ORANGE COUNTY CALIFORNIA GROUNDWATER CHARACTERIZATION AND TREATABILITY

BY

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I dedicate this thesis in an oblique way to the lost souls of Ireland trapped behind Ulster's oppressive walls.

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Abstract

Groundwater in portions of Orange County exhibits a characteristic color attributed to the presence of naturally occurring organic matter. Dissolved organic carbon, largely in the form of humic and fulvic acids, is found at concentrations ranging from 0.3 mg/L to 14.4 mg/L.

Organic rich strata is believed to be the source of dissolved organic carbon (DOC). Removal of DOC from groundwater is necessary to reduce water color and trihalomethane formation potential (THMFP).

Organic carbon characteristics such as average apparent molecular weight and carboxylic acidity appear to effect groundwater treatability and THMFP. Increased organic carbon removal efficiency was realized with decreasing carboxylic acidity and lower apparent molecular weight organic carbon appears to contribute a greater amount of THMFP per milligram groundwater DOC.

Alum coagulation was consistently more successful in removing DOC from solution while ozone oxidation achieved the greatest reduction in sample reactivity.

CHAPTER 1

INTRODUCTION:

The demand for potable water in Southern California has increased steadily with the influx of people to that region. With the reduction in available water from the Colorado River and the California State Project supply, alternative sources are required.

A significant body of virtually unused groundwater lies below portions of Orange County in strata as shallow as several hundred feet and to depths of over 1000 feet. The water has gone unused to date largely because of naturally occurring color which is caused by dissolved humic and fulvic acids. In addition to esthetic concerns with respect to water, humic and fulvic acids are precursors of trihalomethanes (THM's) where chlorination is employed for water disinfection.

This research focuses on the groundwater basin distribution of color, the sources of color (chemical and physical), the interrelationships between various water characteristics and the impacts that water characteristics have on treatment and removal of color and THM precursors.

Beyond color distribution and sources, insight into chemical relationships responsible for THM generation are alluded to. Understanding the mechanisms of THM production and/or likely source molecules may allow for the selection of appropriate treatment alternatives and/or permit the target removal of specific groundwater constituents.

During the course of this research, many questions were raised, prompting recommendations for future research into sources of color for Orange County groundwater and chemical interrelationships between water constituents.

A paucity of information regarding Orange County DOC distribution was available. As a result, speculation as to sources, horizontal and vertical distributions of DOC and other specific relationships, are based on a small amount of information and should be used cautiously.

Physical/chemical sample interrelationships and comparisons have been provided graphically to support the conclusions which were drawn. The majority of the graphs are based on 13-15 data points generated under a constant set of conditions. The interrelationships presented, particularly where good linearity exists, are expected to portray not only conditions in Orange County, but also relationships in other parts of the Los Angeles Basin where groundwater situations and subsurface geology are similar.

CHAPTER 2

LITERATURE REVIEW

Natural waters frequently exhibit a yellow to brownish color which often arises from dissolved organic matter carried in solution. The nature of the color or color imparting compounds appears to vary over a wide range depending on the chemical and physical environment, source of water and the origin of organic molecules. In many waters, humic materials have been found to be responsible for the vast majority of the color present in a sample. In addition, variation in the chemical nature of the color can influence the treatability and THMFP of a water source.

2.1 Dissolved Organic Carbon:

Dissolved organic carbon (DOC) is defined as the organic carbon which passes through a 0.45 um filter (21). DOC can be found in virtually all water sources. Table 2-1 presents average DOC concentrations found in various natural waters. Typically groundwater and seawater contain the lowest concentrations of DOC. Alternately, bogs, marshes and water bodies possessing abundant flora have higher

Table 2-1: Approximate Concentrations of DOC in Natural Waters*

Source	DOC (mg/l)
Seawater	0.5
Groundwater	0.7
Precipitation	1.1
Oligotrophic Lake	2.2
River	5.0
Eutrophic Lake	10.0
Marsh	15.0
Bog	30.0

*Reference #52

corresponding values for DOC.

