. of water sample was added 4 microliters of 5% commercial bleach. This yielded a total chlorine content of 10 ppm. The mixture was allowed to stand for 30 minutes, then quenched with Na<sub>2</sub>S<sub>2</sub>O<sub>3</sub>. The chloroform content was determined as in part (c).

#### 2. Total Organic Carbon

Total organic carbon (TOC) values of the test samples were determined by Gladys Auer, USDA, Water Conservation Laboratory, Phoenix, Arizona and Professor Wallace Fuller, Department of Soils, Water and Engineering, University of Arizona.

#### 3. Phenol Content

The determination of phenols in drinking water posed a serious challenge to us. No one published method is capable of estimating total phenol content. The most widely-used method to monitor the phenolic content of potable waters is the amino-antipyrine colorimetric method (Standard Methods, 1974). Although this "standard" assay is required by many local and state jurisdictions, it is sensitive only to steam volatile phenols which are unsubstituted in the para position. Therefore, it measures a very limited group of phenols and is unreliable even for this group (Van Hall, 1979, p 203).

Simple low-molecular weight phenols and halogenated phenols may also be analyzed by GLC or GC-MS (Van Hall, 1979). No general method exists for the analysis of flavonoids and pigments, although HPLC would seem to be best-suited. For the phenolic macromolecules such as tannin, humic acids, fulvic acids and lignins, there exist no simple screening procedure. Thurman (1979) however, have developed some elegant fractionation schemes for these types of compounds.

We decided to develop a spectrophotometric method for total phenol and total humate content. This analysis is based on the following properties of phenols:

- (a) They are adsorbed on XAD resins in the acid form.
- (b) They are eluted from the resin by base.
- (c) Phenolates (anions of phenols) have maximum extinction coefficients in the 230-280 nm region on the ultraviolet spectrum.
- (d) Humates and fulvates can be determined at 460 nm in the visible spectrum (Kononova, 1961) at which wave-length there is little interference from other phenols.

The following protocol was developed as a screen for phenols and humates:

a. Preparation of resin: Amberlite XAD-8 resin was ground and sieved to 20/40 mesh. It was then batch-washed with 0.1N NaOH for five days to remove monomers and soluble uncross-linked polymers. The wash was changed with fresh NaOH everyday. The resin was then washed with acid and water until neutral, then Soxhlet extracted sequentially with distilled water, methanol, acetonitrile, and ethyl ether for 24 hours

each and stored in methanol until ready for use. It was then slurried in a methanol/water mixture into a 2 cm. x 25 cm. column, washed with 200 ml (approx. 5-6 bed volumes) of 0.1 N NaOH and then 0.1N N HCl. The washings were repeated.

b. Calibration Curves for Humic Acid and Phenol: A series of standard solutions of Suwanee Aquatic Humic Acid and Phenol were made up. One thousand milliliters of each solution (adjusted to pH 1-2 with concentration HCl) were applied to the XAD-8 column, then eluted with 75 ml. of 0.1 N NaOH. The column was washed with 200 ml of base and then 200 ml of acid between samples. The absorbance of the eluted materials were measured at 254 nm and 460 nm.

c. Determination of Humic Acid and Phenol in Water Samples. The water samples were analyzed in an identical manner to the standards shown in (b) above. A blank of distilled water was carried through the entire procedure and was subtracted from the observed values. Humic acid concentrations were estimated from the 460 nm absorbance; total phenol (humate plus phenol) was estimated from the 254 value.

Although the XAD-8 resins theoretically adsorb 100% of the humates, our experiments showed that the percent recovery was 76%, as determined by ultraviolet spectrophotometry. This could be the result of water soluble fractions passing through the column prior to elution with base (e.g. carbohydrate, inorganic salts).

#### 4. Amino-antipyrine Test for Phenols

Although this test for phenols is known to be severely limited in scope of accuracy (Van Hall, 1979) we used it routinely in our water analysis. Since so many governmental agencies use it to monitor water quality, we deemed it necessary to record amino-antipyrine values for our water samples, to establish data comparable to published data as well as to our own phenol values.

