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Reconnaissance Samplings and Characterization of Aquatic Humic Substances at the Yuma Desalting Test Facility, Arizona

(U.S.) Geological Survey
Denver, CO

Prepared for
Bureau of Reclamation
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RECONNAISSANCE SAMPLINGS AND CHARACTERIZATION OF AQUATIC HUMIC SUBSTANCES AT THE YUMA DESALTING TEST FACILITY, ARIZONA

U.S. GEOLOGICAL SURVEY

Water-Resources Investigations 81-42

Prepared in cooperation with the
U.S. Bureau of Reclamation

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Chemical and physical changes in humic substances were extensively studied at four points in the water-treatment process. Humic substances accounted for the largest component (over 25 percent) of organic constituents. Humic substances in the canal source water were similar to other aquatic humic substances present in natural waters. During the treatment process, these substances were brominated and decolorized. The effect of these halogenated humic substances on membrane fouling is unclear, but their presence in the reverse-osmosis product water and reverse-osmosis reject brine along with volatile trihalomethanes has led to environmental concerns.

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RECONNAISSANCE SAMPLINGS AND CHARACTERIZATION OF AQUATIC HUMIC SUBSTANCES AT THE YUMA DESALTING TEST FACILITY, ARIZONA

By R. L. Malcolm, R. L. Wershaw, E. M. Thurman, G. R. Aiken, D. J. Pinckney, and J. Kaakinen

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CONTENTS

ILLUSTRATIONS

TABLES

Page

Page

DEFINITION OF TERMS

Aluminosilicate Clay Minerals—Secondary crystalline minerals composed primarily of Al and Si. These minerals are fine grained and comprise the major part of the clay-size material in most soils and sediments.

Aquatic Fulvic Acid—That colored high-molecular-weight portion of the hydrophobic acid fraction which remains in solution upon acidification to pH 2 with HCl (hydrochloric acid).

Aquatic Humic Acid—That colored high-molecular-weight portion of the hydrophobic acid fraction which precipitates upon acidification to pH 2 with HCl.

Aquatic Humic Substances—The combined humic and fulvic acids in water. Aquatic humic substances should more reasonably be called aquatic fulvic substances because fulvic acids usually predominate by 9:1 in water.

Clay Mineral—Any mineral regardless of composition found in the clay-size range.

Clay or Clay-Size Fraction—Sediment particles less than 2 um in size regardless of composition.

Dissolved Organic Carbon (DOC)—That portion of the organic carbon in water which passes through a 0.45 um (micron) silver membrane filter.

Hydrophilic Fraction—That portion of the DOC in water which passes through or will not sorb onto XAD-8 resin.

Hydrophobic Acid Fraction—That portion of the DOC in water which, when acidified to pH 2 with HCl, sorbs onto XAD-8 resin and is subsequently eluted in 0.1 N NaOH (sodium hydroxide).

Hydrophobic Fraction—That portion of the DOC in water which sorbs onto XAD-8 resin.

Sand or Sand-Size Fraction—Sediment particles in the size range from 60 um to 2 mm (millimeters) regardless of composition.

Silt or Silt-Size Fraction—Sediment particles in the size range from 2 to 60 um regardless of composition.

Specific Low-Molecular-Weight Acids ($C_6 - C_{12}$)—That portion of the hydrophobic acids which are composed of several different organic acids with a carbon skeleton of 6 to 12 carbon atoms in length which should be readily identifiable by gas chromatography.

Suspended Organic Carbon (SOC)—That portion of the organic carbon in water which remains on a 0.45 um silver membrane filter.

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ABSTRACT

Smectite clay minerals were found to be the principal component on the surface of the cellulose-acetate, reverse-osmosis membranes at the Yuma Desalting Test Facility. These clay minerals were not present in the pumped ground water, but were blown into the conveyance canal from adjacent soils. Humic substances from the water and suspended sediments were associated with the clay films on the membrane, but no definitive conclusions concerning their role in fouling were reached. Microbial fouling is believed to be only a minor aspect of membrane fouling.

Chemical and physical changes in humic substances were extensively studied at four points in the water-treatment process. Humic substances accounted for the largest component (over 25 percent) of organic constituents. Humic substances in the canal source water were similar to other aquatic humic substances present in natural waters. During the treatment process, these substances were brominated and decolorized. The effect of these halogenated humic substances on membrane fouling is unclear, but their presence in the reverse-osmosis product water and reverse-osmosis reject brine along with volatile trihalomethanes has led to environmental concerns.

SECTION A - INTRODUCTION

The quantity and quality of desalted water produced by reverse osmosis (RO) membrane processes are dependent on many factors. One of the relatively unknown factors is the effect(s) of organic substances. The possibility that limited organic fouling [illegible] a factor in the slightly decreased performance of RO membranes at the Yuma Desalting Test Facility was postulated, because of the relatively high concentration, 4 mg C/L (milligrams carbon per liter) of organic substances found in the source water, compared to organic concentrations (0.2 mg C/L) in sea water, which is commonly used for desalting.

After several discussions between U.S. Bureau of Reclamation and U.S. Geological Survey personnel from July 1978 through April 1979, a limited organic study was undertaken with the following objectives:

1. The characterization of dissolved organic substances at four points (the canal, RO feedwater inlet, RO product-water outlet, and RO reject-brine outlet) in the Yuma Desalting Test Facility water-processing system at one sampling time.
2. The characterization of suspended organic substances at several points in the treatment process at various times.
3. The characterization of accumulated sediment on and in a dissected spiral-wound RO membrane element that had been in operation for 1 year.
4. The identification of the minerals in various sediment-size fractions from the canal and those accumulated in the spiral-wound RO membrane element before dissection.

The characterization of aquatic fulvic acids was emphasized in the study, because these HMW (high-molecular-weight) substances were postulated to be the most prevalent organic constituents in the water that may interact or precipitate, causing fouling of the RO membranes.

Field Sampling During the Study

The major emphasis of this study was laboratory oriented. Field data in this report are a combination of long-term data accumulated by the U.S. Bureau of Reclamation and intensive short-term cooperative efforts by U.S. Geological Survey and U.S. Bureau of Reclamation personnel. DOC (dissolved organic carbon) and DOC-fractionation data (Supplemental Information) collected during 1979 under the supervision of Howard Salman served as a useful data base for the organic part of this study. Field sampling during the course of this study included:

1. Reconnaissance sampling in May 1979 to determine the DOC composition of water from various points in the treatment system at the Yuma Desalting Test Facility; several producing wells in the Wellton-Mohawk Valley; the Gila River; and the Wellton-Mohawk Canal main conveyance channel (canal).

2. Collection and on-site concentration of humic substances from the water at four points in the treatment system at the Yuma Desalting Test Facility during June 1979 for further characterization; Colorado River water was also sampled for analysis of humic substances.

3. Sludge collection from the solids-contact reactor on June 28, 1979 for analysis of organic and inorganic constituents.

4. Dissection of a 20.3-cm (centimeter) spiral-wound RO membrane element at the Yuma Desalting Test Facility on June 28, 1979; a portion of the particulate material adhering to the membrane was removed by washing and gentle scraping for multiple analyses.

5. Sampling of several producing wells during April 7-10, 1980, for analysis of organic and inorganic constituents; samples also were collected at several points in the treatment system for the analysis of DOC, trihalomethanes, and bromide.

Overview of the Source Water to the Yuma Desalting Test Facility

Water in the canal flowing from the Wellton-Mohawk Valley, which is used as source water for the Yuma Desalting Test Facility, has undergone many changes in water chemistry with location and time. Water diverted from the Colorado River at Imperial Dam is used for irrigation in the valley. A large part of the water infiltrates into the ground water which is then pumped from more than 200 producing wells into a concrete-lined canal leading from the valley to the test facility.

12

Irrigation-Water and Ground-Water Quality in the Wellton-Mohawk Valley. The major part (approximately 90 percent) of the irrigation water used in the valley is from the Colorado River. The water is a calcium sulfate type with a dissolved-solids (DS) concentration of 810 mg/L (milligrams per liter) (table A-1). The other source is the Gila River, which flows every few years as overflow from the Painted Rock Reservoir. This water is of the sodium-chloride type with DS concentrations ranging between 500 and 1,000 mg/L depending on residence time in the reservoir. For the 1979 water year, 80 percent (3.7×10^8 m^3 (cubic meters)), of irrigation water was obtained from the Colorado River and 20 percent (9.3×10^7 m^3) from the Gila River. This water year was unusual because of excessive rainfall in the Gila River basin and discharge of large amounts of flood water from storage through the Gila River to Mexico.

The DOC of the Colorado River was approximately 5 mg C/L (table A-2) for most of the year. This concentration is slightly less than 7 mg C/L, the average DOC for surface water in the United States (Malcolm and Durum, 1976). With decomposition, sorption, and assimilation of selected organic constituents during percolation into the ground water, the DOC is decreased by more than 50 percent to a concentration of 2.3 mg C/L. This concentration is approximately three times the median concentration for ground water (Leenheer and others, 1974).

The proportion of DOC in the Colorado River water and ground water between hydrophobic and hydrophilic fractions is typical of surface and ground waters. Hydrophilic organic solutes predominate in the ground water (66 percent hydrophilic to 34 percent hydrophobic); whereas, both fractions are almost equal in surface water. The decrease in fulvic acid from 0.86 mg C/L in river water to 0.75 mg C/L in ground water contributes to the decrease in hydrophobic constituents in ground water.

Accompanying the decrease in DOC and fulvic acid with percolation into the ground water is the increase in DS from 800 to about 4,000 mg/L. Only one-half of the 5-fold increase in salinity is due to evapotranspiration, because approximately one-half of the amount of water entering the valley must be pumped from the ground to maintain a constant water table. During the 1979 water year, 2.2×10^8 m^3 of ground water (48 percent of the water used for irrigation) was pumped into the canal and flowed out of the valley. The remainder of the ground-water salinity is due to dissolution of soluble salts, and the exchange of calcium for sodium and sulfate for chloride from aquifer solids.

Quality of Canal Water at the Yuma Desalting Test Facility. The DOC of the canal water was relatively constant at approximately 3.5 mg C/L (table A-2 and Supplemental Information). This concentration represents a 1.2 mg C/L (34 percent) increase in DOC during travel in the open canal from the producing water wells to the test facility. This increase is due to extensive growth of algae and diatoms, to humification processes, and to organic debris entering the canal. The most apparent change in water quality from the producing wells to the test facility is the large increase of suspended sediment. The pumped ground water is virtually sediment free. The suspended-sediment concentration in the canal water during June 1979 was in excess of 25 mg/L. This sediment had a SOC (suspended organic carbon) concentration of 2 mg C/L, or 6.1 percent organic carbon by weight; its source is strands of algae and wind-blown debris.

Table A-1.--Normal inorganic chemical water quality at various sampling locations in the Wellton-Mohawk Valley and at the Yuma Desalting Test Facility

Sample	Specific conductance (micromhos per centimeter at 25° Celsius)	Dissolved solids (milligrams per liter at 105°Celsius)	pH (units)	Calcium (Ca^{++})	Magnesium (Mg^{++})	Sodium (Na^{+})	Potassium (K^{+})	Silica (SiO_2)	Bicarbonate (HCO_3^-)	Sulfate ($SO_4^{=}$)	Chloride (Cl^-)
				(milligrams per liter)							
Colorado River at Imperial Dam	1,270	810	7.9	90	35	150	5	10	190	350	150
Gila River near Mohawk	780	500	7.8	50	15	100	5	--	160	80	130
Ground water in Wellton-Mohawk Valley	5,600	3,900	7.8	230	100	930	11	33	450	980	1,180
Canal at Yuma Desalting Test Facility	5,600	3,900	7.9	230	100	930	9	28	450	980	1,180
Reverse-osmosis feedwater	5,300	3,300	7.4	130	90	930	9	20	30	950	1,180
Reverse-osmosis reject brine	12,000	8,200	5.8	350	225	2,250	20	38	17	2,500	2,800
Reverse-osmosis product water	1,200	650	5.3	10	5	220	3	5	8	50	350

Table A-2.--Normal dissolved organic carbon (DOC), suspended organic carbon (SOC), suspended sediment, and fulvic acid concentrations at various sampling locations

Sample	DOC	SOC	Fulvic acid	Suspended sediment
	(milligrams carbon per liter)			(milligrams per liter)
Colorado River at Imperial Dam	5.0	2.0	0.86	50
Ground water in Wellton-Mohawk Valley	2.5	0.01	0.75	0.1
Canal at Yuma Desalting Testing Facility	3.6	2.0	0.98	25
Reverse-osmosis feedwater	3.4	0.01	0.69	0.1
Reverse-osmosis reject brine	6.9	0.01	2.28	0.1
Reverse-osmosis product water	0.7	0.0	0.04	---

The relative proportion of hydrophobic to hydrophilic organic constituents remains virtually the same during travel in the canal, even though the DOC increases by 34 percent. The average hydrophilic : hydrophobic fractionation for 16 canal samples collected for a period of 6 months during 1977 by Howard Salman (Supplemental Information) was 62 percent hydrophilic : 38 percent hydrophobic. These values are within a few percent of those obtained from well reconnaissance (table A-3) and canal-water data (Supplemental Information). The increase of fulvic acid from 0.75 mg C/L in the ground water to 1.08 mg C/L in the canal water at the test facility (table A-2) was associated with these small changes in the percentage of hydrophobic constituents.

The only changes in inorganic water quality from the wells to the test facility were moderate decreases in dissolved silica from 33 to 28 mg/L and potassium from 11 to 9 mg/L. All other inorganic constituents were unchanged. Small changes in inorganic water quality due to evaporation, chemical processes, or eutrophication cannot be determined because of small changes in discharge from pumping wells of different chemical composition. Decreases in dissolved silica and potassium are evident, because almost all of the individual producing wells have relatively constant concentrations of these constituents and these concentrations are significantly greater than those in the canal water at the test facility. These changes are not surprising because of the extensive diatom population in the canal that require large amounts of dissolved silica and potassium for their growth.

Water Quality During Processing at the Yuma Desalting Test Facility. The pretreatment process to remove all suspended solids from the canal water is very effective (table A-2). In addition to suspended solids removal, calcium concentration was decreased by almost 50 percent (from 230 to 130 mg/L, table A-1). Virtually all iron and manganese in the canal water was removed during pretreatment. A slight removal of DOC was achieved; the concentration decreased from 3.6 to 3.4 mg C/L. Implications of the 34-percent decrease in fulvic acid during pretreatment will be discussed later in this report.

During RO treatment, approximately 90 percent of the inorganic substances and 80 percent of the organic substances were removed from the water. A much more efficient exclusion of 95 percent was achieved for fulvic acid (table A-2) than for organic compounds in general.

Table A-3.--Dissolved organic carbon (DOC) and hydrophobic acids in ground water from producing wells varying in discharge and specific conductance

Well number	Discharge (liters per second)	Specific conductance (micromhos per centimeter at 25° Celsius)	DOC May 1979	DOC April 1980	Total of hydrophobic acids, bases, and neutrals	Hydrophobic acids
			(milligrams carbon per liter)			
69B	51	1,360	---	2.9	---	---
68B	65	1,830	---	1.7	0.8	0.8
24	57	2,620	1.9	---	---	---
602	48	2,620	2.3	2.1	---	---
70	105	2,700	---	1.9	0.9	0.6
21A	54	2,830	---	1.4	0.6	0.6
53B	156	3,150	---	2.2	---	---
7	57	3,730	2.7	---	---	---
47	82	3,970	---	3.2	1.2	1.2
58	20	4,700	---	2.6	---	---
38	62	4,810	2.2	---	---	---
624	54	5,530	---	1.2	---	---
9	153	6,530	---	2.0	---	---
2	164	7,390	2.5	---	---	---
39	110	7,850	---	3.2	1.8	1.8
621	82	9,820	3.8	---	---	---
30	74	12,300	---	3.8	1.2	1.2

SECTION B - ISOLATION AND CHARACTERIZATION OF HUMIC AND FULVIC ACIDS

Isolation of Hydrophobic Acids from Four Points in the Water Treatment System

Considerable progress has been made recently in quantitative isolation of organic solutes from water. A schematic diagram for the separation and characterization of organic constituents is given in figure B-1. Separation through level three, resulting in six classes of organic compounds, is called DOC fractionation analysis (Leenheer and Huffman, 1976). This fractionation is achieved by use of an uncharged, macroporous, acrylic, XAD-8 resin (Malcolm and others, 1977). Those solutes sorbed onto the resin are defined as hydrophobic; those passing through as non-sorbed solutes are defined as hydrophilic.

The hydrophobic-acid fraction is important in this study, because it contains the high molecular-weight humic and fulvic acids (Aiken and others, 1979) that were postulated to affect the efficiency of RO-membrane processes. This fraction also contains low molecular-weight specific organic acids. It is isolated by acidification of the filtered water to pH 2 with concentrated HCl (hydrochloric acid), flowing the water sample through a column of XAD-8 resin, and then eluting the resin column with 0.1 N NaOH (sodium hydroxide).

Four points in the treatment system (the canal, RO feedwater inlet, RO reject-brine outlet, and RO product-water outlet) were chosen for the isolation of hydrophobic acids. During the week of June 20 -27, 1979, 855 L (liters) of canal water, 855 L of reject brine, 4,542 L of RO feedwater, 4,905 L of RO product water, and 151 L of Colorado River water were processed on site for hydrophobic acids. Each sample was concentrated by multiple reconcentration to a maximum of 4 L for transport to the laboratory in Denver. The exact volume of each concentrate was determined, and then subsampled for organic carbon analysis (Supplemental Information).

Isolation of Humic and Fulvic Acids from the Hydrophobic Acid Fraction

The hydrophobic acid fraction is composed of three different components: humic acid, fulvic acid, and low-molecular-weight (LMW) specific organic acids with carbon skeletons of 6 to 11 carbon atoms in length per carboxyl (acid) functional group. LMW specific organic acids with less than 6 carbon atoms (C_6) per functional group are hydrophilic; those with more than 11 carbon atoms (C_{11}) are not eluted from the resin column with 0.1 N NaOH.