The spectrum of DOC values is more complex than indicated by Table 2-1. DOC concentrations in natural waters are environment specific. The DOC content of rivers in the Southeast, where currents are slow, fauna is rich and soils are highly organic is typically higher than those of the Southwest where the environment is markedly different.

Organic content of groundwater varies a great deal also. In contrast to surface waters, the DOC content of groundwater appears to be aquifer related. Table 2-2 presents various DOC values associated with different aquifers. From Table 2-2 it can be seen that a strong direct relationship exists between aquifer material and the DOC content of a water.

DOC concentrations range from 0.7 mg/L to 100 mg/L for various aquifers. This scenario is expected because of the intimate contact which occurs between aquifer material and transient groundwater. It has been reported (24,52) that the average groundwater DOC concentration is 0.7 mg/l, although Leenheer et al.,(24) have shown that values in the

Table 2-2: Groundwater DOC Concentrations Resulting from Various Aquifer Materials*

Aquifer Material	DOC (mg/L)
Sand and Gravel	0.7
Limestone	0.7
Sandstone	0.7
Igneous	0.5
Oil Shales	3.0
Humic Colored	10.0
Petroleum Associated	100.0

*Reference #15

United States vary from non-detectable levels to concentrations of 15 mg/l. However, 85% of the values recorded by Leenheer were below 2.0 mg/l.

A similar DOC content for two waters which are separated geographically or stratigraphically does not necessarily imply similar water characteristics. The organic content of soils and water can range in molecular weight (MW) from several hundred to tens of thousands (42). Organic content in itself is a poor measure of the amount of color present in a sample. As early as 1966, Christman et al.,(8) recognized that the chemical structure of organic molecules may have been responsible for the variation in color producing properties of a sample. Aside from color, chemical structure can affect many other properties as well. Humic materials are one of the primary components of DOC which affect the behavior of organic and inorganic materials in solution.

2.2 Humic Materials:

Humic materials have been described as colored, polymeric organic acids which can be separated from solution using XAD resins (52,53). Humic materials are polyfunctional, soluble, and considered to be the relatively stable by-products of microbial decay (7,19).

There are three major divisions which compose humic materials (42). They are; humic acid, fulvic acid and humin. Each group of materials is defined operationally based on its solubility or insolubility in acid and base. Humin represents that material which cannot be extracted by dilute acid or base (42). Fulvic acids are soluble at all pH values and humic acids are soluble in caustic solutions but insoluble below pH 2 (51).

Humic and fulvic acids have been characterized by the presence of multiple aromatic ring structures containing acidic functional groups. Figure 2-1 is a schematic representation of a fulvic acid molecule. The primary acidic functional groups present on humic and fulvic acids are carboxylic and phenolic in nature and as a result humic materials impart a net negative charge at typical pH conditions found in most natural waters (52).

