

Evaluation of THM Precursor Contributions From Agricultural Drains

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More than 200 agricultural drains in the Sacramento River Delta contribute significant levels of trihalomethane (THM) precursors to California State Project water. It has been hypothesized that these drains, associated with crop irrigation involving highly organic peat soils, are probably responsible for the higher levels of dissolved organic carbon and THM formation potential in the California Aqueduct emanating from the delta in comparison with the principal freshwater tributaries entering the delta. The purpose of this study was to evaluate this hypothesis. It was found that the dissolved organic matter from drains is characterized by a higher molecular weight and greater THM reactivity than that found in delta tributaries.

Aquatic humic substances, composed of humic and fulvic acids, account for approximately 50 percent of the dissolved organic carbon (DOC) in most natural waters. The molecular weight distribution of aquatic humic and fulvic acids ranges from approximately 500 to 10,000, with carboxylic and phenolic acidities generally in the range of 5-10 meq/g C. A major water quality concern is that humic substances react with chlorine during water treatment to form trihalomethanes (THMs). The Metropolitan Water District of Southern California (MWD), which uses both California State Project (SPW) water and Colorado River Water (CRW) as sources of water supply, recently converted from the use of free chlorine as a disinfectant to chloramination to reduce THM concentrations to an acceptable level below the current primary drinking water standard. The current maximum contaminant level limits THMs to 100 µg/L; however, it is expected that the US Environmental Protection Agency (USEPA) will promulgate an even more stringent standard by 1991. One problem facing MWD is that the THM formation potential (THMFP) of SPW is about twice that of CRW.

Recent sampling activities by the California Department of Water Resources (DWR) suggest that agricultural drains in the Sacramento River Delta region are

major contributors to THM precursors and humic substances in SPW. Within the delta, there are numerous agricultural tracts containing highly organic peat soils. These agricultural tracts typically exist below sea level with constructed levee systems. Irrigation water is withdrawn from the delta and applied to a tract. The associated drainage accumulates in collector ditches that function as sumps and are located along the perimeter of the tract. Drainage

water is eventually pumped from these sumps and discharged into the delta water system. It has been estimated that there are 262 drains within the upper and lower delta regions. Only three of these drains have been previously sam-



The California Aqueduct constitutes the major freshwater outflow from the delta.

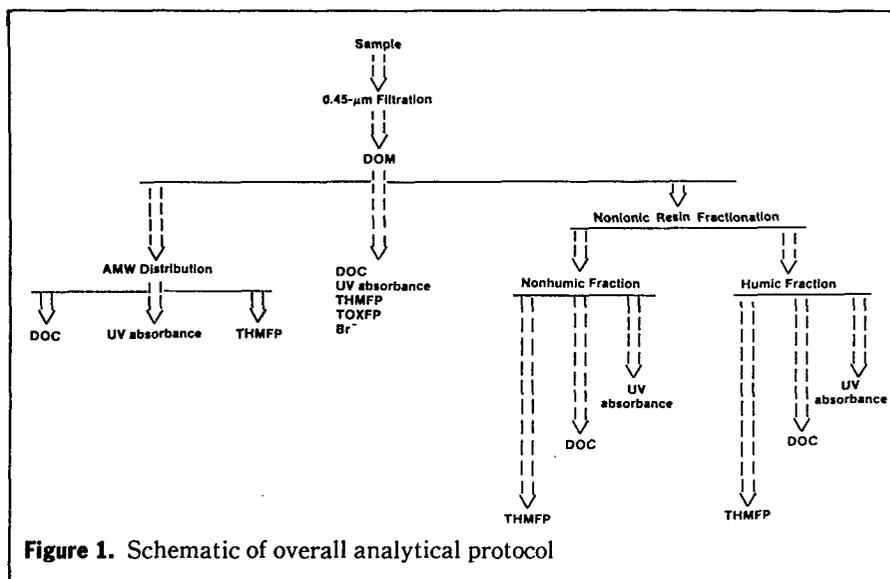


Figure 1. Schematic of overall analytical protocol

TABLE 1
Detailed characterization of samples

Sample	DOC mg/L	UV Absorbance cm ⁻¹	UV Absorbance: DOC	THMFP* µg/L	THMFP µmol/L	THMFP: /DOC µmol/mg	TOXFP µg/L	TOXFP :DOC	Average AMW Based on DOC	Average AMW Based on THMFP	Sampling Date
Drain samples											
Empire 1	22.2	1.08	0.049	2,470	17.1	0.77	9,170	413	5,060	4,720	05/06/87
Grand 1	7.24	0.285	0.039	290	2.37	0.33	1,070	130	2,330	6,930	06/10/87
Tyler 1	7.66	0.298	0.039	456	3.60	0.47	2,690	327	3,140	2,860	06/24/87
Tyler 2	10.4	0.626	0.060	642	5.27	0.51	5,190	499	3,880	5,590	07/08/87
Grand 2	6.38	0.256	0.040	239	1.94	0.30	1,000	157	1,440	2,930	07/28/87
Empire 2	22.3	1.33	0.059	2,690	22.0	0.99	5,180	232	4,530	7,470	07/28/87
Jones 1	10.0	0.375	0.038	637	4.88	0.49	1,110	111	2,550	2,700	08/12/87
Jones 2	6.36	0.255	0.040	433(-)	3.15(-)	0.50	943	148	2,330	2,410	09/28/87
Empire 3	18.7	0.873	0.047	1,800	13.2	0.71	3,470	185	2,780	2,650	09/22/87
Average	12.4	0.598	0.046	1,070	8.17	0.66	3,310	267	3,120	4,250	
River and lake samples											
Sacramento 1	2.12	0.059	0.028	29(-)	0.23(-)	0.05	207	97	730	440	06/10/87
San Joaquin 1	3.67	0.104	0.028	249	1.74	0.47	1,080	294	721	560	06/24/87
H.O. Banks 1	4.10	0.103	0.025	225	1.68	0.41	902	220	790	1,050	05/06/87
Silverwood	3.85	0.132	0.034	213	1.41	0.37	1,430	371	1,850	950	07/01/87
Lake Mathews	3.87	0.067	0.017	198	1.44	0.37	920	238	940	1,620	07/11/87
O'Neil	3.81	0.112	0.029	294	1.91	0.50	980	257	2,020	1,360	07/08/87
H.O. Banks 2	3.37	0.096	0.029	199	2.17	0.64	548	163	940	920	08/12/87
San Joaquin 2	3.54	0.091	0.026	262	1.66	0.47	477	135	2,100	2,270	08/25/87
Sacramento 2	3.14	0.053	0.017	164	1.30	0.41	NA	NA	985	2,440	08/25/87
H.O. Banks 3	3.50	0.110	0.031	241	1.50	0.43	430	123	1,650	2,000	09/22/87
Average†	3.50	0.093	0.026	231†	1.67†	0.46†	835†	223†	1,270	1,440†	

*A positive chlorine residual was observed for all THMFP experiments except Sacramento sample 1 and Jones sample 2.
†Averages do not include Lake Mathews (CRW) or Sacramento River sample 1 (negative chlorine residual at end of THMFP).