As shown in figure B-1, humic acid is separated from fulvic acid and LMW specific acids by acidification of the hydrophobic acid fraction to pH 2 with HCl. Immediately after the hydrophobic acids were eluted from the XAD-8 column, they were acidified to pH 2 with HCl, and placed in an ice bath for transport to the Denver laboratory. Immediate acidification and cooling was essential to prevent possible oxidation of hydrophobic acids in basic solution and

19

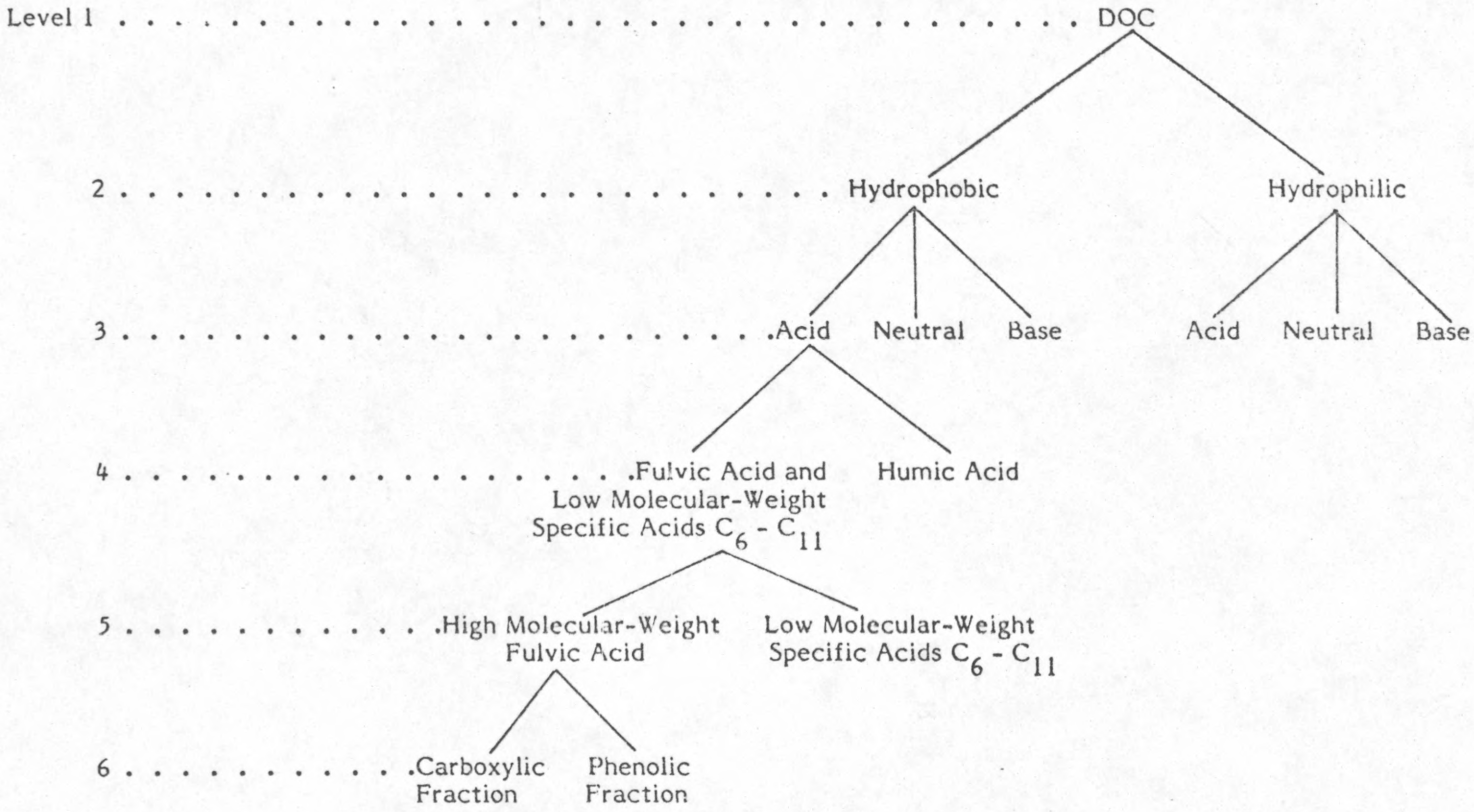

Figure B-1.--Characterization scheme for organic substances in water.

to prevent microbiological growth. Upon arrival at the laboratory, the precipitated humic acids were removed by centrifugation. After washing the precipitate in deionized water, the respective humic acids were dissolved in 0.1 N NaOH, diluted to volume in a volumetric flask, and then subsampled for organic carbon analysis.

Fulvic acid was separated by Enzacryl[1/] gel chromatography from the LMW specific organic acids for only the RO product-water concentrate, because it was the only sample that contained sufficient amounts of LMW acids to require such processing. The separation on Enzacryl gel is achieved by exclusion chromatography. HMW fulvic acid is excluded from the small interior pores of the gel beads, and emerges first from the column. LMW specific acids are small enough to enter into interior pores of the gel beads. The pathway for LMW acids to the end of the column is much longer than for large fulvic acid molecules; therefore, LMW acids are retained a longer period of time in the column and are eluted after the fulvic acid.

Fulvic acids from the canal water, RO feedwater, RO product-water, and RO reject-brine samples were hydrogen-saturated by passing the concentrates through a column of strong-acid ion-exchange resin. The preparations were then freeze-dried. Approximately 1.3 g (grams) of fulvic acid were isolated from the canal water, 4.7 g from the RO feedwater, 2.6 g from the RO reject brine, and 100 mg (milligrams) from the RO product water. These amounts of fulvic acid represent a recovery of 75, 75, 67, and 25 percent, respectively. The amount of humic acid was so small in all samples that the preparations were kept in acid solution for a few characterizations and not freeze-dried. The small amount of fulvic acid from the RO product water also precluded extensive characterization.

[1/] The use of brand names in this report is for identification purposes only and does not imply endorsement by the U.S. Geological Survey.

2

Mass-Balance Considerations

A mass-balance analysis was made for two organic parameters (DOC and hydrophobic acids) for the RO process during June 1979, to evaluate the magnitude of possible organic sorptive processes on the RO membrane. In the ideal case, without sorption, the mass of organic material in the RO feedwater is distributed between RO product water and RO reject brine. This equality is shown by the following expression:

$$\text{RO feedwater} \longrightarrow \text{RO product water} + \text{RO reject brine}$$

For DOC, the recovery was 89 percent:

$$298 \text{ mg C/min} \longrightarrow 38 \text{ mg C/min} + 227 \text{ mg C/min}$$

For hydrophobic acids, the recovery was 120 percent:

$$65 \text{ mg C/min} \longrightarrow 1.9 \text{ mg C/min} + 77 \text{ mg C/min}$$

The recovery values are reasonable and within the expected range when all the variables in the treatment and experimental process are considered. A mass balance for fulvic acid was calculated; it was virtually the same as for hydrophobic acids because fulvic acid is the major component of hydrophobic acids in both the RO feedwater and the RO reject brine. Errors associated with these calculations are large, and no definite conclusions can be made concerning organic sorptive properties of the membrane.

Chemical and Physical Characterization of Humic Substances Isolated from the Yuma Desalting Test Facility

Humic substances are brown organic acids, polymeric in nature, derived from the degradation of plant material and soil organic matter. They vary in molecular weight from 500 to tens of thousands. Humic substances are operationally divided into: (1) fulvic acid, that organic material extractable from soil with 0.1 N NaOH and soluble in acid; and (2) humic acid, that organic material extractable with 0.1 N NaOH, and insoluble in acid (Definition of Terms). Humic substances may be characterized by elemental analysis, infrared spectroscopy, functional-group analysis, and liquid chromatography. In spite of these characterizations, an exact structure is not known; many structures probably exist.

Various methods of characterization distinguish among the types of humic substances, their sources, and chemical changes that they may undergo. The purposes of the characterization of humic substances isolated from waters of the Yuma Desalting Test Facility are: (1) to compare the humic substances isolated from various stages in the treatment system for changes in structure and reactivity; and (2) to determine if there is evidence for membrane fouling from aquatic humic substances. Explanations of the methods precede the characterizations that were done on the aquatic humic substances. Detailed procedures appear in the Supplemental Information section.

Enzacryl Gel Chromatography. A 2 milliliter (mL) sample of hydrophobic acid concentrate was passed through a column of enzacryl gel (Thurman and Malcolm, 1979) at a flow rate of 5 mL per minute. The breakthrough of organic constituents was continually monitored at a visible wavelength of 460 nm (nanometers) and an ultraviolet wavelength of 254 nm, and the effluent collected in 10 mL portions with a fraction collector. DOC was determined on each fraction using a Beckman 915 carbon analyzer.

Enzacryl chromatography serves both as a separation and characterization of the organic acids in samples of the canal water, RO feedwater, RO reject brine, and RO product water (figs. B-2 and B-3). Visible absorbance parallels DOC very closely in the first large peak of fulvic acid, but is insensitive to the uncolored small second and third peaks of the LMW organic acids. As summarized in tables B-1 and B-2, LMW organic acids are a small portion of all samples except for the RO product water. The chromatograms show little change in distribution of hydrophobic acids with sediment removal during pretreatment of the canal water.

The pronounced difference in the RO product-water chromatogram compared to the other sampling points in the treatment system, is due to the preferential movement of LMW organic acids through the RO membrane compared to HMW fulvic acid, the high concentration factor necessary to obtain sufficient detection or resolution, and the presence of small amounts of acrylic acid in the RO product-water sample. Both the canal water and RO feedwater contain small amounts of LMW acids. This LMW portion passes through the membrane; thus, the brine reject is significantly depleted of these constituents. The HMW fulvic acid, however, is largely rejected from passing through the membrane. The HMW fulvic acid concentration is only 0.04 mg C/L in the RO product water compared to 0.69 mg C/L in the RO feedwater. The sample DOC is diluted by approximately one-tenth during passage through the enzacryl column. To attain adequate resolution of the lesser secondary peaks by DOC and spectral analyses, the inital sample DOC concentration needed to be in excess of 1,500 mg C/L. The hydrophobic acid concentrate of the RO product water contained ten times less DOC than the other samples; therefore, in concentrating the RO product-water sample to the same DOC concentration as the other samples, at least a tenfold resolution of the LMW organic acids was attained. A third factor is the presence of small amounts of acrylic acid in the second peak of the RO product-water sample. Acrylic acid is a hydrolysis contaminant from the XAD-8 resin.

The fractionation of the hydrophobic acid concentrates is consistent with the hypothesis that the ground-water system is undergoing rapid or extensive recharge. The canal water (tables A-2 and A-3) is somewhat typical of ground water in that the hydrophilic fraction is much greater than the hydrophobic fraction; the humic acids are in low concentration (0.02 mg C/L); and the

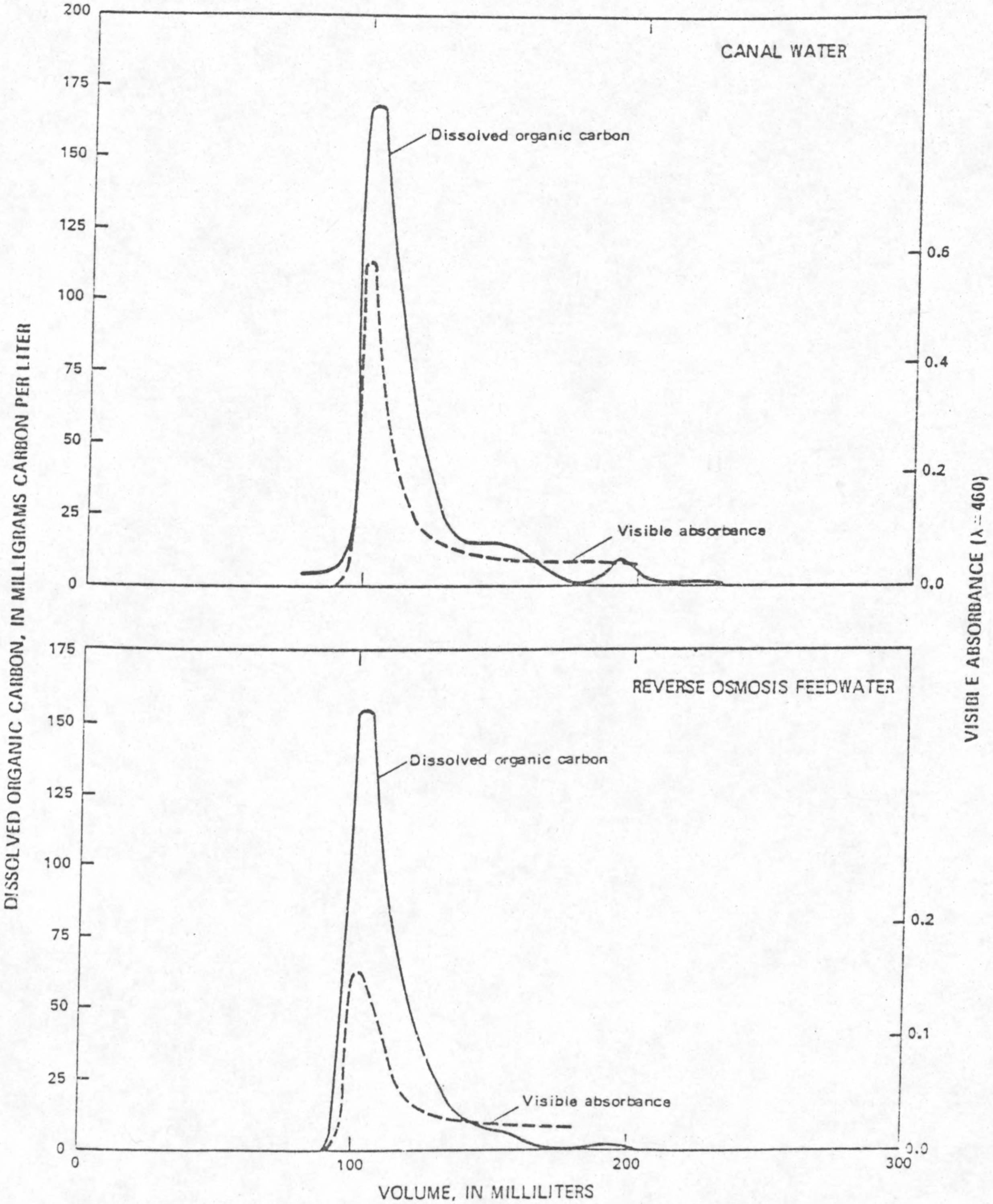

Figure B-2.--Graph showing the enzacryl gel separations of hydrophobic acid concentrates from the canal water and reverse-osmosis feedwater.

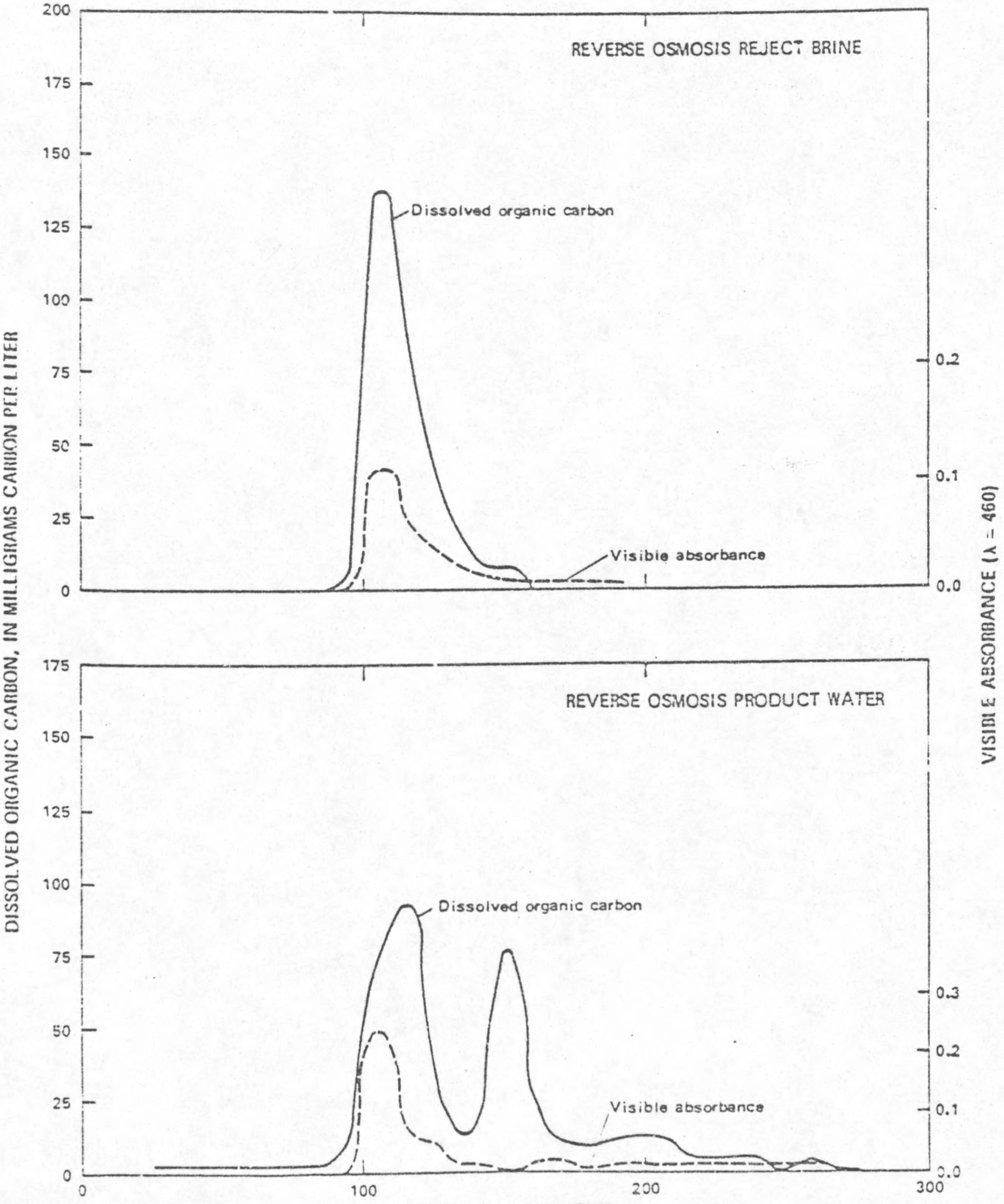

Figure B-3.--Graph showing the enzacryl gel separations of hydrophobic acid concentrates from the reverse-osmosis reject brine and reverse-osmosis product water.