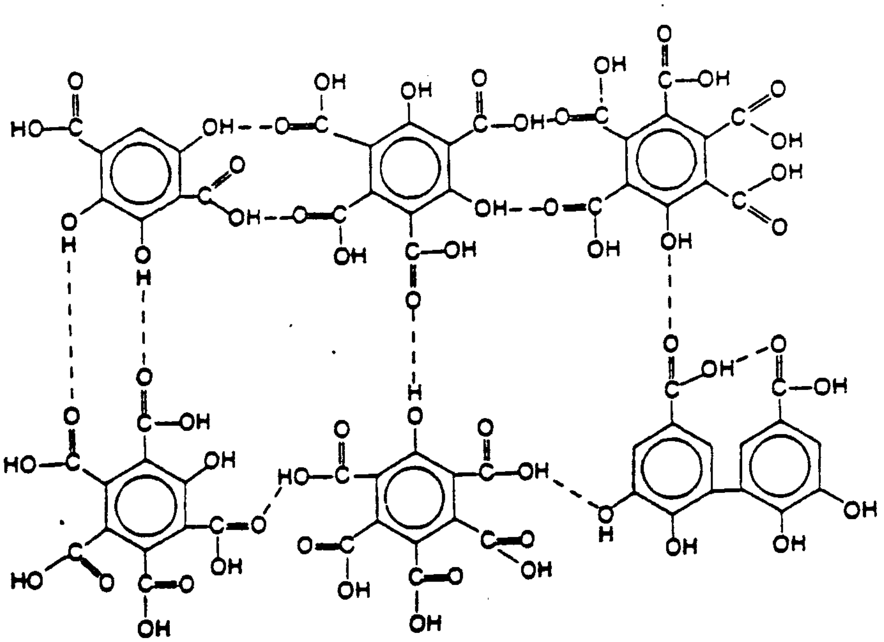


Figure 2-1: Theoretical structure of a fulvic acid molecule

Aquatic humic substances typically account for between 30 and 80% of the DOC present in natural waters (27), although a value as high as 90% (51,56) has been reported. The aqueous concentration of humic substances and the molecular composition are a function of the environment (geographical, climatic and chemical), the degree of evolution, the source or parent organic material and the productivity of the continental and/or marine environment (51).

Many differences between humic and fulvic acids have been reported. There is poor agreement between sources on specific composition and no definitive structural boundry separating the class fulvic acid from the class humic acid exists. The following generalizations have been taken from literature and represent working examples of the variations between humic and fulvic acids.

1. Fulvic acids contain a greater number of carboxylic acid groups than do humic acids (10,42,48,52,55).
2. Fulvic acids contain more elemental oxygen than humic acids (10,40,42).

3. Humic acids have a greater carbon content than fulvic acids (10,40).
4. Fulvic acids have lower molecular weights than humic acids (34,42,54).
5. Humic acids are insoluble below pH 2 where fulvic acids remain in solution (33,51).

Several authors have indicated that humic substances show compositional changes based on position in the hydrologic cycle. For example, Vandenbrouke (51) discussed the apparent lower oxygen to carbon ratios for humic substances found in groundwater when compared to surface water. This situation might be expected because goundwaters are usually oxygen poor while surface water generally is not. Nitrogen and hydrogen to carbon ratios are higher in marine humics when compared to continental humic materials (51). Thurman (51) points out that groundwater humics contain more oxygen and carbon than surface water humics. Thurman goes on to say that groundwater humics possess low color per unit carbon content and that they typically have lost their carbohydrate components apparently through microbial decay.

Table 2-3 (below) presents the approximate elemental composition of aquatic humic materials (52,53). Carbon and oxygen are the dominant elements representing 80-90% of the mass. The distribution of elements in a humic molecule (condensed nuclei vs. side chain) may be responsible for the behavior exhibited by the molecule in the environment. Over generalization should be avoided when defining hydrologic cycle related variations in humic materials due to source related differences and routes of humic maturation. This will be discussed in further detail in the following pages.

Table 2-3: Approximate Elemental Composition for Aquatic Humic Substances.

Element	% by weight
Carbon	50-52%
Hydrogen	4-5%
Oxygen	35-40%
Nitrogen	1-2%
Sulfur	<1%
Phosphorous	<1%

It is probable that humic materials enter the hydrologic cycle via natural water leaching. Organic matter present in soils, rocks and decaying vegitation may be leached by percolating rain water and transported to rivers, lakes or groundwater. Intimate contact between surface waters and particulate or suspended organic carbon may result in slow hydrolysis and creation of DOC, a portion of which is humic in nature. A similar scenario can be drawn for groundwaters in contact with carbon bearing strata. It has been reported that a portion of the humic material in natural waters is autochthonous (7,19) and, that in situ formation of heterocondensates (4,20) may be an additional source of humic substances.

Kerogen, which represents 95% or more of the finely disseminated organic matter in ancient sediments (22), has been identified as an important source of humic substances in groundwater (51,52). The average organic content of ubiquitous sedimentary rocks is 2.1%, 0.29% and 0.05% for shales, carbonates and sandstones respectively (22), although other sedimentary rocks (black shales, coal, etc.) can have organic concentrations which are significantly higher. Another source of groundwater humics is recharge of organically rich waters (51). This is expected to be of greater importance where shallow water tables are present (e.g. Biscayne Aquifer, Florida).

While parent organic material has an affect on the nature and composition of humic matter, the molecular transformations which occur during molecule maturation may dictate the final molecular structure.