TABLE 3
Characteristics of humic and nonhumic fractions

Sample	Nonhumic Fraction (Measured)				Humic Fraction (Calculated)				Humic Content % of DOC
	DOC mg/L	THMFP µg/L	THMFP µmol/L	TOXFP µg/L	DOC µg/L	THMFP µg/L	THMFP µmol/L	TOXFP µg/L	
Drain samples									
Empire 1	10.5	1.040	5.35	6,180	11.7	1,430	11.8	2,990	51.4
Grand 1	2.87	77	0.56	645	4.47	213	1.81	422	61.7
Tyler 1	3.26	252	2.02	879	4.40	204	1.60	1,810	57.4
Tyler 2	4.37	151	1.18	545	6.03	491	4.09	4,650	58.0
Grand 2	3.04	146	1.14	413	3.34	93	0.80	587	47.6
Empire 2	9.00	744	5.63	1,310	13.3	1,950	16.4	3,870	59.6
Jones 1	5.97	224	1.59	NA	4.03	413	3.29	NA	40.3
Average	5.57	376	2.50	1,660	6.75	685	5.68	2,390	53.7
River and lake samples									
Sacramento 1	1.31	NA	NA	143	0.81	NA	NA	338	38.0
San Joaquin 1	2.04	49	0.34	733	1.63	200	1.40	750	44.4
H.O. Banks 1	1.84	31	0.22	NA	2.26	194	1.46	NA	55.1
Silverwood	2.12	118	0.70	452	1.73	95	0.72	1,430	44.9
Lake Mathews	1.74	77	0.50	379	2.13	121	0.94	923	55.0
O'Neil	1.86	152	0.83	411	1.95	142	1.08	980	51.0
Average*	1.97	88	0.52	532	1.89	158	1.17	1,050	48.9

*Averages do not include Lake Mathews (CRW source) or Sacramento sample 1 (negative chlorine residual at end of THMFP).

TABLE 4
DBP formation potential

Sample	Modified THMFP* µg/L	Total DHANs µg/L	DCAA µg/L	TCAA µg/L
Drain samples				
Empire 1	3,580	63	995	885
Empire 2	2,510	130	1,650	1,990
Empire 3	2,700	70	452	389
Jones 1	1,550	27	590	755
Jones 2	770	31	268	340
Grand 1	791	25	240	410
Grand 2	720	10	480	690
Average	1,800	51	668	780
River and lake samples				
H.O. Banks 1	585	4.7	170	120
H.O. Banks 2	426	0.8	57	45
H.O. Banks 3	450	1.6	41	29
Sacramento 2	208	2.7	55	54
San Joaquin 2	504	1.5	58	37
Silverwood	458	1.5	34	24
Average	439	2.1	69	52

*Conditions for these formation tests were Cl₂ = 120 mg/L, 25° C, pH 8.0, and 168 h.

TABLE 2
Additional characteristics of samples

Sample	Bromide µg/L	THM-Br:THM-X percent	THM-Br:Br ⁻ percent	THM-X:TOXFP percent
Drain samples				
Empire 1	3,040*	34	25	25
Grand 1	120*	4	9	24
Tyler 1	32	11		15
Tyler 2	29	5	86	11
Grand 2	22	6	61	21
Empire 2	183	5	41	46
Jones 1	175	17	77	52
Jones 2	130	21	62	41
Empire 3	898	25	45	47
Average	508	14	52	31
River and lake samples				
Sacramento 1	12	7	14	13
San Joaquin 1	127	33	34	21
H.O. Banks 1	100*	18	35	22
Silverwood	66	35		13
Lake Mathews	50	18	68	20
O'Neil	83	36		27
H.O. Banks 2	213	56	48	34
San Joaquin 2	134	48	85	50
Sacramento 2	22	11	73	
H.O. Banks 3	173	50	64	51
Average†	115	36	57	31

*IC data

†Averages do not include Lake Mathews (CRW source) or Sacramento River sample 1 (negative chlorine residual at end of THMFP).