Table B-1.--Concentration of hydrophobic acids, fulvic acid, humic acid, and low-molecular-weight specific organic acids in waters at the Yuma Desalting Test Facility during June 1979

Sample	Amount of water processed (liters)	Initial DOC	Hydrophobic acids	Fulvic acid	Humic acid	Specific low-molecular-weight acids $C_6 - C_{11}$
		(milligrams carbon per liter)				
Canal water	855	3.6	1.12	0.98	0.02	0.12
Reverse-osmosis feed water	4,542	3.4	0.74	0.69	0.01	0.04
Reverse-osmosis reject brine	855	6.9	2.35	2.28	0.01	0.06
Reverse-osmosis product water	4,905	0.7	0.07	0.04	0.01	0.02
Colorado River water	151	5.0	1.00	0.86	0.04	0.10

Table B-2.--Relative percentages of the hydrophobic acid fraction as fulvic acid, humic acid, and low-molecular-weight specific acids (C_6 - C_{11})

Sample	Hydrophobic acid concentration (milligrams carbon per liter)	Percentage of hydrophobic acids as:		
		Fulvic acid	Humic acid	Specific low-molecular-weight acid C_6 - C_{11}
Canal water	1.12	88	2	10
Reverse-osmosis feedwater	0.74	93	1	5
Reverse-osmosis reject brine	2.35	97	0.4	3
Reverse-osmosis product water	0.07	57	14	29
Colorado River water	1.00	86	4	10

2.

Table B-3.--Average percent elemental composition of soil, ground-water, and surface-water fulvic acids compared to aquatic fulvic acids from the Yuma Desalting Test Facility

Sample	Carbon	Oxygen	Hydrogen	Nitrogen	Sulfur
	(percent)				
Soil fulvic acid	50.0	42.8	3.9	1.8	0.5
Average ground-water fulvic acid	62.7	29.1	6.6	0.4	0.5
Average surface-water fulvic acid	53.0	40.0	4.0	0.8	0.5
Canal-water fulvic acid	57.2	35.6	4.8	1.1	0.6
Reverse-osmosis feedwater fulvic acid	54.9	34.6	5.1	1.0	0.2
Reverse-osmosis reject-brine fulvic acid	55.1	34.7	5.0	1.0	0.2

28

proportion of fulvic acid to humic acid is 49:1. This water is atypical in that the DOC is high (3.6 mg C/L) and fulvic acid predominates (88 percent) in the hydrophobic acid fraction rather than LMW specific C_6 - C_{11} acids. The composition of the hydrophobic acids suggests that the ground water pumped into the canal is a complex mixture of older residual ground water and recent additions of rapidly percolating irrigation water.

Elemental Analysis. A basic characterization of humic substances is their elemental composition. Humic substances consist of carbon, oxygen, hydrogen, nitrogen, and sulfur. There are basic differences in elemental composition between aquatic and soil-derived humic substances (table B-3).

Ground-water fulvic acids contain more carbon and hydrogen and less nitrogen and oxygen than soil fulvic acids, because of the lack of carbohydrates and polysaccharides in aquatic material, and the increased number of oxygen-containing functional groups present in soil fulvic acids. These data reflect the anaerobic degradative processes in ground water. Aquatic humic substances are deficient in nitrogen compared to soil fulvic acids.

Elemental analyses of the three samples from the Yuma Desalting Test Facility are very similar in composition, and are intermediate between surface-water fulvic acids and ground-water fulvic acids. This result should be expected because the pumped ground water is a mixture of native ground water and surface water. Surface water is being continually added to ground water by infiltration of irrigation water through the soil zone. There appears to be no fractionation of fulvic acid throughout the treatment process. However, it was found that the RO product-water and RO reject-brine elemental analyses were slightly depleted in oxygen content with respect to the canal sample (canal = 39.6 percent; RO feedwater = 36.8 percent; and RO reject brine = 37.2 percent). This elemental analysis accounts for only 96 percent by weight for the RO feedwater and RO reject-brine samples versus 100 percent for the canal sample; the remainder of the analysis is accounted for by bromine. This is apparently due to the chlorination of the water and will be discussed in detail in SECTION D of this report. The major finding of the elemental analysis is that approximately one bromine atom per fulvic molecule (on the average) was incorporated during the water treatment.

Infrared Spectroscopy. An organic molecule, such as a humic substance, is not a rigid assemblage of atoms, but contains bonds between atoms which can bend or stretch. When infrared light of the same frequency as the bending or stretching of the bond is incident on the molecule, energy is absorbed and the amplitude of that vibration is increased. This is shown as an absorption of light on the spectrophotometer. Various types of bonds between atoms, such as C-C, C=C, C-O, C=O, and C-H, absorb various parts of the infrared spectrum. Therefore, the types of carbon bonds and functional groups present in the molecules of the humic substances can be interpreted by their infrared absorption spectra.

Aquatic humic substances from the canal water, RO feedwater, and RO reject brine are identical in their infrared spectra. They also look very similar to other aquatic humic substances isolated from different surface waters, such as rivers and lakes. A major absorption band occurs at 3,000 to 3,500 reciprocal centimeters (cm^{-1}), the -OH stretching region. Aquatic humic substances contain OH functional groups in: (1) carboxyl groups (COOH); (2) phenolic hydroxyl groups (Ø-OH); and (3) simple hydroxyl groups R-OH). The OH bending region is also seen at 1,200 cm^{-1}, re-inforcing the hydroxyl group as an important functional group in aquatic humic material.

The next important region is at 1,725 cm^{-1}, the carboxyl absorption band. The carboxyl and hydroxyl functional groups are the most important functional groups of aquatic humic material.

Finally, there are absorption bands at 2,960 cm^{-1} and 1,380 cm^{-1} which indicate the stretching and bending of methyl groups (CH_3). These absorption bands differentiate soil humic substances from aquatic humic substances. Methyl or aliphatic carbon absorption bands are not usually found in soil humic substances, which tend to be more aromatic and less aliphatic than aquatic humic substances. In summary, aquatic humic substances from the test facility look very similar to aquatic humic substances that were isolated from other sources; no infrared evidence of degradation of humic material during water processing at the test facility is apparent.

Functional Group Analyses. The humic substances were analyzed by titration for the two most important functional groups: the carboxyl and phenolic-hydroxyl groups. The carboxyl group titration is accomplished by reacting the carboxyl groups with calcium acetate, generating acetic acid in the process. The acetic acid is then titrated with standard base to a pH end point of 8.0. The phenolic hydroxyl group is titrated as an acid-base titration of the aquatic humic substances, and the titer from pH 8.0 to 10.0 is considered to be 50 percent of the phenolic groups. This method determines the minimum number of phenolic groups present.

The carboxyl and phenolic hydroxyl content of the humic material isolated from the canal water, RO feedwater, and RO reject brine is shown in table B-4. The canal sample contains about 10 percent more carboxyl groups than the RO feedwater and RO reject-brine samples, probably because of the increase in weight of the RO feedwater and RO reject-brine samples resulting from the incorporation of bromine. Analytical reproducibility for the carboxyl titration is about ± 0.1 meq/g (milliequivalents per gram).

The phenolic hydroxyl group content is apparently the same for the three samples. This was not expected, because it was postulated that chlorination would probably destroy some of the phenolic hydroxyl sites. It should be kept in mind that all the methods for determining phenolic hydroxyls in humic materials, including the titration method, are not sufficiently precise or sensitive to accurately measure (<1.0 meq/g) low phenolic contents. Therefore, the small differences observed in the phenolic content of the samples may or may not be real.

31

Carboxyl and phenolic hydroxyl group content for all three samples is very similar to other aquatic substances. An important difference between the soil and aquatic materials is in the phenolic hydroxyl content (table B-4). Aquatic material is deficient in phenolic content compared to soil humic material.

In conclusion, it appears that the pretreatment process slightly decreases the carboxyl content of the original canal humic substances. These changes are small and may be the combined result of molecular incorporation of bromine and possible decarboxylation reactions. Slight compositional changes in the carboxyl and phenolic hydroxyl content of the humic substances during pretreatment do not significantly alter the chemistry of these humic substances. Minor differences between these humic substances and average aquatic humic substances should not affect the possibility of membrane sorption.

Molecular Size. Molecular dimensions of the aquatic humic substances were determined by low angle X-ray scattering. The radius of gyration, which is determined by this technique, can be imagined as the sphere swept out by the molecule while it is rotating in solution. The slope of the curve from a plot of the natural log of the intensity of scattering (ln I) versus scattering angle $\frac{2\pi \text{Sin } 2\Theta}{\lambda}$ determines the radius of gyration which is related to the molecular size and molecular weight of the aquatic humic substances (Wershaw and Pinckney, 1973).

Fulvic acid from the canal has a radius of gyration of 6.1 A^{O} (angstroms); fulvic acid from the RO feedwater and the RO reject-brine are 6.4 A^{O}. This corresponds to a molecular weight in the range of 800 to 1,200 grams per mole. The similarity in molecular size of fulvic acid among the samples suggests that there is no fragmentation of humic material during the treatment process.

These samples from the Yuma Desalting Test Facility are somewhat smaller than most other aquatic humic substances which have molecular dimensions of 5 to 10 A^{O}. This is probably due to the source of the aquatic humic substances and their natural variation. These substances are markedly different from soil humic substances, which have a larger radius of gyration (8 to 25 A^{O}).

In conclusion, aquatic humic substances in the Yuma Desalting Test Facility waters are of low molecular weight, in the range of 800 to 1,200 grams per mole, and there are no apparent changes in molecular size due to water treatment.

Ultraviolet-Visible Spectroscopy. The ultraviolet-visible (UV-VIS) spectrum of aquatic or soil humic substances is generally uninformative and simply shows increasing absorbance with decreasing wavelength. However, the extinction coefficient of aquatic humic material may be useful at 460 nm to determine an

3,

Table B-4.--Functional group content of various humic substances

Sample	Carboxyl (calcium acetate method)	Carboxyl (titration)	Phenolic hydroxyl
	(milliequivalents per gram)		
Canal	6.6	5.9	0.8
Reverse-osmosis feedwater	5.9	5.6	0.5
Reverse-osmosis reject brine	5.9	5.5	1.0
Average aquatic fulvic acid	7.0	6.0	1.0
Average aquatic humic acid	6.0	5.0	2.0
Average soil fulvic acid	8.3	6.5	3.0
Average soil humic acid	3.6	3.3	3.9

extinction coefficient for visible color. The extinction coefficient is a measure of absorbance of the material at a specific wavelength, normalized to carbon concentration, and is a measure of the colored portion of the humic material. Beer's Law is used to calculate the extinction coefficient for the humic material:

$$\text{Absorbance} = Elc$$

where E is the extinction coefficient; l is the path length; and c is the concentration in moles per liter. When one substitutes milligrams carbon per liter for c and uses a path length of 1 cm, the units for the extinction coefficient are absorbance units per centimeter per milligram carbon per liter.

Extinction coefficients of the three samples show that there is a dramatic difference between the canal-water fulvic acid and the RO feedwater and RO reject-brine fulvic acids (table B-5). The extinction coefficient of the canal-water fulvic acid is nearly three times higher than the extinction coefficient of either the RO feedwater or the RO reject-brine fulvic acid. These differences are most likely due to loss of color centers within the molecule during the water-treatment process. It is known that at least four conjugated double bonds are required to produce a chromophore in the visible region of the spectrum (Dyer, 1965). It is hypothesized that the color-producing centers, that is, these conjugated double-bond systems, are being disrupted by bromination, causing a marked decrease in color and extinction coefficient. A typical reaction would be the bromination of an olefin shown in equation 1.

Table B-5.--Extinction coefficients of the humic materials from the Yuma Desalting Test Facility

Sample	Extinction coefficient at 460 nanometers (absorbance units per centimeter per milligram carbon per liter)
Canal-water fulvic acid	0.00097
Reverse-osmosis feedwater fulvic acid	0.00038
Reverse-osmosis reject-brine fulvic acid	0.00035

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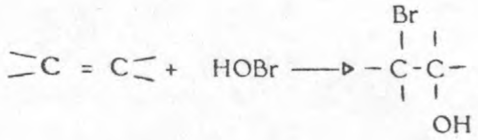

$$>C=C< + HOBr \longrightarrow -\overset{Br}{\underset{|}{\overset{|}{C}}}-\underset{OH}{\underset{|}{\overset{|}{C}}}- \qquad (1)$$

When double bonds in a conjugated system are added across by hypobromous acid, conjugation is disrupted and the color centers of the molecule are destroyed.

In conclusion, it can be stated that hypobromous acid is most likely adding across both conjugated olefin systems and aromatic rings in the fulvic acid molecule to destroy color in both the RO feedwater and RO reject-brine fulvic acid samples.

Liquid Chromatography. Aquatic humic substances may be analyzed by pH gradient liquid chromatography. Various organic acids present in the humic material are adsorbed at the head of the chromatographic column. A pH gradient is established using the titration of phosphoric acid with sodium hydroxide (MacCarthy and others, 1979). Aquatic humic substances are separated into two fractions based on the pK_a of the acidic functional groups present on the molecules. This method, usually gives two chromatographic peaks which are related to the principal acidic functional groups present in the molecule: the carboxylic and phenolic-hydroxyl groups. A typical soil humic acid will fractionate into approximately 50 percent first-peak material, the carboxylic-acid fraction; and approximately 50 percent second-peak material, the phenolic-hydroxyl fraction. Soil fulvic acids vary from 75 to 90 percent as first-peak material.

Table B-6 shows the pH gradient analysis of aquatic humic substances from the Yuma Desalting Test Facility; both humic and fulvic acid components were fractionated by this technique. Because only 200 µL (microliters) of sample are required with a DOC of 250 mg C/L, it was possible to run the small amount of the humic fraction as well as the fulvic fraction. The Colorado River fulvic acid contains slightly more second-peak material than the canal, RO feedwater, and RO reject-brine fulvic acids, which may indicate that more phenolic and hydrophobic materials are removed by adsorption on sediments when the water is applied for irrigation. The concentration of aquatic humic material in the Colorado River is 1.0 mg C/L and the ground water going into the canal varies from 0.5 to 1.0 mg C/L, with a mean of 0.8 mg C/L, suggesting adsorption on soil and aquifer solids. This interpretation is also supported by DOC data. The DOC of the canal water (3.6 mg C/L) is 1.4 mg C/L less than the value for the Colorado River (5.0 mg C/L).

The pH gradient analyses do not indicate any significant changes occurring during water treatment. This is somewhat surprising, because it would be expected that the more hydrophobic second-peak material would be removed during the lime-precipitation procedure. Apparently, natural processes occurring in the soil, aquifer, and canal have adsorbed or salted out these fractions. Only the more hydrophilic, water-loving, species are present in the water.

Table B-6.--Characterization of humic substances from the Yuma Desalting Test Facility by pH gradient analysis

Sample	Fulvic		Humic	
	First peak (percent of total)	Second peak	First peak (percent of total)	Second peak
Colorado River water	94	6	85	15
Canal water	97	3	83	17
Reverse-osmosis feedwater	97	3	86	14
Reverse-osmosis reject brine	97	3	86	14
Reverse-osmosis product water	75	25	--	--

It is interesting to note that there is an important shift toward more second-peak material in the RO product-water fulvic acid. This suggests that the membrane is allowing more phenolic material to pass. These data are consistent with model compounds which have been tested by Sourirajan and Matsuura (1977) where they showed that phenolic model compounds are selectively allowed to pass through a cellulose acetate membrane. Although the RO product water contains more second-peak material, the final concentration is about 1/40 of the RO feedwater.

The humic acid fraction, which precipitates in acid, shows considerably more second peak material. This is not surprising, because the precipitation procedure should enrich the sample in hydrophobic constituents.

In conclusion, the aquatic fulvic acids which are predominant in the Yuma Desalting Test Facility waters are less hydrophobic in nature than soil fulvic acids and almost entirely first peak carboxylic material. The very small amount (about 3 percent) of humic material, which passes through the RO membrane, is enriched in second-peak phenolic material.

Amino Acid and Carbohydrate Analyses. Aquatic humic substances isolated from the Yuma Desalting Test Facility waters were characterized by their amino acid and carbohydrate content. Typically, aquatic humic substances contain low amounts of these compounds, with free amino acid content less than 0.1 percent and carbohydrates less than 5 percent.

Table B-7 shows amino-acid analyses for three fulvic-acid hydrolysates. Aspartic acid is typical of 18 of 22 amino acids analyzed, in which enrichment occurred from the canal sample to the RO reject brine and RO

Table B-7.--Characterization of fulvic acids from the Yuma Desalting Test Facility by amino acid analysis

Amino acid	Canal	Reverse osmosis feedwater	Reverse osmosis reject brine
	(nanomoles per milligram)		
Glutamic acid	2.4	11.3	10.8
Alanine	3.1	14.4	13.9
Leucine	1.5	14.8	14.2
Aspartic acid	3.9	15.3	15.1
Glycine	8.1	10.9	9.9
Threonine	1.4	4.9	4.5
Serine	1.2	3.1	2.9
Phenylalanine	0.6	6.3	5.7
Proline	1.5	7.7	7.1
Lysine	0.5	0.7	0.7
Isoleucine	0.9	8.3	7.6
Arginine	0.2	0.2	0.2
Valine	1.8	12.1	11.2
Histidine	trace	----	----
α-amino adipic acid	0.2	4.0	3.8
Tyrosine	0.3	trace	trace
Ornithine	trace	0.4	0.4
Glutamine	----	----	----
γ-amino butyric acid	0.4	0.8	0.7
Hydroxyproline	0.4	0.4	0.4
Methionine	0.2	0.1	0.1

36

feedwater samples. Enrichment factors varied from two to ten. Three possible explanations for their enrichment are: (1) lysis of diatomaceous cells during treatment and chlorination may yield increased amino acid concentration; (2) certain portions of the fulvic acid molecule, including certain amino acids, may be more labile during chlorination than other portions of the molecule; and (3) effects of chlorination on the fulvic acid molecule may improve the hydrolysis (in 6 N HCl) which is done prior to amino-acid analysis.