The formation of humic substances is poorly understood (48) although several theories exist. Groundwater humic formation is more complex because two or three routes of genesis are possible. The first scenario involves alteration (via decay) of existing organic material. The second possibility encompasses the first scenario plus diagenesis (post-depositional changes in organic material by geologic forces). The final scenario incorporates one and two and includes dissolution of diagenetically altered carbon. Scenario number three also involves post-dissolutional chemical and/or biological changes which occur in the aquifer.

2.3 Formation of Humic Materials:

There exists at least four primary theories on the formation of humic material. The classical theory suggests that humics are modified lignins which follow a decompositional pathway from lignin to humic acid to fulvic acid (48) and eventually to CO_2 and H_2O (42). The initial step is microbially mediated and results in the loss of methoxyl groups and oxidation of aliphatic side chains to form carboxyl groups (48). The oxidative generation of carboxylic acid functional groups increases solubility (52) and results in a stable, ionized molecule in solution.

The second theory holds that phenolic aldehydes are formed when lignin is subjected to microbial decay. This process is followed by enzyme mediated formation of quinones which polymerize to create humic materials (48). Beck et al., (4) indicates that several original biochemical compounds can undergo condensation reactions to form fulvic acid.

The third scenario is essentially the same as the second except non-lignin materials (e.g. cellulose) acts as the starting point in humic generation (48). A fourth theory suggests that microbial by-products initiate non-enzymatic polymerization (48) resulting in humic like polymers.

Krom et al., (20) suggests a similar pathway to biologically mediated polymerization. Degraded cellular material is transformed to low molecular weight dissolved organic matter (DOM) via fermentation reactions. The DOM (e.g. amino acids) undergoes condensation reactions forming fulvic acids. Further condensation results in the formation of humic acids. Degens (22) supports condensation reactions of metabolic and hydrolysis products as a primary step in the formation of humic materials. Teichmuller et al., (22) states that humic acids can be formed from lignins via auto-oxidation condensation reactions in a weakly acidic environment. The authors go on to say that the process can also proceed via chemical reactions in neutral or weakly alkaline environments.

Whether one process dominates over the others or all four scenarios occur independently, it appears that aquatic humic substances are the refractory end products of diagenesis of plant and microbial organic matter (7,19,27,30).

Where deep groundwater is concerned, post-depositional changes to humic materials may be the most important step in the creation of DOM in groundwater.

The end products of the sedimentary evolution of organic matter are largely the post-depositionally modified humic substances kerogen and coal (19). The presence and relative abundance of original hydrophilic biological materials (amino acids, sugars, etc.) in a carbon source may indicate the stage of diagenesis (22). During peat formation, organic material is characterized by a high oxygen content. With progressive diagenesis, organic matter loses mainly nitrogen and oxygen (51). The slow inorganic maturation is accompanied by a loss in functional groups with heat being the primary cause of alteration (19,22,48,51). In conjunction with this process, the aromaticity of the humic matter increases (19).

Apparently, a narrow physical/chemical environment separates organic acid destruction from organic acid generation. Spirakis and Heyl (46) point out that beyond the bacterial thermal limit of 80 degrees celsius, high concentrations of organic acids can form and have been found in subsurface solutions. The source of these acids is apparently thermocatalytic degradation of kerogen (16). Certain kerogens (Type II) have high oxygen/carbon ratios which are great enough to account for the organic acid concentrations. Spirakis and Heyl also says that continued temperature increases will degrade the organic acids.

The implications of this information are important. Information provided by Spirakis and Heyl may indicate that groundwater humic acids can contain higher functional group concentrations than their terrestrial counterparts and that no surface water companion humics may exist.

2.4 Kerogen:

The progression of diagenesis to the point where humic material is insoluble in alkali or other solvents corresponds to the creation of kerogen (19). Increased metamorphism results in the generation of coal or other by-products which are increasingly aromatic, hydrophobic and significantly reduced in side chain aliphatics (22).