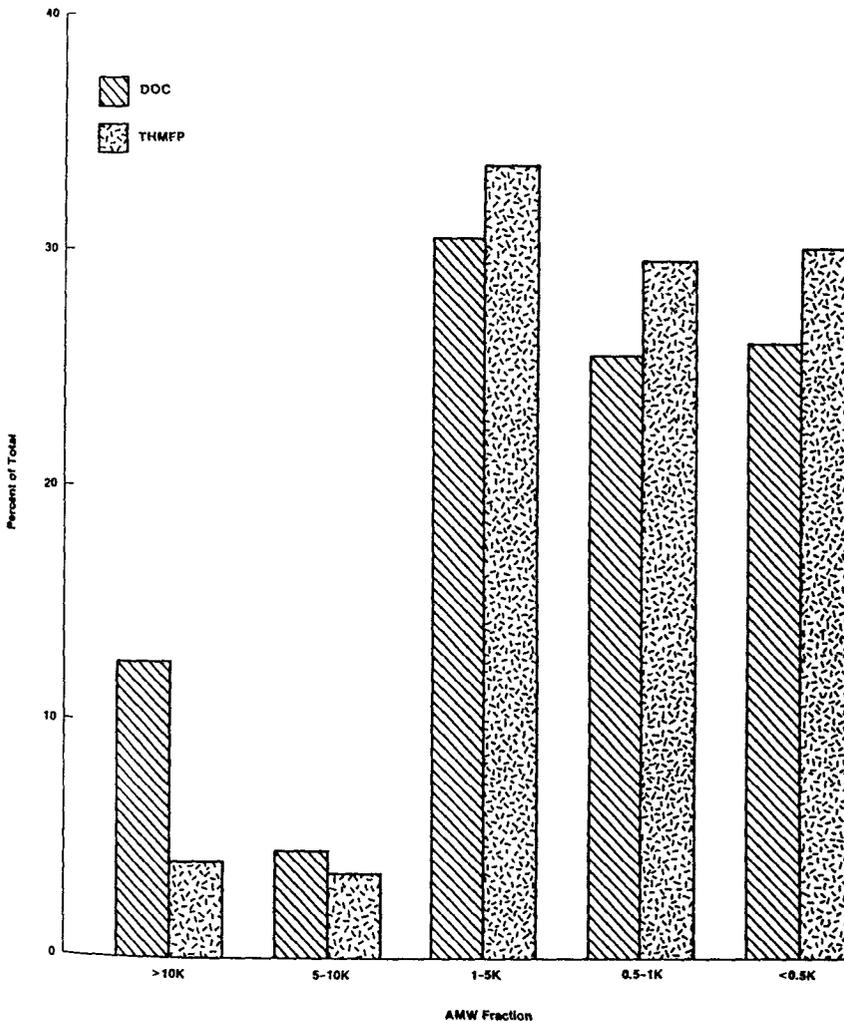


Figure 2. AMW distribution of DOC and THMFP in San Joaquin River (average of two samples)

pled for detailed characterization of the humic substances present. Moreover, little is known about the volumetric flow contributions of these drains.

The two principal freshwater inflows are the San Joaquin and Sacramento rivers; the major freshwater outflow is the California Aqueduct. The Sacramento River Delta represents the beginning of the estuarine system that is inherently San Francisco Bay.

Research objectives

The objective of the proposed research was to delineate the contribution of agricultural drains to levels of THM precursors and humic substances found in Sacramento River Delta and California State Project waters. Through molecular weight and other characterizations, the goal was to identify possible "fingerprints" of agricultural versus nonagricultural sources.

Experimental methods and procedures

Samples for characterization were acquired from a series of agricultural drains and from key river and lake components of the delta system. For comparison purposes, a Colorado River source was also sampled. Nineteen samples were characterized during the research—nine agricultural drains and ten river and lake samples.

All samples were collected by representatives of the DWR. Samples were collected* from May 6, 1987, to Sept. 22, 1987, and sent by air freight in an ice chest to the University of Arizona. Ten sampling locations were evaluated during the research: Tyler Island Drain, Grand Island Drain, Empire Tract Drain, Upper Jones Tract Drain, Sacramento River, San Joaquin River, Clifton Court Forebay (H.O. Banks Pumping Plant), Silverwood Reservoir, O'Neill Forebay, and Colorado River (Lake Mathews). Three sets of samples were obtained from the Empire Tract and H.O. Banks sources. Two sets of samples were acquired from the Tyler, Grand, Upper Jones, San Joaquin, and Sacramento sources. Single samples were obtained from the remaining sources.

The sampling points were selected based on the hydrologic regime embodied by the delta: an estuary with two principal inflows and one freshwater outflow (the California Aqueduct). The DWR conducted a preliminary monitoring survey before this study was conducted. Its preliminary results were used to select samples representative of high-, medium-, and low-humic agricultural drains. The two rivers selected represent the principal tributaries to the delta, and the H.O. Banks Pumping Plant represents the principal freshwater outflow.

Upon receipt, each sample was filtered

*Nalgene Containers, Nalge Co., Rochester, N.Y.

through prewashed 0.45- μ m membrane filters, providing an operational definition of dissolved organic matter (DOM), and refrigerated at 4°C. Complete analytical characterization of a sample was achieved within two weeks. (The humic fraction of the DOM can be considered biorefractory under these conditions, whereas the nonhumic fraction should be stable during this time because of the filtration step and low-temperature storage.) Aliquots of the overall DOM were then characterized according to: non-purgeable dissolved organic carbon (DOC); ultraviolet (UV) absorbance (1-cm path length, pH 7.0, 254 nm); THMFP (Cl_2 :DOC = 3:1 [mass basis], pH 7.0, 20°C, 168 h; and qualitative analysis for a positive Cl_2 residual); total organic halide formation potential (TOXFP, same conditions as THMFP); and bromide.

A second aliquot of the DOM was characterized according to apparent molecular weight (AMW) distribution (as determined by ultrafiltration [UF]). The technique described in Amy et al¹ was used to process samples in parallel through 200-mL stirred cells* with UF membranes having molecular weight cutoffs of 500, 1,000, 5,000, 10,000, and 30,000. This parallel processing approach produced a series of corresponding permeates that were first analyzed for DOC and UV absorbance. Based on measured values of DOC, aliquots of the permeates were then analyzed for THMFP (using Cl_2 :DOC = 3:1). Each of the retentates derived from UF was also analyzed for DOC, permitting a mass balance of DOC as an analytical control.

A third aliquot of the DOM was fractionated into humic and nonhumic fractions using the technique of Thurman and Malcolm,² based on adsorption of humic substances onto a column of non-ionic resin† under acidic conditions. Both the influent and the column effluent containing material not retained on the resin were first analyzed for DOC and UV absorbance and then analyzed for THMFP after determination of the DOC level (using Cl_2 :DOC = 3:1). The material retained on the resin was subsequently eluted with NaOH. The eluent was also analyzed for DOC; DOC and corresponding sample volume data permitted mass balance calculations as an analytical control.

In summary, analytical characterization involved DOC, UV absorbance, and THMFP characterization of the overall DOM, the humic and nonhumic fractions of the DOM, and molecular weight fractions of the DOM. In addition, the overall filtered samples were characterized according to TOXFP and bromide ion. The overall analytical protocol is described in Figure 1.