Methionine and tyrosine (table B-7) are exceptions to the enrichment trend. This finding is consistent with the predicted susceptibility of these compounds to oxidation and substitution during halogenation with chlorine or bromine. Tyrosine, which has a phenolic side chain, would be readily substituted by bromine. Methionine, a sulfur-containing amino acid, also would be easily oxidized, and has been depleted by a factor of two.

Carbohydrate analysis shows that the canal fulvic acid is typical of an average aquatic humic substance and contains about 4.4 percent carbohydrate by weight (table B-8). There, is a marked depletion in carbohydrate content during water treatment, probably because of oxidation of the carbohydrate material by chlorination, and subsequent separation from the fulvic acid. Therefore, the conclusion is that chlorination and bromination are having an important effect on amino acid and carbohydrate components of fulvic acid.

Table B-8.--Carbohydrate content of fulvic acids at the Yuma Desalting Test Facility

Sample	Percent carbohydrate
Canal fulvic acid	4.4
Reverse-osmosis feedwater fulvic acid	2.2
Reverse-osmosis reject-brine fulvic acid	2.9

SECTION C - SEDIMENT ORGANIC ANALYSES

Three suspended-sediment samples were analyzed during this study. Two of the samples were obtained from the Wellton-Mohawk main conveyance channel (canal): the first sample was collected during the reconnaissance trip in May 1979, and the second sample was collected during June, 1979. The third sample was obtained from a 20.3-cm diameter, spiral-wound, cellulose acetate membrane element dissected on June 28, 1979. This element was manufactured by Fluid Systems division of UOP Corporation; it had been part of the domestic water system at the Yuma Test Facility. It was operated for approximately 5,400 hours prior to dissection. In addition to these sediments, a sample of the sludge from the solids contact reactor was taken on June 28, 1979.

The canal suspended-sediment samples were collected on 0.45 μm silver filters (Supplemental Information). In addition to filtering water from the canal, the RO feedwater in the treatment train was also filtered through a silver filter; however, no appreciable amount of sediment was collected. This filter was examined by scanning electron microscopy. The most predominant features observed on the filter were diatom frustules. Inorganic crystals seen in some of the photomicrographs were analyzed by the X-ray microprobe attachment to the scanning electron microscope. Calcium was found in the crystals, indicating that the crystals are most likely calcium carbonate. Diatoms were also observed in the canal sediment.

Reconnaissance Sample of May 1979

The May sample consisted of 1.1 g of sediment that was carefully scraped from two 142-mm (millimeter) silver filters, which had been used to filter 10 gallons of water. This reconnaissance sample was used to develop procedures for processing of samples taken during the June sampling, and to determine what parameters should be measured. The filters were scraped and washed in the field immediately after the filtering process. The sediment sample and water washings were collected in a polyethylene bottle and immediately chilled on ice. Upon receipt in the laboratory, the sample was sieved through a 60 μm (micrometer) sieve to remove twigs and leaves, and then lyophilized; 0.987 g of the 1.1 g of starting material passed through the sieve. The sample was extracted with NaOH to isolate the humic and fulvic acids.

Data in table C-1 show that approximately one-third of the organic carbon in the sediment is humic and fulvic acid. Data in table C-2 show that the sediments have a low-to-moderate organic content. Canal sediments have a high inorganic-carbon content that is almost completely removed during water treatment. An attempt was made by acid hydrolysis to identify the remaining 67 percent of the organic carbon, which is not extractable in 0.1 N NaOH. Ten mL of 12 N HCl was added to 0.0533 g of NaOH extracted sediment and refluxed for 3.5 hours. This treatment resulted in the removal of approximately 92 percent of the remaining organic carbon.

Table C-1.--Organic and inorganic carbon composition of canal and reverse-osmosis membrane sediments

Sediment parameter	May 1979 canal sample	June 1979 canal sample	June 1979 scrapings from reverse-osmosis membrane element
	(percent by dry weight)		
Organic carbon	2.32	6.11	3.53
Inorganic carbon	4.06	3.68	0.02

Table C-2.--Extractable organic constituents of canal and reverse-osmosis membrane sediments

Sediment parameter	May 1979 canal sample	June 1979 canal sample	June 1979 scrapings from reverse-osmosis membrane element
	(percent of organic carbon)		
Fulvic acid	21	18	49
Humic acid	6	2	4
Amino acids	--	21	6
Carbohydrates	--	5	2

The portion of the organic carbon in soil which is not soluble in basic solution is called the humin fraction. Part of this fraction is soluble in NaOH, after the soil has been treated with strong acids. Repeated treatment generally results in increased solubilization of humin in NaOH. Most of the humin that is released by acid hydrolysis is not soluble in acid solution; however, in the case of the canal sediment, a considerable amount of the organic material released by acid hydrolysis was soluble in acid solution. This finding indicates that the majority of the organic material dissolved by the HCl cannot be classified as humin.

Efforts to measure concentrations of carbohydrates and proteins by direct analysis in the sediment phase were unsuccessful; specific carbohydrates and amino acids were identified after acid hydrolysis to obtain definitive results.

The sample for carbohydrate analysis was hydrolyzed in 2 N HCl and then analyzed by cellulose thin-layer chromatography (Supplemental Information). Results of this analysis showed the presence of mannose, glucose, galactose, arabinose, and rhamnose. Amino acids were analyzed on an automatic amino-acid analyzer after hydrolysis in 6 N HCl; results of this analysis are listed in table C-3.

Based on the results of this reconnaissance sample it was decided to analyze future samples for humic and fulvic acids, carbohydrates, and amino acids. In addition, elemental analyses for carbon, hydrogen, oxygen, and nitrogen would be done during various stages of the processing and extraction of the samples.

Sampling During June 1979

The most striking characteristic of this canal-suspended sediment was the high content of diatomaceous frustules exhibited during microscopic examination. At least 50 percent of the sediment by volume was diatomaceous remains; the remainder was aluminosilicate clay. Sediment scrapings from the RO membrane surface contained comparatively few diatoms.

These two samples were examined by Dr. J. Platt Bradbury of the Paleontology and Statigraphy Branch of the Geological Survey. His results are given in tables C-4 and C-5. Dr. Bradbury made the following comment in his report concerning these species, "The species in both samples are dominantly benthic diatoms that live attached to convenient substrates. I suspect that a massive growth of diatoms is present on the sides and bottom of the canal, and that during unfavorable periods for growth, large numbers of them become detached and are carried down the canal by water currents. The diatom flora reflect the high pH, alkalinity and dissolved solids content of the water." Diatoms were also observed on the silver membrane filters that were used to filter the RO reject brine and RO feedwater. To facilitate identification of the diatom species, the suspended sediment samples were digested in nitric acid (Supplemental Information).

Table C-3.--Amino acid composition of the May 1979 canal suspended sediment after NaOH extraction

Amino acid	Nanomoles per milligram of extracted sediment
Glutamic acid	31.0
Alanine	49.6
Leucine	24.2
Aspartic acid	29.6
Glycine	55.6
Threonine	23.0
Serine	30.8
Phenylalanine	11.8
Proline	20.8
Lysine	14.8
Isoleucine	9.0
Arginine	13.2
Valine	13.6
Histidine	4.6
Tyrosine	1.0
Glutamine	1.6
Galactosamine	36.4

Table C-4.--Diatom species found in canal sediment sample (June, 1979)[1/]

- *Biddulphia laevis*[*]
- *Cyclotella meneghiniana*[*]
- *Nitzschia frustulum*[*]
- *Gyrosigma nodiferum*[*]
- *Fragilaria sp.*
- *Navicula tripunctata var. schizonemoides*[*]
- *Terpsinoe musica*
- *Diploneis sp.*
- *Surirella ovalis*
- *Achnanthes hauckiana var. rostrata*[*]
- *Amphora veneta*[*]
- *Amphora coffaeiformis*
- *Nitzschia denticula*
- *Gomphonema parvulum*
- *Nitzschia palea*
- *Navicula cryptocephala*
- *Amphora angusta*[*]
- *Amphora macilenta*
- *Nitzschia obtusa*
- *Achnanthes lanceolata var. dubia*
- *Gomphonema affine*
- *Nitzschia intermedia*
- *Synedra ulva*

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[*] Most abundant species.

[1/] Identified by J. P. Bradbury of the U.S. Geological Survey.

Table C-5.--Principal diatom species found in the scrapings from the reverse-osmosis membrane (June, 1979)[1]

Navicula tripunctata var. schizonemoides
Amphora angusta

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[1] Identified by J. P. Bradbury, U.S. Geological Survey.

Data in tables C-1 and C-2 show that the June canal sample had almost three times as much organic carbon as the May sample, but the concentration of fulvic acid in the two samples was similar (21 percent in May and 18 percent in June). Humic acid concentration in both is low, but substantially higher in the May sample than in the June samples; however, in both samples, the fulvic acid concentration is at least three times higher than humic acid concentration, which is the opposite of the usual alkaline extract of a soil. On the other hand, in aquatic humic materials, the fulvic acid concentration is normally several times higher than humic acid concentration. This close similarity of sediment humic substances to aquatic humic substances strongly suggests that sediment humic substances are derived from aquatic humic material and do not represent humic material associated with soil particles that were blown into the canal. The mechanism for incorporation of the dissolved humic material into the sediment could be through adsorption of the humic material on clay mineral surfaces; proteins that are abundant in these sediments can bind humic materials to clay surfaces.

Humic acids isolated from the canal sediment and from the membrane gave a fractionation pattern similar to soil humic acids when fractionated on Sephadex G-50 (Supplemental Information). Fractionation obtained by this procedure is dependent both on adsorption and size exclusion (Wershaw and Pinckney, 1973).

Infrared spectra of the humic and fulvic acids obtained from the sediments are shown in figures C-1, C-2, and C-3. They are similar to those of other soil and aquatic humic materials with only a few broad peaks in the spectra. The most prominent peaks are those between 2,960 to 2,840 cm^{-1} (CH_3 and CH_2 stretching modes of aliphatic compounds); 1,730 to 1,600 cm^{-1} (carbonyl oxygen stretching modes of carboxylic acids and carboxylates); 1,600 to 1,540 cm^{-1} (carboxylate); 1,150 to 1,000 cm^{-1} (Si-O and Al-O stretching modes; and some C-O stretching modes).

Fractions 1 and 2 of the canal and RO membrane sediment humic acids have particularly strong bands in the region between 1,000 to 1,100 cm^{-1}. These bands are probably indicative of the presence of clay minerals complexed to the humic acids (Wershaw and Pinckney, 1980). Clay-humic complexes were expected in these sediments.

The ratio of humic acid to fulvic acid suggests that the humic material in the sediment was derived from dissolved humic materials and from degradation of the organic compounds that are produced in the canal or in the treatment system by aquatic organisms. If a single identifiable group of diatoms is contributing the bulk of the organic compounds in the canal, then the relative concentrations of amino acids and carbohydrates present in the sediments of the canal should closely approximate those of the diatoms in the canal.

The carbohydrates isolated after hydrolysis with 2 N HCl were analyzed as alditol acetates by gas liquid chromatography (Supplemental Information). Total carbohydrate in the hydrolyzate was determined by the phenol-sulfuric acid method, using L-rhamnose as a standard (Dubois and others, 1956). The contribution of carbohydrate to the total organic carbon was determined by multiplying the total carbohydrate concentrations by 0.4 (table C-1). Relative concentrations of the various carbohydrates are given in table C-6. Darley (1977) has compiled analyses from several different sources on concentrations of simple sugars in diatoms (table C-7). Comparing analyses of the two sediment hydrolyzates and the averages in table C-7, two conclusions can be reached: (1) canal sediment and the membrane sediment have dramatically different carbohydrate concentrations; and (2) neither of the sediments is similar to average values published by Darley. This is not surprising, because there were wide quantitative differences between the various species included in the averaging, and copious strands of algae were observed in the canal.

Samples of the June canal sediment and the RO membrane sediment were analyzed for amino acids prior to extraction with NaOH; results of these analyses are given in table C-8. Darley (1977) found that the amino acid suite from diatoms is generally characterized by a greater abundance of serine than other amino acids, glycine concentration higher than glutamic acid and aspartic acid, arginine higher than aspartic acid, and isoleucine higher than lysine. As with the saccharides, it appears that most of the organic material in the canal and on the membrane is not derived from diatoms.

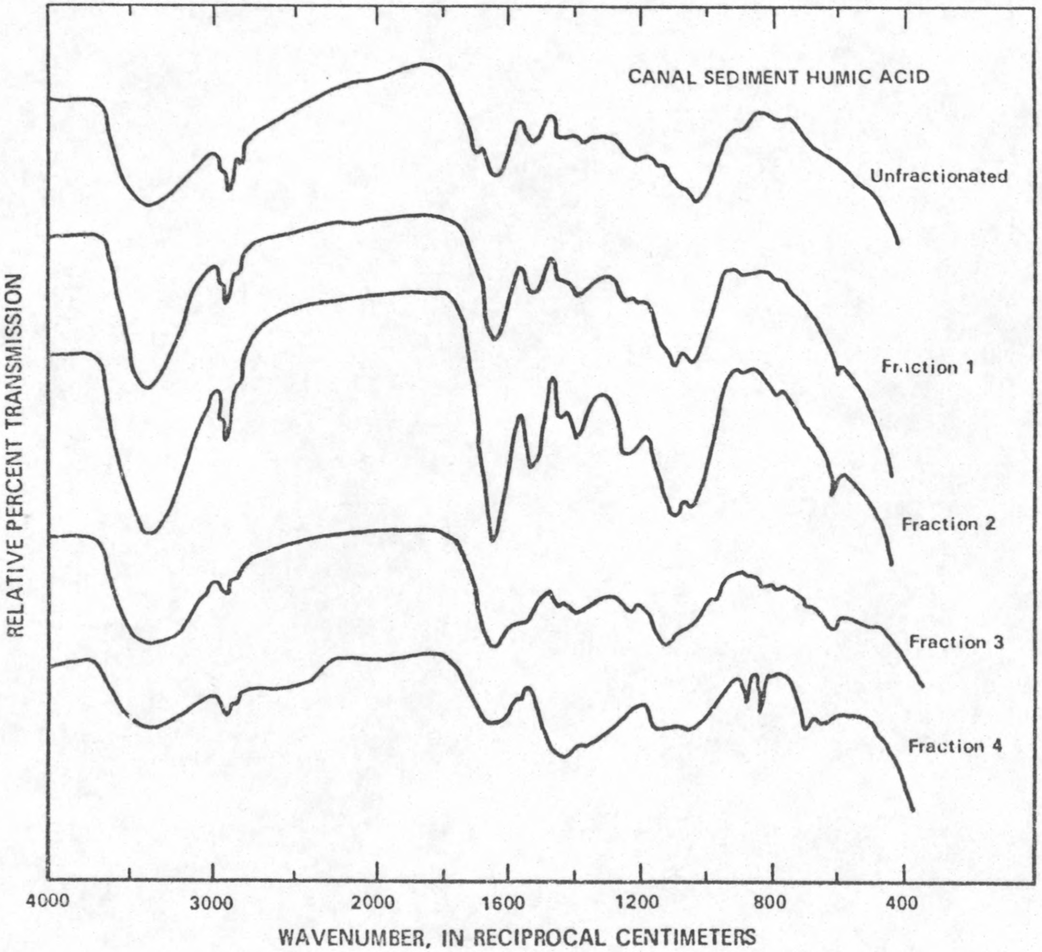


Figure C-1.--Infrared spectra of canal sediment humic acid fractions.

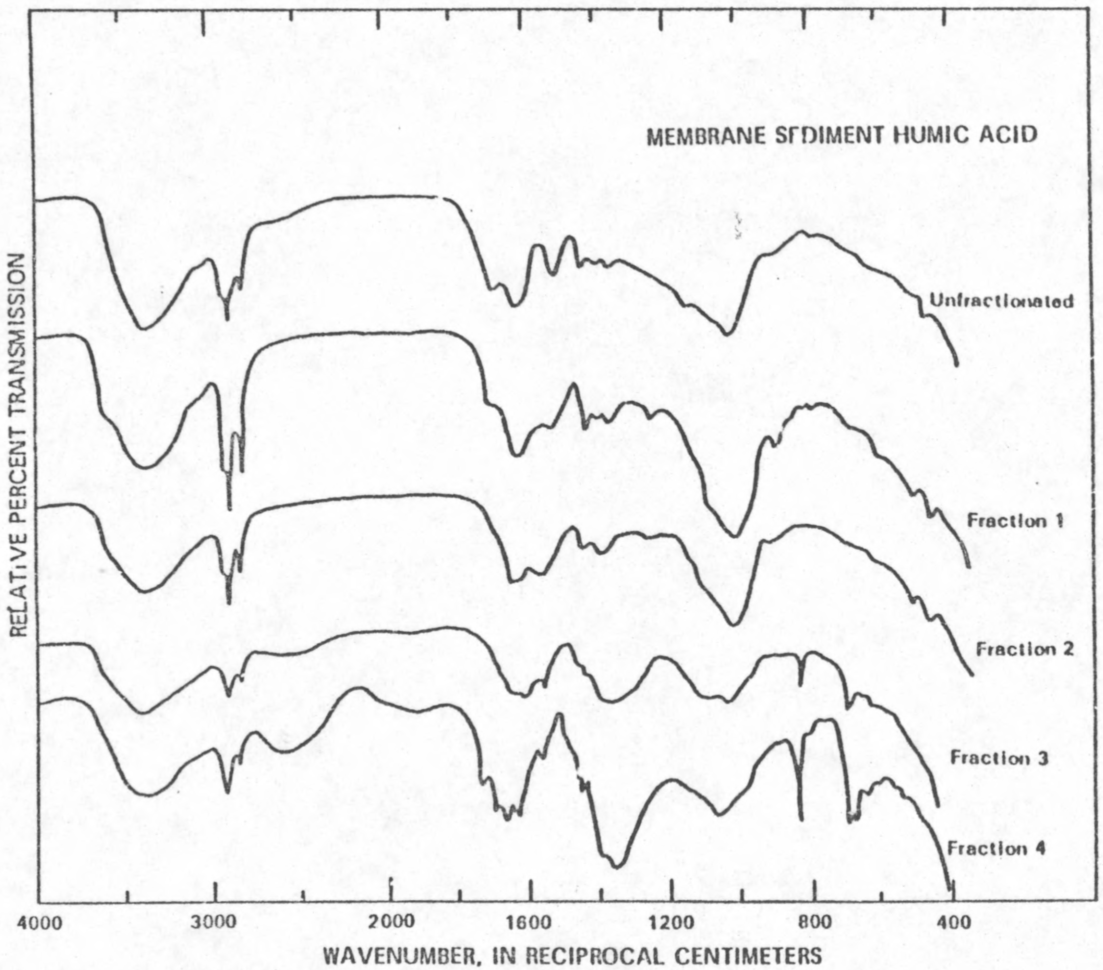


Figure C-2.--Infrared spectra of reverse-osmosis membrane sediment humic acid fractions.