As with humics, kerogen properties vary from rock to rock. Typical kerogen composition ranges from 65-90% carbon, 5-12% hydrogen and 5-25% oxygen (5). Kerogen can be subdivided into two primary classes: 1) Sapropelic or amorphous kerogen formed from plankton and 2) humic kerogen from continental sources which consists largely of plant remains (especially lignin) (5).Type II kerogen is more refractory because it contains much less hydrogen than Type I Kerogen (16).

If, as Thurman (52) points out, kerogen is an important source of humic substances in deep groundwater then the biological and/or chemical relationships which result in re-suspension/alteration must be understood to positively identify the source material. Isolation of these mechanisms may also lead to a greater understanding of potential removal mehcanisms for dissolved humic materials.

2.5 Implications of Organic Carbon Characteristics:

Because the degree of maturation or diagenesis strongly affects molecular characteristics such as carboxylic acidity, molecular weight, hydrophobicity and color it also affects treatability and trihalomethane formation potential (THMFP). Oliver et al., (33) points out that chloroform production after chlorination changed with molecular weight and that low molecular weight fulvic acids (<30,000) were the major chloroform precursors. Miller et al., (28) states that groundwater fulvic acids have the lowest THMFP and that they represent the oldest organic material. Collins et al., (11) and Chadik et al., (6) indicate that high MW materials (which are the most reactive THM precursors), are most easily removed during water treatment and that lime treatment only removed lesser charged humic materials. Kuo et al., (21) states that DOM characteristics such as MW and humic content were found to influence removal by alum coagulation.

As demonstrated by these authors, the physical/chemical nature of DOM (and hence humic materials) significantly influences the treatability and THMFP of a water source. The causes of these variations must be understood to successfully develop treatment stratagies.

CHAPTER 3

GEOLOGIC DESCRIPTION:

3.1 Los Angeles Basin:

The Los Angeles Basin is an alluviated depression which is bounded by mountains on the north, east and southern sides and the Pacific Ocean on the western edge. The drainage basin has been the site of fluvial deposition, largely marine in nature, since middle Miocene time (57). The structural depression extends approximately 50 miles in length from the San Joaquin Hills near Laguna Beach to the Santa Monica Mountains. The width of the Los Angeles Basin is roughly 35 miles, starting at the Palos Verdes Hills and stretching to the San Gabriel Mountains (45) (Figure 3-1).

Lithologically, the basin is subdivided into 3 distinct units. The basal unit consists of crystalline rocks (igneous and metamorphic) with the distinctive Catalina Schist (a sodium-rich metamorphic rock) in the basins western complex (45). Above the basement rocks lie 17,000 feet of pre-basin sedimentary rocks. These rocks are characterized by conglomerates, sandstones and shales (45).