Nonpurgeable DOC was determined with an organic carbon analyzer,‡ and UV absorbance was measured with a

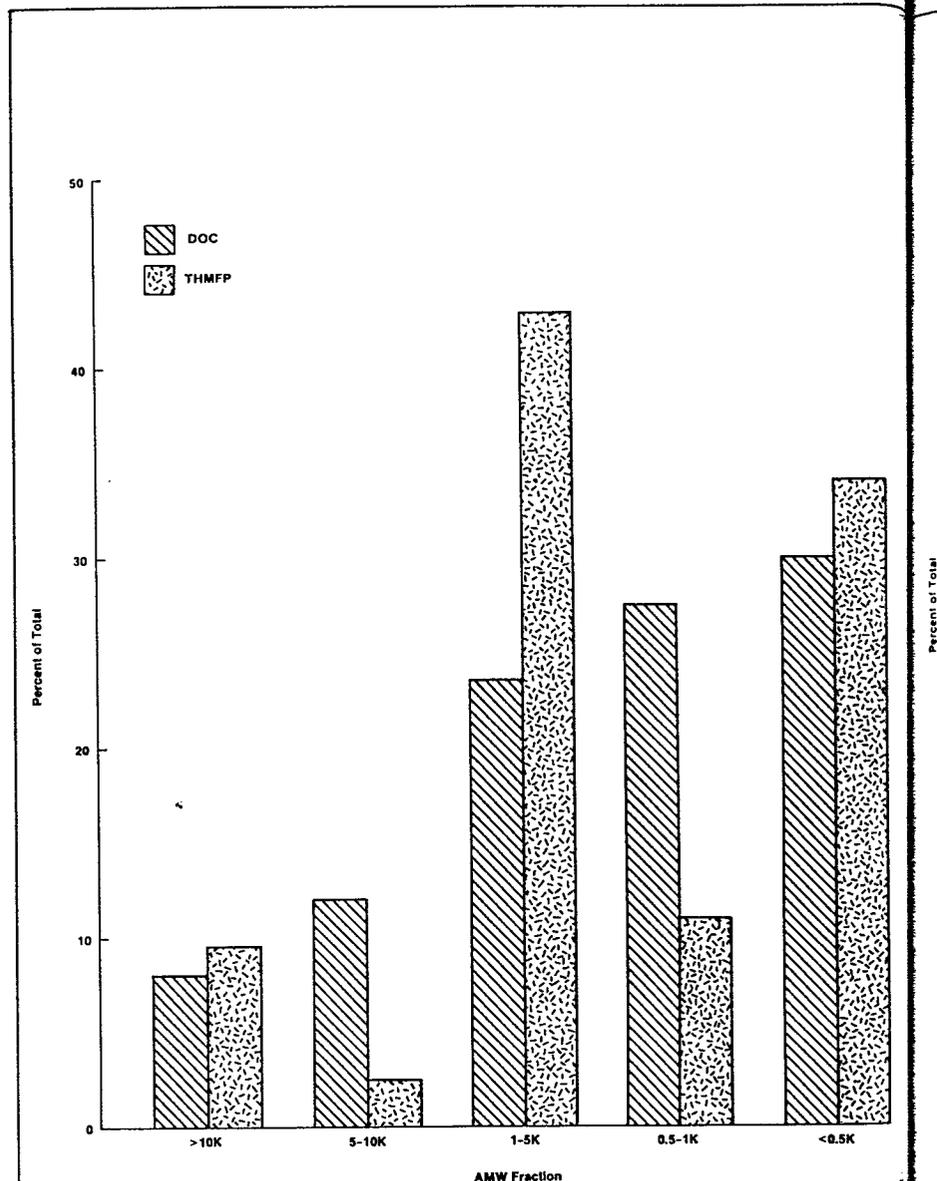


Figure 3. AMW distribution of DOC and THMFP in Sacramento River (average of two samples)

spectrophotometer.§ Trihalomethanes were measured with a gas chromatograph and electron capture detector** using the standard USEPA procedure—the liquid-liquid extraction technique with pesticide-grade pentane and a large-bore capillary column. Bromide ion was determined by an ion-specific electrode†† or, in some cases, an ion chromatograph (IC).‡‡ An organic halide analyzer§§ was used for TOX determinations.

The UF procedure involved parallel processing of identical aliquots of DOM through each of the indicated UF membranes, yielding permeates with molecular weight ranges of <500, <1,000, <5,000, <10,000, and <30,000. Thus, the procedure does not provide discrete AMW

fractions but instead generates a series of cumulative fractions. The amount of DOM associated with each cumulative fraction was determined by direct measurement of the respective permeates, and the amount associated with each discrete fraction was calculated.

Analytically, it becomes progressively more difficult to distinguish between AMW fractions if the overall DOC of the

*Amicon Inc., Lexington, Mass.

†XAD-8, Rohm & Haas, Philadelphia, Pa.

‡Model DC-80, Dohrmann Envirotech, Santa Clara, Calif.

§200-UV-visible spectrometer, Perkin-Elmer, Norwalk, Conn.

**Model 5794 GC and ECD, Hewlett-Packard, Avondale, Pa.

††Model 94-35, Orion Research Inc., Cambridge, Mass.

‡‡Model 10, Dionex Corp., Sunnyvale, Calif.

§§Model DX-20, Dohrmann Envirotech, Santa Clara, Calif.