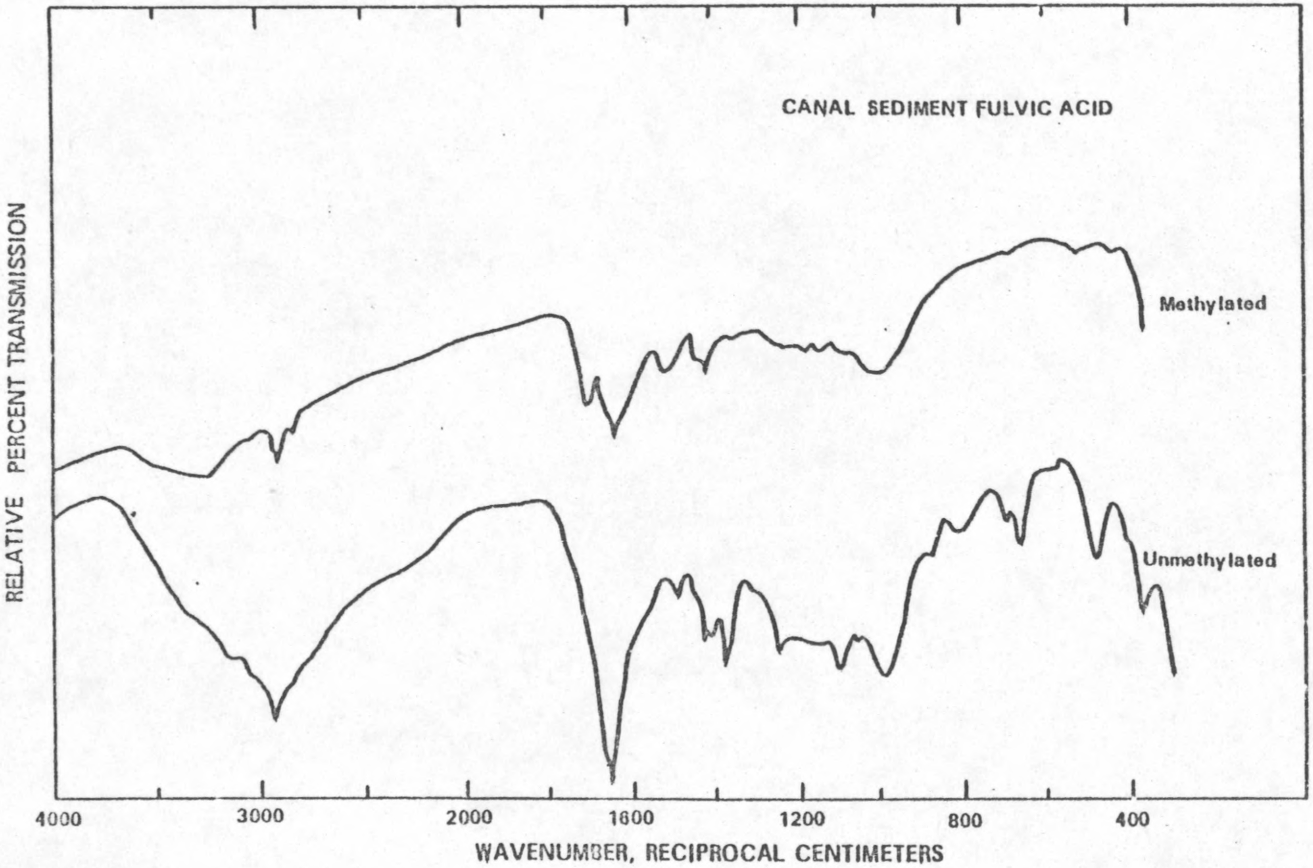


Figure C-3.--Infrared spectra of canal sediment fulvic acid fractions.

Table C-6.--Carbohydrate composition of canal and reverse-osmosis membrane sediments during June 1979

Carbohydrate	Canal sediment	Membrane sediment
	(percent of total carbohydrate)	
Glucose	27.3	53.6
Galactose	19.5	6.1
Mannose	16.5	27.7
Xylose	13.7	5.0
Arabinose	3.8	2.7
Ribose	3.3	1.2
Fucose	5.3	1.2
Rhamnose	9.8	2.5

Table C-7.--Average simple carbohydrate composition of six species of diatoms[1/]

Carbohydrate	Whole cell average	Cell contents	Cell wall
	(percent of total carbohydrate)		
Glucose	53	63	24
Galactose	12	10	11
Mannose	10	13	30
Xylose	2	4	16
Arabinose	--	trace	trace
Ribose	4	2	1
Fucose	4	4	15
Rhamnose	14	3	3

[1/] Data from Darley (1977).

Table C-8.--Amino acid composition of canal and reverse-osmosis membrane sediments during June 1979

Amino acid	Canal		Membrane	
	(nanomoles per milligram)	(weight percent of total amino acids)	(nanomoles per milligram)	(weight percent of total amino acids)
Glutamic acid	25.2	11.8	4.5	13.7
Alanine	31.4	9.1	6.0	11.1
Leucine	21.2	8.9	5.3	20.3
Aspartic acid	22.0	9.3	3.2	8.8
Glycine	31.9	7.7	3.7	5.7
Threonine	17.1	6.5	2.1	5.2
Serine	19.3	6.5	2.2	4.8
Phenylalanine	10.2	5.4	2.1	7.3
Proline	13.7	5.0	2.1	4.9
Lycine	13.8	6.5	0.5	1.6
Isoleucine	11.6	4.9	2.8	7.7
Arginine	9.5	5.3	0.3	1.2
Valine	17.1	6.4	---	---
Histidine	3.2	1.6	---	---
α-amino adipic acid	---	---	1.7	5.7
Tyrosine	6.3	3.6	---	---
Ornithine	1.0	0.4	0.3	0.9
Glutamine	0.9	0.4	0.1	0.4
γ-amino butyric acid	---	---	0.3	0.7
Hydroxyproline	1.5	0.6	---	---
Methionine	0.2	0.1	---	---

Relative concentrations of various amino acids are very similar in the two canal samples; however, there are some marked differences between the canal samples and the membrane sample, especially in the case of leucine, arginine, α-amino adipic acid, and tyrosine.

Although results of the amino acid and carbohydrate analyses cannot be interpreted, they provide baseline data for comparison with future data; in turn, it may be possible to interpret departures from these results, especially during periods of unusual diatom or bacterial activity.

SECTION D - HALOGENATION OF ORGANIC SUBSTANCES IN THE WATER AT THE YUMA DESALTING TEST FACILITY

Chlorinated organic compounds were assumed to be present in the treated water of the Yuma Desalting Test Facility during our first visit, because the canal water was chlorinated during pretreatment. Aquatic humic substances in the presence of free chlorine are postulated to be the major precursor of three groups of chlorinated organic compounds: (1) nonvolatile chlorinated high-molecular-weight aquatic humic substances; (2) chlorinated nonvolatile low-molecular-weight organic acids and ketones; and (3) volatile trihalomethanes (THMs). THMs are the only group for which quantitative chemical analyses are routinely performed, because these volatile compounds are easily determined by gas-chromatographic and mass-spectrophotometric techniques. Determination of nonvolatile chlorinated organic compounds is still a research undertaking; no routine analytical procedures have been widely accepted.

The procedures developed and used for the concentration of aquatic humic substances on XAD-8 resin are effective for high-molecular-weight chlorinated compounds. In most fresh waters, it has been observed that chlorination of drinking and waste waters produces chloroform as the principal THM, along with various chlorinated acids. Small amounts of chlorine in the fulvic acid isolates from the treated waters of the Yuma Desalting Test Facility were expected; large amounts of bromine were found in the isolates and only small amounts of chlorine (Section B).

Recent research (Minear, 1980) has shown that brominated products of chlorination can be significant when the bromide concentration in water is 0.3 mg/L or greater. Additional samples of water were taken from various points at the test facility to establish the bromide concentration. Three possible sources of bromide at the test facility are: (1) natural bromide background-level in the canal water; (2) bromide as a contaminant in the chlorine used for chlorination; and (3) bromide as a contaminant in the lime treatment process for sediment removal from the canal water. Bromide or bromine contamination of the chlorine gas was determined to be only a trace because of the high analyzed purity of the gas. Bromide addition during the lime treatment process is still being investigated, but calculations based on the amount of lime added and water processed indicate that possible bromide additions from this source could contribute no more than a few hundredths mg/L. A natural background concentration of approximately 0.5 mg/L in the pumped ground water is believed to be the major source of bromide at concentrations adequate to produce bromination rather than chlorination of fulvic acids. The bromide concentration is stated as approximately 0.5 mg/L, because of analytical difficulties in accurate bromide measurement in the presence of high chloride concentrations in water (chloride concentrations in the canal exceed 1,000 mg/L). The presence of bromide is common in marine sediments and geothermal areas similar to those in the Wellton-Mohawk Valley.

If bromination rather than chlorination were the dominant halogenation reaction, bromoform rather than chloroform should be the principal volatile THM. This hypothesis was tested and confirmed to be positive; test data will be presented later in this section.

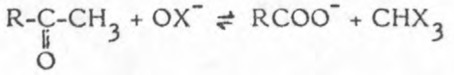
The Chlorination Problem

In previous sections of this report, it has been shown that the concentration of fulvic acid in the canal is high enough for it to be a major precursor of chlorinated high-molecular-weight fulvic acid as isolated from the RO feedwater and the RO reject brine. No attempt was made in this study to isolate low-molecular-weight nonvolatile chlorinated acids. The following portion of this section will be devoted to a more detailed discussion of the formation of bromine and the bromination process with special emphasis on THM formation.

THMs have a chemical formula of CHX_3, where X may be any possible combination of Cl, Br, or I. THMs have been surveyed in drinking waters around the world (Trussell and others, 1979) and have been found to be a world-wide problem, affecting drinking waters from a variety of sources and locations. The widespread use of chlorine to disinfect drinking waters and municipal wastes makes this a water problem of large dimensions and, perhaps, serious consequences. Consequently, the Environmental Protection Agency has set limits on the total concentration of THMs in water not to exceed 100 μg/L.

The discovery that halogenated methanes were generated in water chlorination (Rook, 1974) has been well-documented, although mechanisms of the reaction are not clearly understood. Aquatic humic substances are known to be one important precursor of THMs; however, reactions that produce THMs from aquatic humic substances are still an important subject of research. Two important reactions which produce THMs are: (1) the haloform reaction, and (2) the oxidative chlorination of phenolic constituents in aquatic humic substances.

The haloform reaction is the reaction of methyl ketones to form THMs:



$$R\text{-}\underset{\underset{O}{\|}}{C}\text{-}CH_3 + OX^- \rightleftharpoons RCOO^- + CHX_3$$

where the methyl ketone reacts with OX^- to form an acid salt and a THM. Methyl ketones are present in the humic material, are also present in specific low-molecular-weight acids in water, and are likely to react with excess OX^- present in the water at the test facility.

Oxidative chlorination of phenolic constituents in humic substances has been shown to be important (Christman and others, 1980). Chlorine attacks the phenolic ring and yields many products, including dicarboxylic acids as well as THMs. Therefore, it is apparent that both mechanisms may be occurring in the water at the test facility.

Chlorine has been assumed to be the significant oxidant in the chlorination of organic matter in water and in the production of THMs. However, it has been shown that if Br^- is present at concentrations as low as 0.1 mg/L, the following reaction occurs:

$$HOCl + Br^- = HOBr + Cl^-.$$

The reaction of Br^- with HOCl is much faster than the reaction of HOCl with organic matter; thus, the principal species is HOBr which reacts with the organic matter. The reaction between organic matter and HOBr is thought to be primarily one of halogenation rather than oxidation, with HOBr being the most important halogenating species. Chlorine and bromine are incorporated and remain as part of the fulvic acid by similar mechanisms, and by addition to double bonds.

Sampling for THMs at the Yuma Desalting Test Facility

After large amounts of bromine were found in the fulvic-acid isolates of the treatment facility, samples were taken during April 1980 for THM analyses at various points in the water-treatment process. The test results are shown in table D-1.

Table D-1.--Trihalomethane concentrations at various points in the water-treatment process[1]

Sample	$CHCl_3$	$CHCl_2Br$	$CHClBr_2$	$CHBr_3$
	(micrograms per liter)			
Canal water	0.3	--	--	--
Train influent	1.1	3.6	12	12
Reverse-osmosis feedwater	3.6	14	40	40
Reverse-osmosis reject brine	3.1	12	33	33
Reverse-osmosis product water	3.5	14	42	40

[1] Data from James Montgomery Labs, Pasadena, California.

The major THMs are brominated compounds, dibromochloromethane, and bromoform. This indicates that the formation of HOBr is occurring in water treatment, and that oxidation and bromination is occurring to both humic substances and low-molecular-weight acids present in the water. Fulvic acids isolated from the water appear to be important precursors, because bromine accounted for 3.1 to 3.9 percent by weight of the hydrophobic acids. In the characterization of humic substances earlier, it was shown that the major changes occurring to the high-molecular-weight humic substances were due to bromination during water treatment. Therefore, substantial data support the conclusion that humic substances are a major precursor for THMs in the water at the test facility.

General Discussion

The importance of these findings are: (1) total concentration of THMs in the water exceeds the Environmental Protection Agency standard of 100 µg/L (micrograms per liter); (2) bromination of the humic material in the water is occurring, and this water, with accompanying humic material, will be disposed of as brine, which will eventually be disposed of in the Gulf of California; (3) low-molecular-weight brominated acids, which we have not sampled, may have significant environmental importance; these acids will most likely be present in both the product and brine waters; and (4) bromination does not seem to be affecting the membrane itself, nor does bromine appear to be concentrating on the membrane.

The concentration of THMs may be lowered to meet EPA standards by treating the product-water in a purge tower, and by dilution with Colorado River water. Possible toxicity of the brominated humic material is not known, and should be investigated by the Ames test on isolates from the RO feedwater and the RO reject brine. The question of possible bromination of hydrophilic acids might be worth pursuing with further sampling and toxicity studies.

Finally, the membrane itself is not apparently being damaged by the bromination process; in fact, bromine forms a more powerful bactericide than chlorine, and probably does a better job preventing slime, algal, and bacterial growth on the membrane.

SECTION E - MINERALOGICAL ANALYSES

Gross Mineralogy

Two suspended sediments from the canal (May 1979 and June 1979) and sediment from the dissected RO membrane element (June 28, 1979) were examined by X-ray diffraction by J. Hartwell (Bureau of Reclamation) to determine gross mineralogical composition. Air-dried unfractionated samples were ground and resulting powders were examined; minerals in each sample are listed in table E-1.

The two canal samples are similar mineralogically, except the halite concentration is less in the May sample. The May sample was analyzed after extraction with 0.1 N NaOH for isolation of humic substances. An unextracted sample portion was not available because of the small amount of total sample. Major minerals in the canal were calcium carbonate, quartz, and halite. Halite and clays were dominant in the membrane sediment. The presence of halite in these samples is somewhat puzzling; it probably resulted from evaporation of the water retained with the suspended sediment samples after drying, and does not represent minerals present in the sediments when they were suspended in the water.

Detailed Mineralogical Analyses

Sample Preparation. Two samples were intensively analyzed for mineralogical composition. The suspended canal sediment that accumulated on the silver membrane filters during the June 20 - 25, 1979 filtration was washed and scraped from the filters with a rubber policeman. The second sample was sediment that was scraped from the dissected RO membrane element of June 28, 1979. The sediment scrapings as collected were suspended in approximately 1.5 L of water. Several pieces of pipe turnings and lint were included in the sample. These artifacts were removed from the sample and discarded by passing the suspended sample through a 60-um sieve. A known volume of each sample was freeze-dried to determine total dry weight for each sample.

Representative portions of each sample were treated with 30 percent hydrogen peroxide for removal of organic matter (Jackson, 1956, page 35). Approximately 90 percent of the organic matter can be removed by this wet-oxidation procedure. The surface of most mineral grains contain amorphous coatings of both organic matter and sesquioxides. These coatings are removed to prevent scattering of the X-ray beam during X-ray diffraction analysis. After removal of organic matter, the suspended sediments were treated with sodium dithionite for removal of Fe (iron) and Mn (manganese) sesquioxides (Jackson, 1956, pages 47-49). The amount of Fe and Mn in the extract was determined by atomic absorption.