A number of analyses were carried out on known concentrations of model phenols to determine the accuracy and scope of the anti-pyrine method. The experimental details are in Standard Methods, 1974. The official method requires that the water sample be distilled; the distillate is collected and treated with the amino-antipyrine reagent and  $K_3Fe(CN)_6$ . A color develops in the presence of phenolic compounds; the intensity of the color is measured at 510 nm, and is directly related to the concentration of the phenol. Analyses were also carried out with the distillation step omitted. The results of the tests of model compounds are shown in Table I.

It can readily be seen from Table I that the colorimetric readings of concentration (based on a calibration curve for phenol itself) are all consistently lower than the actual concentrations of model phenols, some by a factor of twenty! Distillation lowered colorimetric readings of natural water samples by factors of five or more. Furthermore, the absorption maximum of the antipyrine complexes of the model phenols all differed from those of phenol itself. Therefore, only phenol and perhaps a few mono-chloro derivatives of phenol can be estimated with any degree of confidence by this method. All other phenols would give falsely low values.

Therefore, we concluded that the amino antipyrine method establishes a lower limit for phenols in drinking water. Our analyses of water samples were performed without the distillation step.

### RESULTS AND DISCUSSION

#### 1. Haloform analysis

The chloroform levels of water samples collected on 2/8/80; 2/14/80 and 12/12/80 are shown in Table II. Other haloform contents are shown in Table III. Samples were taken from the Verde and Salt Rivers (about 5 miles upstream from the Granite Reef Dam), at the Val Vista Treatment plant, at the Deer Valley Treatment plant, at the 35th Avenue Sewage Treatment plant (secondary effluent just before it flows on the Flushing Meadow recharge basin) and from wells 60-80 feet deep into the recharge basin. Samples from Cave Creek (2/8/80) and Sycamore Creek (2/8/80) are included, although these were atypical runoff samples. The latter two samples are provided by Dr. Quon Chin, chemist for the City of Phoenix Water Production.

Chloroform levels are also shown for samples which were chlorinated in our laboratories. Other haloforms are shown in Table III.

The results clearly reveal that no chloroform appears in the raw surface waters

TABLE I

ASSESSMENT OF AMINOANTIPYRINE PROCEDURE FOR A GROUP OF MODEL PHENOLS

Sample	Original Concentration (in ppb)	Absorption at 510 nm	Phenol Conc. * (ppb)	Max.
Catechin	50	-	-	475 nm
	100	-	-	
	500	0.003	37	
	1000	0.0055	47-8	
	5000	0.0275	220	
	10000	0.0735	575	
Resorcinol	20000	0.165	1200	476 nm
	8000 (distilled)	0.022	260	
Catechol	10000	0.119	930	420 nm
	5000	0.063	493	
p-chlorophenol	9000	0.720	5600	
	9000 (distilled)	0.665	5100	
m-nitrophenol	10000	0.015	120	475 nm
Secondary effluent				
	2/8/80 unfiltered	0.074	580	
	2/8/80 filtered	0.018	140	
	2/8/80 distillate	0.003	25	
Phenol	1400	0.189	1400	
	1400 (distilled)	0.170	1300	
Tap water		0.001-0.004	0-35	

\* aminoantipyrine reading

entering the Val Vista treatment plants. After treatment of the water, at either the Val Vista or Deer Valley plants, the levels of chloroform rise in the finished water, as would be expected from the chlorination process. The levels between sampling dates vary markedly, which may be due to a lot of causes. Seasonal variation in chloroform levels have been reported to vary by a factor of 10 or more (Arguello, 1979).

When these water samples are chlorinated in our laboratory, chloroform is produced. This indicates that some haloform precursor (THMP) still remains in the water. Cave Creek and Sycamore Creek are dramatic examples of this phenomenon, although they are probably atypical of the Phoenix Water system. Both Creeks run infrequently and are high in organic matter.

Probably the most interesting result is found in the data from the ground recharged water. It is quite evident that these waters contain no chloroform, even though the source, secondary effluent, does have haloform. Thus the ground recharge system effectively removes all haloforms.