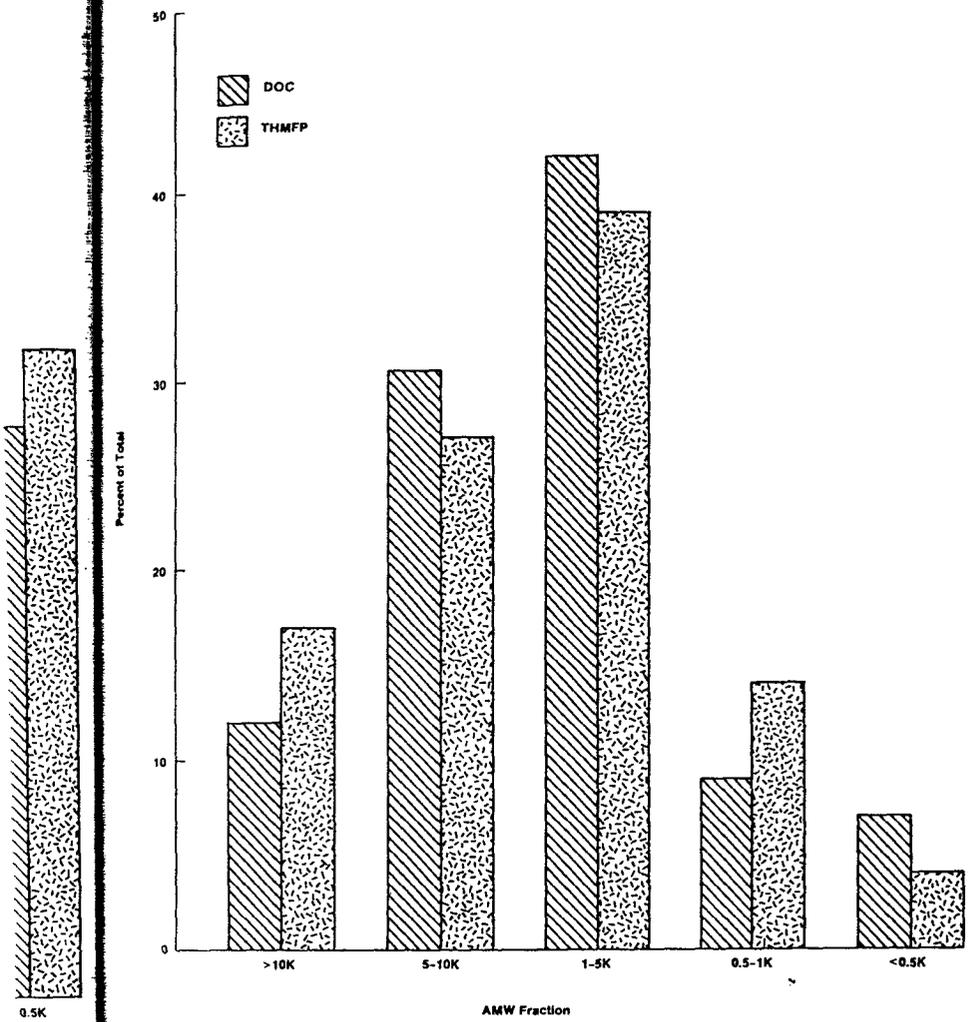


Figure 4. AMW distribution of DOC and THMFP in Empire Tract drain (average of three samples)

of SPW. Important characteristics of the four drain sources are contrasted with those of various rivers and lakes inherently related to the California State Project or important to the overall water resources "pool" of MWD.

AMW distributions, based on DOC or THMFP, can be portrayed in the form of bar diagrams representing discrete MW fractions. The calculation of average MW based on DOC should differ from that based on THMFP if, as expected, different MW fractions exhibit different THM yields and reactivities (μg THMFP/mg DOC). A higher average MW based on THMFP rather than DOC indicates that the higher MW material is more reactive in forming THMs.

An AMW distribution functions as a fingerprint and provides insight into the average AMW as well as the variation in AMW. Several illustrative examples are presented in Figures 2-5 for the San Joaquin River (average of two samples), the Sacramento River (average of two samples), Empire Drain (average of three samples), and H.O. Banks (average of three samples). The averages indicated in the figures are actually arithmetic averages from several different samples collected on different occasions, as opposed to replications. Figures 2-5 portray the percentage of either the DOC or THMFP that occurs in association with each of five discrete molecular weight fractions. As a general rule, the AMW fingerprints indicated a higher molecular weight for the DOM in drain samples than in nondrain samples. For many of the agricultural drain samples, the two predominant AMW ranges were the 5,000-10,000 and the 1,000-5,000 fractions. Other agricultural drain samples exhibited a single predominant AMW fraction of 1,000-5,000. As a general rule, the three predominant AMW ranges for river and lake samples were 1,000-5,000, 500-1,000, and <500. Particularly noteworthy is that much of the DOM in river and lake samples was characterized by a molecular weight of less than 1,000.

A molecular weight cutoff of 1,000 is often used to differentiate between hydrophilic "low" MW and more hydrophobic "high" MW molecules. The former are generally more difficult to remove in water treatment processes.

A summary of the important characteristics of the 19 samples studied during this research is presented in Table 1. The column average values reported do not reflect the Colorado River source (i.e., Lake Mathews) to clearly show the relative influences of delta tributaries and agricultural drains on SPW quality. In a comparison of agricultural drain with river and lake samples, drain samples exhibited greater levels of DOC, UV absorbance, THMFP, and TOXFP. Also shown in Table 1 are calculated values of AMW based on either DOC or THMFP.

water is only several milligrams per litre. In such cases, it was necessary to first concentrate samples by rotary evaporation. Only two samples, both of the Sacramento River series, were subjected to rotary evaporation at 60°C because of their relatively low DOM levels. Only moderate degrees of concentration were accomplished to ensure that no precipitation occurred. Appropriate volume measurements and corresponding DOC determinations were conducted to ensure that there was no significant loss because of volatilization. Although MW-oriented control experiments were not conducted, polymerization during rotary evaporation at this temperature was considered unlikely.

An important stipulation of the THMFP test is the need to maintain a positive chlorine residual over the 168 h. For most water sources, a Cl_2 :DOC ratio of 3:1 (mass basis) was adequate for this purpose, although a higher ratio was necessary for one source (the Sacramento River). Collins et al³ found that a ratio of 3:1 was adequate for a series of Colorado River samples.

Results and discussion

In the discussion that follows, the general characteristics of "drain" samples as opposed to "nondrain" samples are contrasted. The objective is to identify possible fingerprints of agricultural contributions to the THM precursor load

These values also support the observation that the DOM in drain samples is characterized by a higher molecular weight.

Data were used to calculate specific absorbance, defined as the ratio of UV absorbance to DOC. This parameter is indicative of the humic substances content of the "DOC pool." It is based on the premise that humic matter absorbs UV light more effectively than nonhumic organic matter. This parameter indicates that the DOM in drain samples had a higher percentage of humic substances than that in river and lake samples.

Data were also used to calculate values of THM yield, expressed as mass THMFP:mass DOC. This parameter provides insight into the reactivity of the DOM with chlorine. The average THMFP:DOC ratio was higher for drain samples than for river and lake samples. Thus, drain samples exhibited more DOC, and this material was also more reactive in forming THMs. Values of TOXFP:DOC indicated that drain samples generally exhibited a higher propensity to form organic halide. About 80 percent of the TOX occurred in the form of nonpurgeable organic halide, presumably chlorohumic material. Measured values of the four THM species accounted for almost all of the purgeable organic halide observed.