57

Table E-1.--X-ray powder diffraction analyses of sediments[1]

Canal Sediment (May 14, 1979)
(After extraction with 0.1 N sodium hydroxide)

Major Minerals	Minor Minerals	
Calcium carbonate	Micas	Anhydrite (?)
Quartz	Clays	Amphiboles (2)
Feldspar	Zeolites (?)	Halite
Gypsum		

Canal Sediment (June 20-25, 1979)

Calcium carbonate	Clays	Gypsum
Quartz	Micas	Zeolites (?)
Halite	Feldspars	Anhydrites
		Amphiboles

Membrane Sediment (Dissected June 28, 1979)

Halite	Quartz	Zeolites (?)
Clays	Feldspars	Gypsum (?)
	Micas	Amphiboles (?)
		Anhydrite (?)

---

[1] Performed by J. Hartwell, U.S. Bureau of Reclamation.

The canal sample was then wet-sieved through a 60-μm (280 mesh) sieve. The sand-size particles greater than 60 μm were washed from the screen into a small beaker and dried at 60°C. The 2-μm clay-size fraction was separated from the silt-size fraction by repeated sedimentation by Stokes Law. The clay-size fraction of each sample was divided into two equal portions. One portion was saturated with K^+ as the only counter or exchangeable ion (monoionic saturation) by repeated washing with 1 N KCl salt solution; the other portion was Mg-saturated by repeated treatment with 1 N $MgCl_2$ salt solution. The residual interstitial salt solution was removed from the respective clay samples by repeated washing in distilled water, and centrifuged until the wash solution gave a negative test for chloride with silver nitrate solution.

The clay samples were suspended in 5 mL of distilled water. A 1 mL portion of each sample was applied evenly to a pre-weighed glass slide. After air drying, the slide was reweighed to obtain the weight of clay in each of the two fractions of each sample.

X-ray diffraction analysis was conducted using Cu to K a radiation. Diffraction of the Mg-saturated slide was obtained at room temperature and after ethylene glycol solvation. The K-saturated series were run at room temperature, after heating to 350°C, and after heating to 550°C. Monoionic saturation and heat treatments are essential to exacting mineralogical analyses, especially for mixed and randomly interlayered species. (For a more complete discussion of the procedure refer to Jackson, 1956, pages 179-188 and pages 210-213).

Size-Fractionation Analyses. Size-fractionation or particle-size distribution analyses for the canal and membrane sediment samples are presented in table E-2. Silt is the major size fraction of the canal suspended sediment; clay is the dominant fraction on the RO membrane. During pretreatment, suspended sediment in the canal water is very effectively removed to below the μg/L concentration. Only a small portion of the finely dispersed fine silt and clay particles that pass through the treatment system is either filtered-out onto the membrane surface or passes through in the reject-brine stream.

Extractable Iron and Manganese. The percent Fe and Mn as coatings on the whole canal sample of sand, silt, and clay was determined to be 3.1 percent for Fe, and 0.8 percent per Mn. Before Fe and Mn removal, the canal sample was a much darker red than the membrane sample. The membrane sample was determined to be 1.2 percent Fe and 0.25 percent Mn. Fe and Mn, determined by this extraction procedure, are thought to be amorphous oxides on the surface of sediment particles.

Table E-2.--Particle-size analyses of suspended sediment from the canal (June 20-25, 1979) and reverse-osmosis membrane element (dissected June 28, 1979)

Size fraction	Canal	Membrane
	(percent by dry weight)	
Sand (2 millimeter - 60 micrometer)	32	0
Silt (60 micrometer - 2 micrometer)	54	20
Clay (<2 micrometer)	14	80

Quantitative Mineralogy. The most precise quantitative mineralogy requires considerable optical mineralogy, dissolution chemistry, differential thermal analyses, thermal gravimetric analyses, and infrared analyses in addition to X-ray diffraction analyses. Such extensive analyses were not required for this study, but gross mineralogy was insufficient. The mineralogy in the report may be considered to be detailed and semi-quantitative in nature. For these reasons, the relative abundance of minerals in the silt and clay fractions will be discussed in the terms listed in table E-3.

X-Ray Analyses of Silt and Clay-Size Suspended Sediments. Size separation at 2 µm is useful in partitioning predominately secondary clay minerals below 2 µm and predominately primary minerals greater than 2 µm. This partitioning was accomplished in both the canal and membrane samples, because clay minerals are in trace amounts in the silt fractions; K-feldspars and plagioclase feldspars are only minor components of clay fractions.

Table E-3.--Designation of relative abundance of minerals in the silt and clay-size fractions

Trace	less than 5 percent
Small	5 - 20 percent
Moderate	20 - 40 percent
Abundant	40 - 60 percent
Dominant	greater than 60 percent

Silt fractions of the canal and membrane samples shown in figure E-1 are different in kind and amount of minerals. The canal silt has an abundance of carbonates; whereas, the membrane has none. The carbonate is predominately calcite ($CaCO_3$) as indicated by the strong 3.03 A^{o} peak. Small amounts of dolomite are also indicated by the 2.88 A^{o} peak. This abundance of carbonate is supported by chemical data for the whole canal sample, which contained 20 percent carbonate by weight. Even though sample pretreatment was conducive to carbonate dissolution, it remains abundant in the silt fraction of the canal.

Several explanations for the absence of carbonate in the membrane silt fraction are possible. These small particles of carbonate which pass through the mixed filter could slowly dissolve during storage in the clearwell. The most plausible explanation is that any carbonate particles in the RO feedwater would be held onto the membrane and then dissolved by the pH 5.5 acid water. A third possible explanation is that carbonate was dissolved in pretreatment of the sample for mineralogical analyses. This third explanation is unlikely, because the carbonate in the canal silt persisted so well during sample treatment.

A second major difference in the canal and membrane silt-size franctions is that mica and feldspar minerals are in much larger amounts in the membrane sample. Feldspars are abundant in the membrane sample but are present in only small amounts in the canal sample. Both K-feldspars and Ca-Na feldspars (plagioclase feldspars) are indicated by the peaks between 3.15 and 3.28 A^{o} and the peak at 4.0 A^{o}. The increased amount of mica is probably because it floats readily and is preferentially swept into the RO feedwater from the clearwell.

Quartz is present in moderate amounts in both silt samples. Aluminosilicate clay minerals are also present in small amounts in both samples.

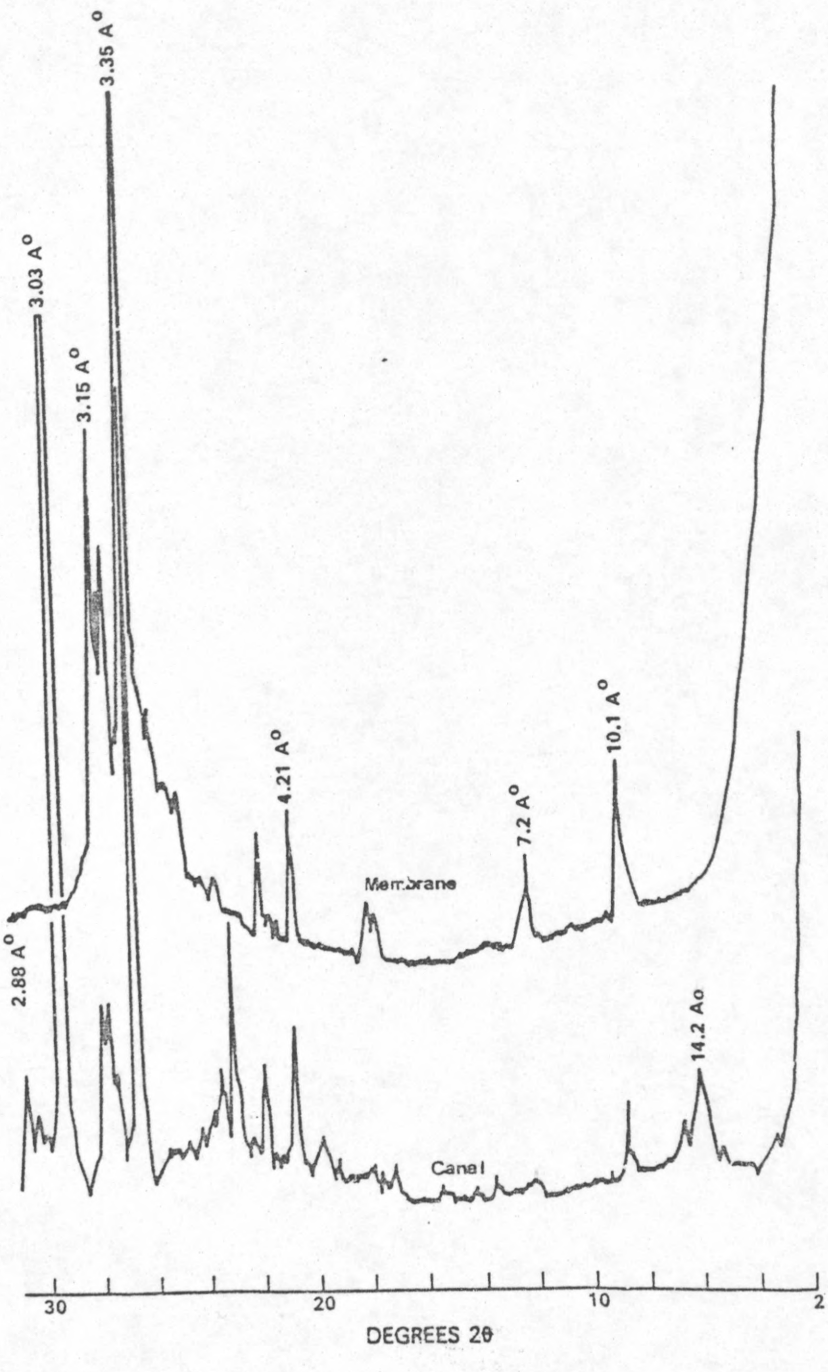


Figure E-1.--X-ray diffraction patterns of canal and membrane silt.

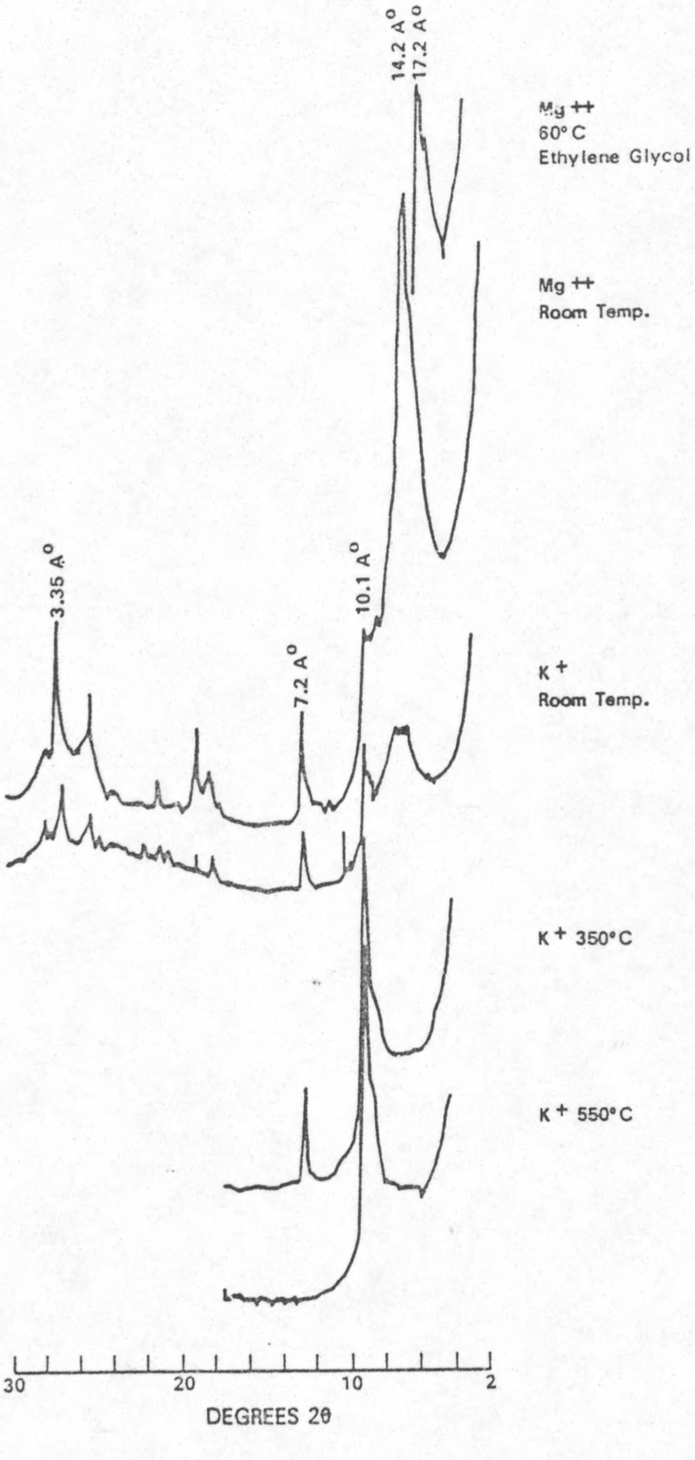


Figure E-2--X-ray diffraction patterns of canal clays.

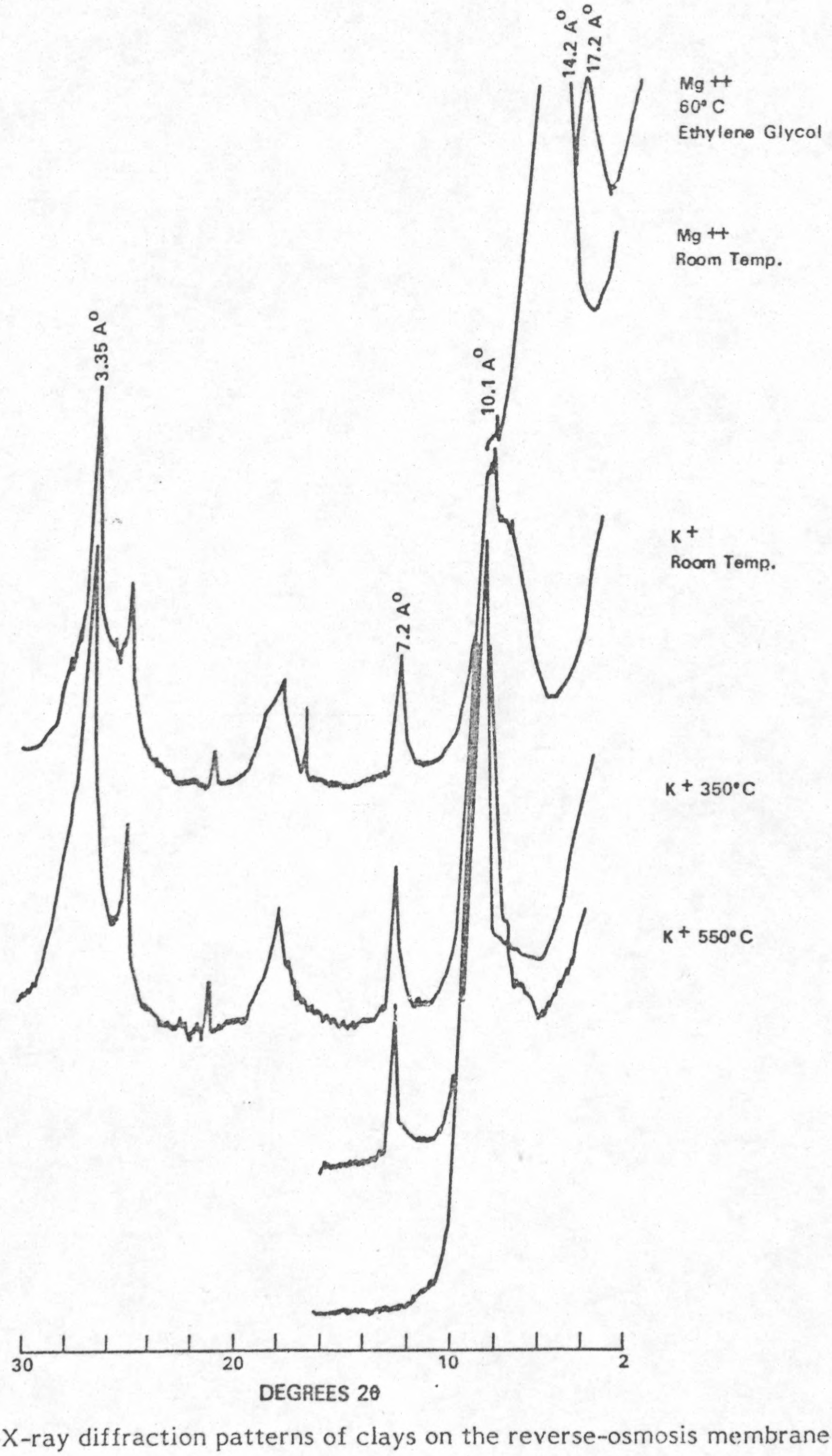


Figure E-3.--X-ray diffraction patterns of clays on the reverse-osmosis membrane element.

The most striking aspect of the mineralogy of both clay-size fractions is the dominance of smectite (montmorillonite-like) minerals. This closely associated group of minerals is composed of montmorillonite, regular or random-mixed layered minerals containing montmorillonite, and some swelling intergrades or montmorillonite containing hydroxy-interlayers. These smectites have a negative charge density in the range of 0.8 to 1.2 meq/g (milliequivalents per gram). The smectite in the canal sample is somewhat different from that in the membrane, even though they both give 14.2 A° spacings with Mg-saturation at room temperature, and readily expand to 17.2 A° upon ethylene glycol solvation. Smectite on the membrane more closely resembles montmorillonite, because a large portion of it collapses to 10 A° with K-saturation at room temperature. Smectite from the canal is probably randomly interstratified or randomly mixed-layered with a mica or vermiculite weathering product other than montmorillonite. This is shown by the dramatically decreased intensity of the 12 to 14 A° region with K-saturation at room temperature and the lack of collapse to 10 A°. Random interstratification is also shown by the decreased intensity of the 14.2 A° peak with Mg-saturation at room temperature in the canal sample compared to the membrane sample, even though the summation of other minerals in the sample is relatively the same.