Further chlorination of ground recharged and secondary effluent produces very little chloroform, even though both waters have high contents of organic carbon. Evidently, the organic matter no longer contains haloform precursors.

TABLE II

CHLOROFORM LEVELS IN DRINKING WATERS OF THE PHOENIX  
WATER SYSTEM<sup>a</sup>

<u>Source</u>	<u>2/14/80 Collection</u>		<u>12/12/80 Collection</u>	
	<u>CHCl<sub>3</sub></u>	<u>After Chlorination</u>	<u>CHCl<sub>3</sub></u>	<u>After Chlorination</u>
Salt River	0	202	0-1	83
Verde River	0	222	0-1	64
Val Vista Raw	0	575	19	60
Val Vista Finish			26	69
Secondary Effluent	0	48	14	43
Ground Recharged	0	39	0-1	20
Deer Valley Raw	0	413		
Finish	196	461		
Sycamore Creek <sup>b</sup>	0	612		
Cave Creek <sup>b</sup>	230	791		

<sup>a</sup>In ppb

<sup>b</sup>Collected 2/8/80

2. Phenolic Content

The value for total phenol (humates plus phenolics), humates alone and "amino-antipyrine phenolics" are shown in Table IV. Included in this table are the TOC (Total Organic Carbon) values of the water samples. A number of conclusions can be drawn from these data.

1. Phenolic compounds may constitute up to 50% of natural waters. However, humates are only a small fraction of the total phenols.

2. Treatment of raw water dramatically reduces the phenolic and humic acid content, but NOT the total organic carbon. This seems to be an anomolous result. Perhaps chlorination converts phenols to non-phenolic substances which no longer adsorb in the ultraviolet range, but which are still detected as total organic carbon. The conversion of certain phenols to unsaturated acids would be an example of such a reaction.

3. Ground recharging reduces the total organic matter by a factor of four. It also reduces the phenolic substances and humates by a factor of three, as well as simple or chlorinated phenols by a factor of three. These compounds are no longer able to produce haloforms upon chlorination, although they are still technically classified as phenols and humates. It would be interesting to determine what structural changes they have undergone in the dewage treatment; that determination, however, must await another major research project.

TABLE III

## OTHER HALOFORMS DETECTED IN PHOENIX WATER SYSTEM

<u>Source</u> <sup>a</sup>	<u>Halofoms Detected</u> <sup>b</sup>
Salt River	CCl <sub>4</sub>
Verde River	CCl <sub>4</sub>
Val Vista Raw	CHCl <sub>3</sub> , CCl <sub>4</sub> , CHBrCl <sub>2</sub> , CHBr <sub>2</sub> Cl
Val Vista Finished	CHCl <sub>3</sub> , CCl <sub>4</sub> , CHBrCl <sub>2</sub> , CHBr <sub>2</sub> Cl
Secondary Effluent	CH <sub>2</sub> Cl <sub>2</sub> , CHCl <sub>3</sub> , CCl <sub>4</sub> , CHBrCl <sub>2</sub>
Ground Recharged	CCl <sub>4</sub>

<sup>a</sup>Samples collected 12/12/80

<sup>b</sup>Only CHCl<sub>3</sub> was quantitated in the analyses

TABLE IV

PHENOLIC CONTENT OF PHOENIX DRINKING WATERS<sup>a</sup>

<u>Source</u>	<u>TOC</u>	<u>Antipyrine Phenol</u>	<u>Total Phenol</u>	<u>Humic Acid</u>	<u>Humic Acid as % of Phenols</u>
Salt River	2000	30-35	1050	50	9
Verde River	1200	120-125	1050	50	9
Val Vista Raw	2000	190	750-800	50-75	10-18
Val Vista Finish	2500	30-35	350	less than 1 ppb	---
Secondary Effluent	16,800	730	7500	1600	55
Ground Recharged	4000	315	2700-2800	500	43

<sup>a</sup>In parts per billion (ppb).

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