Table 1 indicates that some of the agricultural drain samples contained substantial levels of THM precursors (e.g., Empire), whereas others (e.g., Grand) exhibited THMFPs that were not very different from those of river and lake sources. Other samples (e.g., Tyler and Jones) fell between these two extremes in their propensity to form THMs. A comparison of SPW (H.O. Banks samples 1, 2, and 3) with CRW (Lake Mathews) indicates a lower THM reactivity (i.e., THM:DOC) in the latter source used by MWD.

Additional characteristics of the agricultural drain and river and lake samples are summarized in Table 2. The bromide levels are particularly noteworthy. Bromide effects on THM formation have been studied previously. On a mass basis, the presence of bromide increases THM yield, all other factors being equal. Bromide concentrations in drain samples were highly variable; very low levels were found in the Grand and Tyler sources and much higher levels were observed in the Empire and Jones sources. Presumably, this trend may reflect the effect of saltwater intrusion into regions of the delta. The average Br concentration observed in the H.O. Banks samples was 162 $\mu\text{g/L}$, whereas averages for the two major tributaries to the delta, the Sacramento and San Joaquin rivers, were 130 and 17 $\mu\text{g/L}$, respectively. Thus, it appears that there are

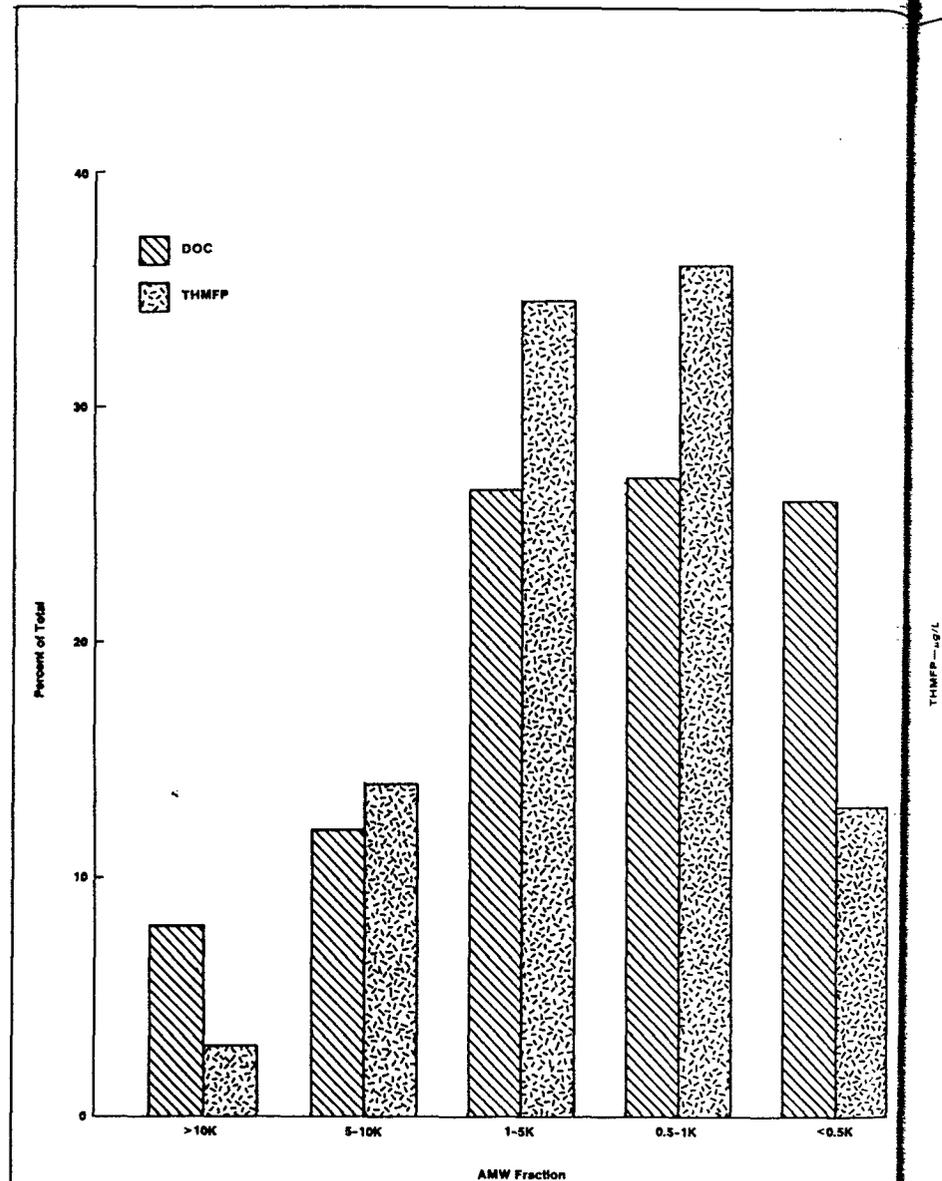


Figure 5. AMW distribution of DOC and THMFP in H.O. Banks River Pumping Plant (Clifton Court Forebay; average of three samples)

significant delta contributions to bromide levels in SPW. Brominated THM species generally accounted for a greater percentage of THMFP in river and lake samples than in drain samples. For both drain and river and lake samples, about half of the ambient bromide was eventually incorporated into THM species. The measured THM species generally accounted for about 30 percent of the measured TOXFP.

A summary of the important characteristics associated with the humic versus nonhumic fractions of the DOM in each sample is presented in Table 3. The calculation of humic fractions was based on DOC analysis of both the water ap-

plied to a nonionic resin column (total and the column effluent (nonhumic) with calculation of the humic fraction by difference. The material subsequently eluted from the column was also characterized for mass balance purposes. Typical recoveries of >90 percent of the DOC were observed. On a DOC basis, humic substances made up approximately half the DOM found in either drain or river and lake samples. Moreover, about two-thirds of the THMFP was observed to occur in association with the humic fraction of the DOM in either drain or river and lake samples, indicating the higher reactivity of the humic fraction in forming THMs. It is important

Other disinfection by-products

Stevens et al^{7,8} found a variety of other halogenated organic by-products in chlorinated drinking water. These include haloacids such as trichloroacetic acid (TCAA) and dichloroacetic acid (DCAA), and dihaloacetonitriles (DHANs) such as dichloroacetonitrile, dibromoacetonitrile, and bromochloroacetonitrile. Stevens also observed several haloaldehydes and haloketones.