Another small difference between the canal clay and the membrane clay is that the canal sample contains a small amount of amorphous material; whereas, the membrane sample has no evidence of any amorphous material by X-ray analysis. The amorphous material is manifested in the X-ray diffractogram by upward curvature of the baseline between 12 and 30 degrees 2 θ.

The other minerals in the clay fractions are common to both samples with only minor variations in the small amounts of each. These minerals include kaolinite at 7.2 A°, illite (clay-size mica) at 10.1 A°, quartz at 3.35 A°, and a trace amount of feldspar.

Data indicate that the source of the sediment on the membrane is the canal. The water-treatment process not only removes practically all of the sediment from the water, but also fractionates the clay-size fraction. The randomly mixed-layered smectite and the amorphous fractions are coarser-grained than the more montmorillonite-likely smectite. The very fine-grained smectite, with particle sizes < 0.02 µm, would be less likely to be flocculated by the treatment process and would be more likely to pass through the dual media or mixed media filtration, and thus be filtered out onto the RO membrane.

The smectite-clay mineral is believed to be a significant aspect of RO membrane fouling because of its platey nture, its large surface area, and its presence in significant amounts on the dissected membrane. The silt fraction is believed to be relatively unimportant because of the small amount found on the membrane, its relatively low surface area, and its relatively angular-grain configuration. A total of 6.2 g of sediment was scraped from the entire membrane; 80 percent was clay size; and 80 percent of the clay-size minerals (4 g) was smectite. Surface area for smectite clay is in the range of 150 to 200^2/g (square meters per gram). The total surface of the spiral RO membrane element was approximately 325 ft^2 (square feet). If a 50 percent recovery of sediment from the membrane is assumed, the smectite clay would be 15 to 20 layers in thickness over the entire membrane. Such a thickness of clay-filter cake should result in considerable decrease in water flux through the membrane.

SUMMARY AND CONCLUSIONS

Physical fouling by smectite-clay minerals may be an important factor in the decreased performance of cellulose-acetate RO membrane elements at the Yuma Desalting Test Facility. Smectite clay is prevalent in soils of the region and is blown into the canal by frequent gusts of wind. A small portion of the less than 0.2 µm smectite clay fraction, which is not removed by the water treatment system, is physically filtered out on the RO membrane. This extremely fine, particulate, smectite clay mineral has a large surface area of between 150 and 200 m^2/g. The buildup of a multilayer clay filter cake with time has the potential to limit the transport of water to the membrane surface.

The physical fouling by smectite clay is augmented by humic substances and microbial matter admixing to form a sticky gelatinous film on the RO membrane. Even after extensive washing and scraping, the membrane remains discolored. This indicates that some of the clay and organic material either is chemically attached to the RO membrane or that some of the material penetrates into the matrix of the membrane.

The possible fouling of RO membranes by aquatic humic substances was tested in several ways without definitive results. The sediment scrapings which caused limited fouling were moderately high in organic content, humic and fulvic acids, carbohydrates, and amino acids; yet, compared to the amounts found in either the reject-brine stream or passing through the membrane, the amount of the respective organic compounds accumulating on the membrane was low.

High molecular-weight aquatic humic substances were isolated and characterized from four points in the water treatment system. These humic substances were found to be generally similar to other aquatic humic substances, except that they were extensively brominated (2 to 3 percent by weight) during water treatment. Halogenation of the humic substances disrupted the conjugated double-bond chromophore system within the molecule and resulted in a less colored brominated humic material. Halogenation (principally bromination) produced relatively high concentrations of THMs (trihalomethanes), in the product water produced at the test facility. The halogenated and unhalogenated humic substances adhered to the membrane and could not be removed with extensive washing and scraping. The relative effect of this material on the decreased performance of the RO membrane remains unknown.

The relative effect of microbial fouling of the RO membrane is also nonquantified, but microbial fouling is believed to be slight, because of: (1) small amounts of microbial cells on the membrane; (2) lack of appreciable slime on the membrane; (3) and marked control of microbial growth by chlorination of the water during treatment. The extensive population of diatoms and algae in the conveyance canal were largely removed by the water treatment process.

Other related chemical phenomena that could be investigated and would possibly be related to chemical fouling of the RO membrane by clay and organic materials are: (1) charge exclusion by net negative clay surfaces; (2) effect of acidity at the clay surface; (3) hydrophobic sorptive capacity of cellulose acetate RO membranes for aquatic humic substances; (4) variation of the previous chemical effects with the variability of cellulose acetylation; (5) sizing effects of natural low-molecular-weight organic solutes; (6) effects of chlorinated or brominated organic solutes versus unhalogenated solutes; and (7) possible reduction in fouling by substituting ozone for chlorine to control microbial growth.

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70

SUPPLEMENTAL INFORMATION

Table SI-1.--Organic carbon fractionation of train grit-basin influent water and clearwell effluent water at the Yuma Desalting Test Facility from June 1977 through December 1977[1]

[Data from the Yuma Desalting Test Facility compiled by the U.S. Bureau of Reclamation]

Sample date (1977)	Dissolved organic carbon	Hydrophobic fraction total	Hydrophobic fraction bases	Hydrophobic fraction acids	Hydrophobic fraction neutrals	Hydrophilic fraction total	Hydrophilic fraction bases	Hydrophilic fraction acids	Hydrophilic fraction neutrals
	(milligrams carbon per liter)								
7-25 A [2]	3.6	< 0.1	0.1	0.1	< 0.1	3.7	0.3	2.2	1.1
7-25 B [3]	3.5	< 0.1	< 0.1	< 0.1	< 0.1	3.6	0.5	1.0	2.1
8- 1 A	3.2	0.6	0.1	0.6	< 0.1	2.6	< 0.1	1.2	1.4
8- 1 B	3.3	< 0.1	0.1	0.1	< 0.1	3.4	0.1	1.3	2.0
8- 8 A	4.0	2.3	< 0.1	0.5	1.8	1.7	0.5	0.6	0.6
8- 8 B	2.6	0.8	0.2	0.4	0.2	1.8	0.6	0.8	0.4
8-16 A	7.6	2.8	0.4	1.6	0.8	4.8	< 0.2	3.6	1.0
8-22 B	3.0	1.2	< 0.2	0.7	0.5	1.8	< 0.2	1.6	0.2
8-29 A	2.8	1.4	< 0.2	1.4	< 0.2	1.4	< 0.2	1.0	0.4
8-29 B	2.9	1.5	< 0.2	0.6	0.9	1.4	< 0.2	< 0.2	1.4
9- 6 A	180	130	< 0.2	0.6	129.3	50	< 0.2	51.4	0.6
9- 6 B	3.4	1.8	< 0.2	1.0	0.8	1.6	< 0.2	1.4	0.2
9-12 A	3.8	2.0	< 0.2	0.8	1.2	1.8	< 0.2	1.8	< 0.2
9-12 B	3.7	1.9	< 0.2	0.8	1.1	1.8	< 0.2	1.6	0.2
9-19 A	3.4	1.4	< 0.2	0.6	0.8	2.0	0.4	1.2	0.4
9-19 B	2.8	1.2	< 0.2	0.6	0.6	1.6	0.4	0.8	0.4
9-26 A	3.1	1.3	< 0.2	0.6	0.7	1.8	0.2	1.4	0.2
9-26 B	3.0	1.6	< 0.2	0.8	0.8	1.4	0.2	1.0	0.2
10-25 A	3.6	1.2	< 0.2	0.6	0.6	2.4	0.2	0.2	2.0
10-25 B	3.2	0.6	< 0.2	0.4	0.2	2.6	0.2	1.2	1.2
10-31 A	3.7	2.5	< 0.2	0.8	1.7	1.2	< 0.2	< 0.2	1.2
10-31 B	3.0	1.4	< 0.2	0.6	0.8	1.6	< 0.2	1.2	0.4
11- 7 A	3.3	0.7	< 0.2	0.4	0.3	2.6	0.2	0.6	1.8
11- 7 B	3.8	1.2	< 0.2	0.4	0.8	2.6	0.2	1.4	1.0
11-14 A	3.3	1.1	< 0.2	0.2	0.9	2.2	0.2	1.2	0.8
11-14 B	3.5	1.3	< 0.2	0.4	0.9	2.2	0.2	1.0	1.0
11-21 A	3.2	1.0	< 0.2	0.4	0.6	2.2	0.2	0.8	1.2
11-21 B	3.2	0.6	< 0.2	0.4	0.2	2.6	0.4	0.8	1.4
11-28 A	3.6	2.2	< 0.2	0.8	1.4	1.4	< 0.2	1.2	0.2
11-28 B	3.3	1.3	< 0.2	0.6	0.7	2.0	< 0.2	1.4	0.6
12- 5 A	3.5	0.9	< 0.2	0.4	0.5	2.6	0.2	1.8	0.6
12- 5 B	2.8	1.2	< 0.2	0.4	0.8	1.6	0.2	1.0	0.4
12-12 A	3.2	1.6	< 0.2	0.4	1.2	1.6	0.2	1.2	0.2
12-12 B	3.2	1.8	< 0.2	0.4	1.4	1.4	0.2	1.0	0.2

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[1] Analyses performed by Huffman Laboratories, Wheatridge, Colorado.

[2] A = Train I grit basin influent - no chlorination.

[3] Clearwell effluent, operator control center.

Table SI-2.--Comparisons of nonfilterable mineral carbon and organic carbon with filter plugging tests at the Yuma Desalting Test Facility from June 1977 through January 1978[1]

[Data from the Yuma Desalting Test Facility compiled by the U.S. Bureau of Reclamation]

Sample date	Mineral carbon[2]	Organic carbon[3]	Plugging factor[4]
	(milligrams carbon per liter)		(percent)
7-25	0.84	1.14	15 to 25
8-17	0.63	1.25	11 to 49
8-29	0.02	0.54	10 to 15
9- 6	0.55	0.38	10 to 25
9-19	0.58	0.38	10 to 25
10-25	1.35	0.00	18 to [5]
10-31	0.50	0.52	5 to 42
11-7	0.65	0.88	5 to 10
11-14	0.34	0.54	5 to 20
11-21	0.37	0.81	10 to 20
12- 5	0.78	0.32	10 to 22
12-12	0.75	0.78	5 to 10
12-19	0.57	0.37	10 to 15
1-3-78	0.38	0.49	No test
1-3-78	0.83	0.27	8 to 30

[1] Material taken at clearwell effluent, operator control center. Retained on a 0.45-micron silver filter.

[2] Determined in a coulometric mineral carbon apparatus. Consists of carbonate and/or bicarbonate compounds.

[3] Determined by heating to 1,000° Celsius in a coulometrics total carbon apparatus. Value is obtained by the difference between total carbon and mineral carbon.

[4] Data taken from monthly operation and maintenance reports from Planning Research Corportation (Train I).

[5] Maximum acceptable.

Table SI-3.--Chemical analyses of canal water before pretreatment at the Yuma Desalting Test Facility from August 1977 through January 1978[1]

[Data from the Yuma Desalting Test Facility compiled by the U.S. Bureau of Reclamation]

Sample date (1977)	Conductivity (micromhos per centimeter)	Dissolved solids at 105° Celsius	Dissolved solids computed	pH (units)	Calcium (Ca^{++})	Magnesium (Mg^{++})	Sodium (Na^{+})	Potassium (K^{+})	Carbonate ($CO_3^{=}$)	Bicarbonate (HCO_3^{-})	Sulfate ($SO_4^{=}$)	Chloride (Cl^{-})
		(milligrams per liter)			(milligrams per liter)							
8-16	5060	3350	3310	8.0	208	90.2	778	13	0.0	406	875	923
8-29	5200	3490	3480	7.9	202	101	825	11	0.0	429	968	987
9-6	5280	3560	3550	7.8	196	114	834	11	0.0	398	971	966
9-12	5320	3560	3490	7.9	200	93.1	823	11	0.0	365	951	1040
10-31	5310	3530	3530	7.9	194	118	854	11	0.0	344	987	1020
11-7	5390	3610	3490	7.7	206	103	851	11	0.0	386	924	1000
11-14	5390	3610	3570	7.7	210	91.7	842	11	0.0	379	990	1040
11-21	5450	3630	3490	7.7	206	93.7	842	11	0.0	379	951	1000
12-5	5410	3500	3650	8.1	224	102	882	11	0.0	407	938	1070
12-12	5410	3520	3630	8.0	216	100	903	11	0.0	421	995	980
12-19	5460	3530	3680	8.1	226	95.6	903	11	0.0	418	993	1020
12-27	5430	3570	3580	8.1	218	121	891	11	0.0	417	902	1010
1-3-78	5220	3670	3560	8.1	216	103	825	11	0.0	442	960	987
1-16-78	5240	3600	3520	8.2	219	95.6	814	11	0.0	419	900	1040

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[1] Wellton-Mohawk water at the Yuma Desalting Test Facility, station A at the Grit Basin influent; no chlorination.

Table SI-4.--Chemical analyses of clearwell effluent water at the Yuma Desalting Test Facility from August 1977 through January 1978[1/]

[Data from the Yuma Desalting Test Facility compiled by the U.S. Bureau of Reclamation]

Sample date (1977)	Conductivity (micromhos per centimeter)	Dissolved solids at 105° Celsius	Dissolved solids computed	pH (units)	Calcium (Ca^{++})	Magnesium (Mg^{++})	Sodium (Na^{+})	Potassium (K^{+})	Carbonate ($CO_3^{=}$)	Bicarbonate (HCO_3^{-})	Sulfate ($SO_4^{=}$)	Chloride (Cl^{-})
		(milligrams per liter)			(milligrams per liter)							
8-16	4540	2990	2814	8.3	107	78	778	11	0.0	43	852	944
8-29	4800	3050	2876	7.9	106	82	795	10	0.0	40	828	1020
9-6	4780	3150	2992	7.7	104	87	834	10	0.0	40	880	1040
9-12	4850	3190	2997	7.9	125	76	842	11	0.0	38	833	1070
10-31	4760	3170	3051	7.9	112	84	817	10	0.0	40	916	1070
11-7	4900	3210	3053	7.9	106	84	823	10	0.0	43	916	1070
11-14	4880	3180	2991	7.5	107	38	795	9.8	0.0	41	900	1050
11-21	4780	2870	3024	7.4	106	92	798	10	0.0	45	902	1070
12-5	4670	3150	3019	7.5	102	94	806	11	0.0	41	930	1040
12-12	4690	3120	2969	7.4	106	80	789	9.8	0.0	41	872	1070
12-19	4850	3190	2885	7.5	106	100	795	9.8	0.0	42	798	1040
12-27	4900	3210	3014	7.7	102	92	795	11	0.0	46	897	1070
1-3	4850	3190	3015	7.6	112	87	778	10	0.0	43	913	1070
1-16	4760	3100	2923	7.5	115	76	770	11	0.0	40	875	1040

[1/] Wellton-Mohawk water at the Yuma Desalting Test Facility, station B at the clearwell effluent, operator control center.

Field Methods for the Isolation of Humic Substances

DOC Filtration. All water samples in this study were filtered with nitrogen pressure through 0.45 μm silver-membrane filters.

Isolation of Hydrophobic Acids. After filtration, water samples were acidified to pH 2 with concentrated HCl. The canal, RO reject-brine, and Colorado River samples were concentrated on 1,200-mL columns of XAD-8. Seventy-six L of water were passed through the column before elution with 3.8 L of 0.1 N NaOH. After elution, the hydrophobic acids were acidified to pH 2 with HCl and stored on ice until reconcentration. After 11 runs, the combined 41.8 L of concentrate of each sample were reconcentrated on the XAD-8 column and eluted with 3.8 L of 0.1 N NaOH. This sample was acidified, kept on ice, and transported to the laboratory in Denver.

Hydrophobic acids from the RO feedwater and the RO product water were concentrated on 10-liter columns of XAD-8. Three hundred and eighty L of water were passed through the columns before elution with 19 L of base. This concentrate was acidified and reconcentrated on 1,200-mL columns of XAD-8 until the final reconcentration was reduced to 3.8 L. This concentrate for each sample was acidified to pH 2, kept on ice, and transported to the laboratory in Denver.

Laboratory Methods for the Characterization of Humic Substances

Elemental Analysis. Elemental analyses for carbon, hydrogen, oxygen, sulfur, nitrogen, and bromine were conducted by Huffman Laboratories, Wheatridge, Colorado.

Infrared Spectroscopy. The freeze-dried humic materials were incorporated into KBr micropellets and analyzed on a Perkin Elmer model 580 infrared spectrophotometer.

Functional Group Analysis. Carboxylic acid functional groups were determined by mixing 10 mg of humic material with 2 mL of 0.1 N $Ca(CO_2CH_3)_2$, shaking the mixture overnight, then titrating to pH 8 with 0.01 N NaOH. Phenolic functional groups were determined by acid-base titration of 10 mg of humic material and measuring the amount of titrant required to increase the pH from 8 to 10. This amount of titrant was assumed to have titrated one-half of the phenolic functional groups; total phenolic groups were twice this amount.

UV-VIS Extinction Coefficients. The optical density of a known concentration of humic material was measured at 460 nm using a Cary model 118 UV-VIS spectrophotometer. This optical density was normalized to a path length of 1 cm per mg C per liter of solution to determine the extinction coefficient.

Liquid Chromatography. A Varian 8500 liquid chromatograph with Variscan UV-VIS detector was used to generate the pH gradient chromatograms for the samples of humic materials (McCarthy and others, 1979). A 1-meter column of XAD-8 resin (40 to 60 micron) was used for the separation.

Methods of Analysis of Organic Sediment Constituents

Hydrolysis with 2 N HCl. Three mL of 2 N HCl was added to approximately 0.05 g of sediment in a 1 cm x 10 cm glass hydroloysis tube with Teflon plunger seal at the top of the tube. After addition of the sample and acid, the tube was closed and heated to approximately 90°C (degrees Celsius) in a boiling water bath, or 100°C in an aluminum block heater. After heating for approximately 2 hours, the tube was allowed to cool to room temperature and the supernatant was poured off and dried in a rotary evaporator or freeze-dried.