A summary of disinfection by-products (DBPs) found in drain versus river and lake samples appears in Table 4. These results were derived in MWD's Water Quality Laboratory using analytical methods described elsewhere for DBPs.^{7,8} Note that the modified formation potential conditions used for these experiments differed from the standard THMFP conditions described previously (see Table 4 footnote). As a general rule, much higher levels of DBPs were found in drain samples. Although drain samples exhibited THMFPs that were four times greater than river and lake samples, the DBPs reported in Table 4 were 10 or more times greater.

Projected effects of agricultural drains on delta water quality

The two major sources of freshwater inflow into the delta are the Sacramento River (approximately 70 percent of the total annual flow) and the San Joaquin River (approximately 30 percent of the total annual flow). The San Francisco Bay system constitutes the major natural outflow. Water quality in certain regions of the delta is affected by the estuarine system that is inherently a part of San Francisco Bay (i.e., seawater intrusion). The major artificial diversion of water from the delta is the California Aqueduct (originating at the H.O. Banks Pumping Plant), a major component of the California State Water Project.

In the overall delta system described previously, levels of DOM are lowest in the Sacramento River. The higher levels of DOM found in SPW can be attributed to both San Joaquin River inflow and water quality transformations along the flow path through the delta. It has been hypothesized that agricultural drains affect water quality more than any other feature of the delta.

A schematic representation of a DOC balance and a THMFP balance conducted for the delta is shown in Figure 7. This schematic portrays the average DOC and THMFP levels for the two principal inflows into the delta and the major artificial outflow from the delta. (The average THMFP for the Sacramento River was assumed to be equal to that of the second sample because the first sample violated the criterion of a positive chlorine residual.) Assuming that the outflow at H.O. Banks is derived in the pro-

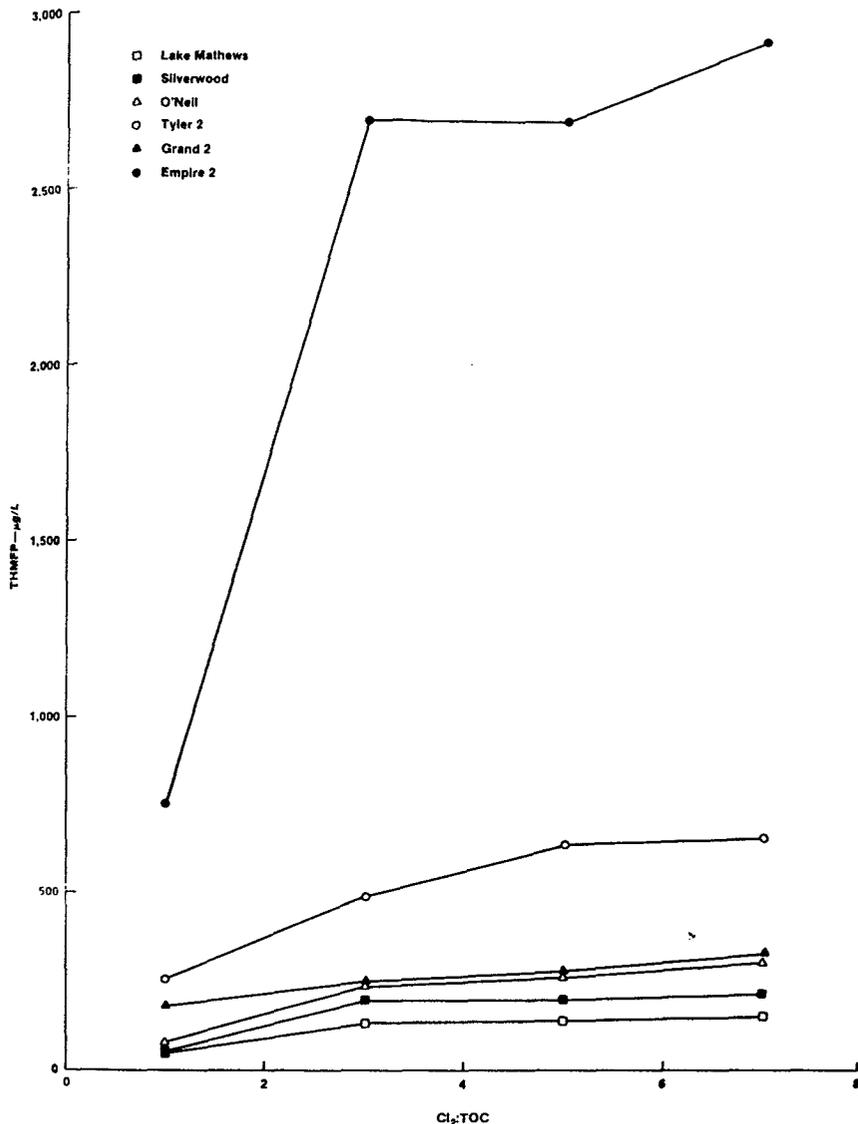
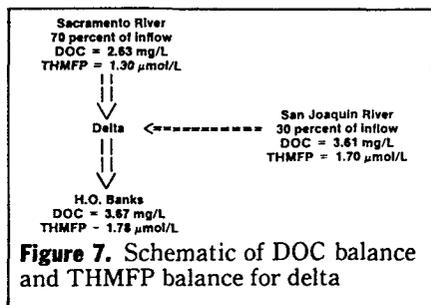


Figure 6. Effects of chlorine dose on THMFP

(total) recognize that the resin isolation technique used provides, at best, an operational definition of aquatic humic substances. The fraction of the DOM that adsorbs onto the nonionic resin under the specified conditions is designated as the humic fraction. Previous research⁴ has shown that the humic fraction of the DOM is more amenable to removal by chemical coagulation or activated carbon adsorption. As indicated previously, values of specific absorbance, the ratio of UV absorbance to DOC, are indicative of the humic content of a water. The higher humic contents reported in Table 3 for drain samples are consistent with the higher values of specific absorbance

for drain samples that are reported in Table 1.