Water was added to the dried material and the sample was redried. This process was repeated three to four times to remove all of the residual HCl.

Hydrolysis with 6 N HCl. This hydrolysis was similar to the 2 N HCl hydrolysis except that 6 N HCl was substituted for 2 N HCl. Hydrolyses for the amino acid analyses on all samples except the reconnaissance sample were performed in sealed glass ampoules that had been evacuated prior to sealing in a flame. These ampoules were heated at 110°C in an oven for 16 hours.

Amino Acid Analysis of Hydrolyzate. The amino acid analyses were performed on a Beckman Model 121-M Amino Acid Analyzer using lithium citrate buffers in the laboratory of Dr. Stephen I. Goodman of the Department of Pediatrics at the University of Colorado Medical Center.

Carbohydrate Analysis by Thin-Layer Chromatography. The sample, with suitable standards, were spotted on a 20 cm x 20 cm Merck cellulose thin layer plate and were developed with a solvent consisting of six parts by volume butanol, four parts pyridine, and three parts water. After one hour, the plate was removed from the tank, allowed to dry, sprayed with aniline oxalate, and heated for 10 minutes at 105°C to form the colored spots.

Humic and Fulvic Acid Extraction. Sediment samples from the June sampling were received in the laboratory mixed with some of the water that had been used to wash the sediment from filters, or, in the case of the reverse osmosis cell, from the membrane surface. These samples were chilled immediately after collection and were maintained chilled until analyzed. The extraction process was started for all the samples on July 5, 1979. The sample containers were shaken and an aliquot was taken from each one. The suspensions were sparged with nitrogen, and enough NaOH pellets were added to make the solutions 0.1 N NaOH. The solutions were placed in closed teflon or polyethylene containers and allowed to stand for 16 hours. After extraction, the solutions were centrifuged and filtered through a Whatman #1 filter to remove floating debris. The pH of the supernatant solution was lowered to pH 1 and allowed to stand overnight for precipitation of the humic acid fraction. The solutions were centrifuged and the humic precipitate was washed and recentrifuged. The wash water was combined with the supernatant. Organic carbon analyses were made during various stages in the process to determine the amount of carbon extracted, and the amounts of organic carbon in the humic and fulvic acid fractions in each sample.

Fractionation of the Humic Acid. The humic acid was fractionated using the procedure of Wershaw and Pinckney (1973); because of the small amount of humic acid in the sample, only the first part of the fractionation procedure was used. This involved dissolving approximately 0.01 g of humic acid in 1 mL of pH 11.5 NaOH solution and applying the solution to Sephadex G-50 Superfine column (0.9 cm diameter x 7 cm long). The fractionation pattern on the column was observed and drawn when the first fraction reached the bottom of the column. Each fraction was collected and infrared spectra of the fractions measured.

Small Angle X-ray Scattering Measurements. Small angle X-ray scattering measurements were made using the method developed by Wershaw and Pinckney (1973). Solutions containing 1 percent by weight concentrations of the humic material in water or in suitable buffer were used. Measurements were made on a Kratky small angle X-ray scattering goniometer using a 150 um entrance slit and a 400 um receiving slit. Sample solutions placed in a 1-mm diameter quartz glass capillary tube were irradiated with Cu to K α radiation. Partial monochromatization of the X-radiation was achieved by using a nickel filter and proportional detector coupled to a pulse-height analyzer. The experimental data were smoothed by use of a sliding five-point least-squares fit of the curve to a third-degree polynomial, and the collimation effects were eliminated by a computer program developed by Schmidt (1965) for Gaussian weighting functions; weighting functions for the goniometer configurations were evaluated by the computer program of Buchannan and Hendricks (1967).

Extraction of Humic and Fulvic Acid. Thirty mL of 0.1 N NaOH was added to 0.921 g of sediment and extracted overnight under nitrogen. The mixture was centrifuged and the resulting clear supernatant decanted off. This treated sediment was rinsed with water and centrifuged six times and the supernatant combined. Organic carbon analysis was made of the supernatant; then it was adjusted to pH 1 with HCl to precipitate the humic-acid fraction. Organic carbon analysis was made of the fulvic acid remaining after the humic acid precipitated out.

Deamination with HNO_2. In this experiment, 1 g of $NaNO_2$ was added to a suspension of 100 mg of the sediment in 10 mL of water. While this mixture was being stirred, 3 mL of 6 N HCl was slowly added and stirring was continued for 2 hours, after which the excess nitrous oxide of the supernatant solution was removed by boiling, and organic carbon was measured on the Beckman analyzer.

Preparation of Sediment Samples for Diatom Identification. The samples were suspended in concentrated nitric acid and the suspension was heated for 2 minutes in a Bunsen burner flame. Nitric acid was decanted off and the sample washed with distilled water until the wash water had a pH of 7. After each addition of distilled water, the sample was centrifuged and the supernatant decanted off. The cleaned diatoms were placed on a scanning electron microscope stub, coated with palladium, and placed in the scanning-electron microscope. Some of the samples prepared this way were also examined by light microscopy.

Gas Chromatographic Analysis of Carbohydrate Hydrolyzates. Alditol acetates were prepared according to the procedure of Brennan and Goren (1979). In this procedure, hydrolyzate is deionized with ion-exchange resins and reduced with $NaBH_4$ in 0.01 N NaOH overnight. The reaction was stopped with a few drops of acetic acid and the boric acid removed by evaporation of methyl borate from methanol. The solution was deionized with Amberlite MB-3 resin and vacuum-dried over P_2O_5. The alditols were acetylated with pyridine-acetic anhydride (1:1) at 100 - 110°C for 30 minutes. After evaporation and chloroform-water partition, the chloroform extract was analyzed by gas-liquid chromatography. These analyses were performed in the laboratory of Dr. Patrick Brennan at National Jewish Hospital.

Mineralogical Analyses of Sediments from the Fluid Systems Membrane Element Dissected May 20, 1980

The membrane scrapings were collected in 500 mL of 0.5 percent formaldehyde in which the membrane was preserved. Of this volume 150 mL was given to Dr. Winters, a microbiologist from Fairleigh Dickinson University; 50 mL to the U.S. Bureau of Reclamation; and 300 mL to the U.S. Geological Survey for analyses. Several large flakes of scale were observed in the scrapings. The Survey's portion of sample was wet-sieved through a 60 um screen. The sand-size fraction greater than 60 μm is believed to be an artifact of scraping, because it is fiber-like material which weighed 160 mg; it was not included in any of the reported analyses. An aliquot of the less than 60 μm sieved fraction was freeze-dried. Based on the aliquot, 1,532 mg of sediment was recovered from the RO membrane.

1. Organic Carbon Analysis. The sediment was 14.2 percent C by weight. This organic matter is not a separate phase, but occurs almost entirely as coatings on inorganic clay-size minerals and as bacterial and fungal biomass.

2. Inorganic Carbon Analysis. The sediment contained only a trace (0.1 percent) inorganic carbon as carbonates.

3. Size-Fractionation Analysis.

2 mm - 60 μm (sand-size fraction) = 0 percent

60 μm - 2 μm (silt-size fraction) = 8 percent

2 μm (clay-size fraction) = 92 percent

The silt was separated from the clay by repeated sedimentation by Stokes Law.

4. Mineralogical Analysis of Silt-Size Fraction. The results of X-ray diffraction analyses were:

Quartz	65 percent
K-feldspars	15 percent
Plagioclase feldspars	15 percent
Mica	5 percent

5. Mineralogical Analysis of Clay-Size Fraction. The results of X-ray diffraction analyses were:

Smectite (montmorillonite plus mixed-layered swelling clays)	65 percent
Amorphous clay minerals	10 - 15 percent
Kaolinite	5 - 10 percent
Illite (clay-size mica)	5 - 10 percent
Quartz and feldspar	10 percent

6. Iron and Manganese Oxides. Fe and Mn oxides are also coatings on clay-size minerals in addition to organic matter. The filter sediment scrapings were dark-reddish brown in color, which indicated Fe and Mn oxide coatings.

Fe as coatings on minerals = 1.34 per

Mn as coatings on minerals = 0.64 percent

7. The Br, Cl, carbohydrate, and amino-acid analyses are yet to be reported.

Conclusions: The fine-grained smectite-clay minerals may be a major factor in membrane fouling. They are typically 0.2 to 0.02 µm in size with a surface area of 150 to 200 m^2/g. If we assume 33 percent recovery of sediment from the RO membrane and 1,275 ft^2 of membrane surface, there are approximately three to five layers of clay over the membrane. This could have a marked effect on membrane performance in a number of ways.

The organic material (primarily humic and fulvic acids) and the small amount of microbes could have an additive effect to the clay in membrane fouling.

Mineralogical Analyses of Sediments from the Hydranautics Membrane Element Dissected June 18, 1980

The RO membrane had been preserved by cooling; no formaldehyde perservative was added. Distilled water was added to the membrane surface to facilitate removal of the sediment by a hard rubber scraper. The sediment scrapings collected were in a total suspension volume of 2,650 mL. Of this volume, 850 mL were given to Dr. Winters, 425 mL to the U.S Bureau of Reclamation, and 1,375 mL reserved for the U.S. Geological Survey analysis. Few flakes of scale were observed on the membrane. Visual evidence suggested strands of fungal growth, but no colonization of the membrane per se by fungi or bacteria was observed. The Survey's portion of the sample was wet-sieved through a 60 µm screen. The sand-size fraction greater than 60 µm is believed to be an artifact of scraping, because it is fiber-like material weighing 120 mg. It is not included in any of the reported analyses. A 600-mL aliquot of the less than 60 µm sieved fraction was freeze-dried. Based upon this aliquot, 1,080 mg of sediment was recovered from the membrane. Considering the number of membrane leaves which were sacrificed and not scraped for other types of sampling, and the efficiency of the sediment scraping technique, approximately 50 percent of the sediment was recovered from the membrane.

1. Organic Carbon and Nitrogen Analysis. The sediment was 19.96 percent C (carbon) and 0.38 percent N (nitrogen) by weight. A small amount of lint fibers scraped from the membrane was observed in the dried sample; therefore, the organic carbon is not completely representative of microbial biomass plus natural humic substances. Additional evidence for this conclusion is the low nitrogen content of the sediment.

2. Inorganic Carbon Analysis. The sediment contained only a trace (0.19 percent) inorganic carbon as carbonates.

3. Size-Fractionation Analysis.

2 mm - 60 µm (sand-size fraction) = 0 percent

60 µm - 2 µm (silt-size fraction) = 15 percent

2 µm (clay-size fraction) = 85 percent

The silt was separated from the clay by repeated sedimentation by Stokes Law.

4. Mineralogical Analysis of the Silt-Size Fraction. The results of the X-ray diffraction analysis were:

Quartz	30 percent
K-feldspar	30 percent

Plagioclase feldspar	30 percent
Mica	5 percent
Aluminosilicate clay minerals	5 percent

5. Mineralogical Analysis of the Clay-Size Fraction. The results of the X-ray diffraction analysis were:

Smectite (montmorillonite plus mixed-layered swelling clays)	70 percent
Amorphous clay minerals	5 - 10 percent
Kaolinite	5 - 10 percent
Illite (clay-size mica)	5 - 10 percent
Quartz and feldspars	10 percent

6. Iron and Manganese Oxides. After collection, this sediment sample visually was not as reddish-brown as the sediment from the RO membrane dissected on May 19, 1980.

Fe as coatings on minerals = 4.0 percent

Mn as coatings on minerals = 0.96 percent

7. The Br, Cl, carbohydrate, and amino acid analyses are yet to be determined and will be reported by Wershaw.

Conclusions. The membrane scrapings were similar to those from the May 19, 1980, and June 28, 1979, samplings, in that smectite clay was the dominant material on the membrane. This membrane contained approximately three times as much sediment as the May membrane. The higher carbon content of the scrapings, along with visual observations, indicated that microbial growth was more abundant on the membrane than the May membrane.

If 50 percent recovery of sediment from the RO membrane and 300 ft^2 of membrane surface are assured, there are approximately eight to ten layers of clay over the membrane. The clay, along with humic acids and microbial growth, probably has a marked effect on the performance of this membrane.

Organic Analyses of Sediments from the Membrane Elements Dissected in 1979 and 1980

Data reported here represent results obtained from the examination of the sediment deposits from three different membrane elements which were dissected and scraped to recover the sediment. The first element was dissected on June 28, 1979, the second on May 19, 1980, and the third on June 18, 1980.

The sediments were analyzed for the following organic parameters: (1) amino acids after hydrolysis; (2) carbohydrates after hydrolysis; (3) humic and fulvic acids, (4) total organic carbon hydrolyzable in 6 N HCl; and (5) total organic carbon.

The most meaningful results were obtained from the amino acid, carbohydrate, and total organic carbon analyses. Reproducible results for the humic and fulvic acid analyses could not be obtained, apparently because of partial hydrolysis of the proteins and carbohydrates by the NaOH used for extraction of the humic and fulvic acid. The procedure that was used for the extractions was developed from soils and sediments where the concentrations of carbohydrates and proteins are relatively low with respect to the humic and fulvic acids. However, this was not the case in the second and third membrane sediments.

Data for the carbohydrate and amino-acid analyses are given in tables SI-5, SI-6, and SI-7. It will be noted that concentrations of carbohydrates and amino acids were highest in the third sediment and lowest in the first, with the second having intermediate values. The same was true for organic carbon concentrations (table SI-8). Sediment carbohydrate compositions were: 2.2 percent of the organic carbon in the first sediment, 2.8 percent in the second sediment and 6.6 percent in the third sediment. Amino acids accounted for 6.2 percent of the organic carbon in the first sediment, 6.2 percent in the second sediment and 7.5 percent in the third sediment. Part of the remaining organic carbon is humic and fulvic acid; however, they probably are not the major constituents. At this time, it is not possible to say what are major constituents are.

Tables SI-5 and SI-7 show that, with few exceptions, relative concentration of the various simple sugars and amino acids identified in the hydrolyzates were very similar in all three of the sediments. Relative concentrations of the carbohydrates and amino acids in the canal-sediment hydrolyzates are very different from those of the membrane sediment; therefore, the constancy of the relative concentrations in the different membrane samples cannot be accounted for by saying that they simply reflect a constant source from the canal sediment.

Table SI-5.--Relative percent carbohydrate concentrations of sediments from the reverse-osmosis membrane elements dissected in 1979 and 1980

Carbohydrate	Dissection date June 28, 1979	May 29, 1980	June 18, 1980
Glucose	53.6	55.5	51.8
Mannose	27.7	9.7	9.2
Galactose	6.1	5.7	5.5
Xylose	5.0	10.6	11.8
Arabinose	2.7	7.5	10.0
Rhamnose	2.5	9.0	6.7
Fucose	1.2		
Ribose	1.2	0.4	4.9

Three possible explanations for this consistency are: (1) carbohydrates and amino acids are being biologically produced in the canal, treatment train, or reverse osmosis system and are being concentrated in the RO units; (2) there is a physical chemical fractionation in the treatment train, and RO system which results in relatively constant ratios of the components; or, (3) a combination of the first two mechanisms.

The relatively high concentration of polar organic compounds, such as humic and fulvic acids and amino acids or proteins in the sediment will alter the properties of the clays in the sediment; however, it is not generally possible to predict the effect.

Table SI-6.--Amino acid concentrations of sediments from the reverse-osmosis membrane elements dissected in 1979 and 1980

	Dissection date		
Amino acid	June 28, 1979	May 29, 1980	June 18, 1980
	(nanomole per milligram)		
Aspartic acid	3.22	14.7	26.9
Threonine	2.11	10.0	12.5
Serine	2.22	12.2	20.1
Glutamine	0.1	0.0	0.0
Proline	2.08	8.4	16.6
Glutamic acid	4.54	20.7	35.7
Glycine	3.71	20.5	29.2
Alanine	6.02	21.0	40.4
α-amino adipic acid	1.72	8.2	15.9
Valine	+	+	0.0
Galactosamine	+	+	0.0
Methionine	0.0	0.0	0.3
Isoleucine	2.84	10.2	18.9
Leucine	5.26	20.0	34.8
Tyrosine	+	0.0	0.0
Phenylalanine	2.13	8.4	10.7
γ-amino butyric acid	0.33	0.0	4.4
Ornithine	0.33	2.9	4.6
Lysine	0.52	3.3	6.2
Arginine	0.33	2.0	3.6
Histidine	0.0	0.0	0.8
	37.46	162.5	281.6

Table SI-7.--Relative amino acid concentrations of sediments from the reverse-osmosis membrane elements dissected in 1979 and 1980

Amino acid	Dissection date		
	June 28, 1979	May 29, 1980	June 18, 1980
	(mole percent)		
Aspartic acid	8.60	9.05	9.55
Threonine	5.63	6.15	4.44
Serine	5.53	7.91	7.14
Glutamine	0.27	0.0	0.0
Proline	5.55	5.17	5.89
Glutamic acid	12.1	12.7	12.68
Glycine	9.90	12.6	10.4
Alanine	16.1	12.9	14.3
α-amino adipic acid	4.59	5.05	5.65
Valine	0.0	0.0	0.0
Galactosamine	0.0	0.0	0.0
Methionine	0.0	0.0	0.11
Isoleucine	7.58	6.28	6.71
Leucine	14.0	12.3	12.36
Tyrosine	+	0.0	0.0
Phenylalanine	5.69	5.17	3.80
γ-amino butyric acid	0.88	0.0	1.56
Ornithine	0.88	1.78	1.63
Lysine	1.39	2.03	2.20
Arginine	0.88	1.23	1.28
Histidine	0.0	0.0	0.28

Table SI-8.--Percent by weight of organic carbon in sediments from the reverse-osmosis membrane elements dissected in 1979 and 1980

Dissection date	Percent by weight organic carbon
June 28, 1979	3.53
May 19, 1980	14.2
June 18, 1979	19.96

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