All of the THMFP and TOXFP data presented were based on a Cl₂:DOC ratio of 3:1. It is well known that THM yield varies as a function of the applied chlorine dose.^{5,6} Six samples (three drains and three river and lake samples) were evaluated over a range of Cl₂:DOC ratios (Figure 6). In all cases, a negative chlorine residual (i.e., no measurable residual) was observed at a Cl₂:DOC ratio of 1:1; positive residuals were observed at all other ratios. THMFP values appear to increase somewhat linearly with Cl₂:DOC up to a ratio of 3:1, at which point they begin to level off.



portion of 70 percent to 30 percent from the Sacramento and San Joaquin rivers, a DOC:THMFP balance analysis indicates that only 80 percent of the DOC and, likewise, only 80 percent of the THMFP can be accounted for by the major freshwater inflows. Although based on limited data, this analysis suggests that the delta may contribute as much as 20 percent of either the DOC or the THMFP found in SPW.

The DOC-based average molecular weights of the Sacramento and San Joaquin rivers were 860 and 1,410, respectively. A DOC balance analysis predicts a DOC-based average molecular weight of 1,030 for H.O. Banks. In actuality, the experimentally determined average molecular weight based on DOC for H.O. Banks was 1,130—a higher value possibly reflecting the higher molecular weight DOC found in association with agricultural drain samples. (A similar analysis of THMFP-based molecular weights proved inconclusive.)

The key data necessary to make an irrefutable statement about drain contributions to the delta, volumetric flow data from each drain, do not exist. Thus, only indirect analyses (i.e., THMFP or DOC balances) are possible. The results of these indirect analyses are suggestive although not conclusive of the effect of drains on delta water quality.

An original objective of this study was to establish molecular-weight fingerprints characteristic of both agricultural drains and freshwater inflows into the delta (i.e., the Sacramento and San Joaquin rivers), and then to try to identify the effect of drains by examining a representative fingerprint of the H.O. Banks samples. The first set of samples, (i.e., San Joaquin 1, Sacramento 1, Empire 1, and H.O. Banks 1) partly met this original objective. Generally low-molecular-weight fingerprints were observed for the San Joaquin and Sacramento rivers, a high-molecular-weight fingerprint was found for the Empire Drain, and an intermediate-molecular-weight fingerprint was ascertained for the H.O. Banks sample. However, this same trend was not observed for a second set of samples; the desired trends may have been masked by differences in water quality associated with the slightly different sampling dates.

The molecular-weight fingerprints presented in Figures 2-5 are inconclusive in supporting the hypothesis that agricultural drains significantly affect the THM precursor pool found in SPW. Clearly, the AMW fingerprint for the Empire Tract (Figure 4) was considerably different from those of the inflowing rivers (Figures 2 and 3). However, it is difficult to discern any effects embodied in the AMW fingerprint for the delta outflow at H.O. Banks (Figure 5).

The correlations shown below, which were based on 19 samples and subsets thereof, were established by simple linear regression between THMFP ($\mu\text{mol/L}$) and DOC (mg/L) as a surrogate parameter. (Curvilinear regressions were not attempted.) The magnitudes of the statistically determined regression coefficients (1.07 versus 0.70 for drain versus river and lake samples) indicates the higher THM reactivity of drain samples.

$$\begin{aligned} \text{Drain samples } (n = 9): \\ \text{THMFP} = -5.00 + 1.07 (\text{DOC}) \\ r^2 = 0.98 \end{aligned}$$

$$\begin{aligned} \text{River and lake samples } (n = 10): \\ \text{THMFP} = -0.95 + 0.07 (\text{DOC}) \\ r^2 = 0.58 \end{aligned}$$

$$\begin{aligned} \text{All samples } (n = 19): \\ \text{THMFP} = -2.31 + 0.91 (\text{DOC}) \\ r^2 = 0.94 \end{aligned}$$

Implications for water treatment

The higher-molecular-weight material making up the DOM in drain samples may lend itself to removal by certain water treatment processes. Chemical coagulation is most effective for removing humic substances of a higher molecular weight.⁹ MWD's experience in removing humic substances by chemical coagulation has, however, been limited; past results have indicated coagulation will not be sufficient to meet the projected 1991 THM regulations. Activated carbon adsorption is also effective in removing higher-molecular-weight material, although pore size exclusion phenomena may inhibit adsorption of high-molecular-weight species.¹⁰ Generally, the most viable alternative for removal of low-molecular-weight and hydrophilic THM precursors is the use of an oxidant such as ozone to reduce the reactivity with chlorine.¹⁰

Conclusion

Agricultural drains in the Sacramento River Delta represent potentially significant contributors to THM precursors in SPW. DOM associated with drain samples exhibited much higher levels of THMFP than a series of related river and lake samples, although a wide range in THM precursor levels was observed among the four agricultural drains sampled and analyzed. DOM in drain

samples had a higher AMW than that found in river and lake samples. The THMs produced represent only 30 percent of the TOX formed. Because future regulations will probably involve maximum contaminant levels for other DBPs, any increase in the reactivity of humic materials caused by agricultural drains could prove significant.

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Issam N. Najm
Chung H. Lee,

The objectives of the activated carbon (PAC) particle size and backwash of PAC. Results show PAC but that the rate of occurring humic substance removal of trace organic equilibrium and close and using an equation

Many synthetic (SOCs), including chemicals (VOCs), of interest because mutagenicity, carcinogenicity. These compo

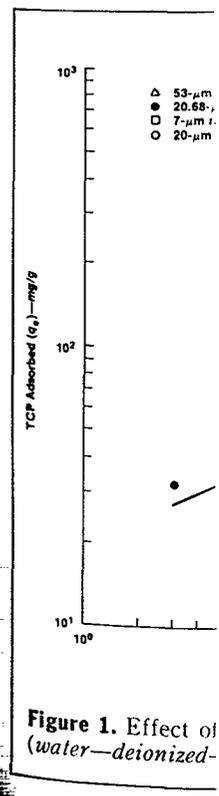


Figure 1. Effect of (water-deionized-