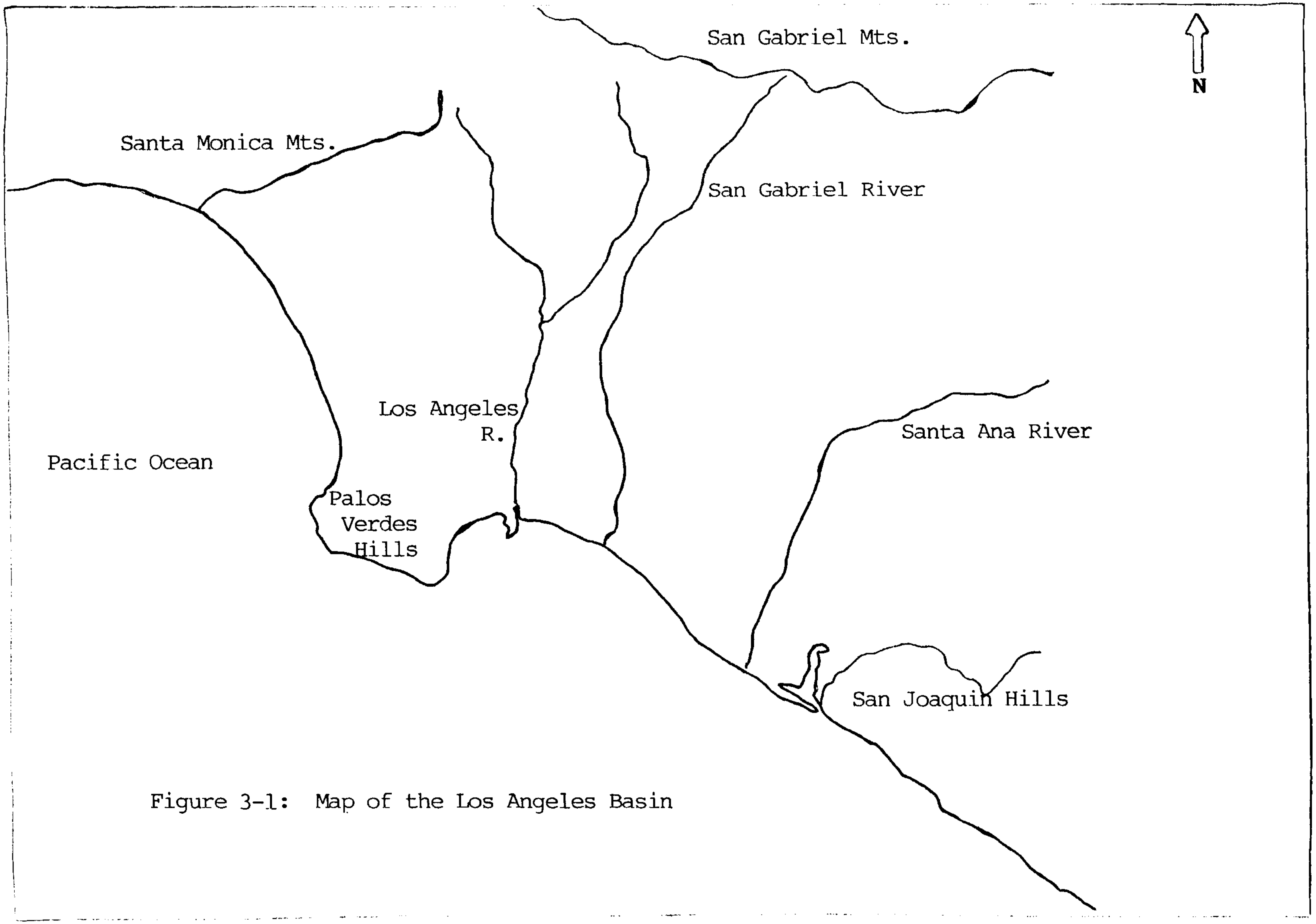


Figure 3-1: Map of the Los Angeles Basin

The final stratigraphic unit is composed of basin sediments/fill material which is both marine and terrestrial in nature. The majority of this upper unit was deposited by the Los Angeles, San Gabriel and Santa Ana Rivers. Structurally, the basin consists of a huge north-dipping syncline with its axis extending from the city of Beverly Hills to Santa Ana.

3.2 Orange County Area:

The portion of the Los Angeles Basin which covers Orange County has been named the "Central Block" (29,57). It extends from Beverly Hills southeast to the San Joaquin Hills, and is bounded on the east by the Whitter Fault Zone (29).

Basin lithology consists of slightly metamorphosed sedimentary basement rocks which have been intruded by the Southern California Batholith, a granite plutonic body of Cretaceous age (29). Lying above the basement rocks are up to 32,000 feet of marine and non-marine sedimentary rocks from late Cretaceous to Pleistocene age. Structurally, central Orange County is underlain by a broad synclinal sag which is roughly 10-14 miles wide (29). The most recent deposits in Orange County consist of 500-1200 feet of alluvial fan material deposited from the San Gabriel Mountains (17) and Santa Ana River deposits many of which consist of buried stream channels (57).

3.2.1 Groundwater Occurrence:

The Central Block consists of consolidated and unconsolidated aquifers with separate groundwater producing strata subdivided by faults. In addition, impermeable beds below the surface act as barriers to groundwater movement (14). This complex system of aquifers is a dynamic hydrologic environment impacted by artificial and natural recharge, groundwater extraction and natural losses. Aquifers and aquicludes in this area are continuous and discontinuous with barriers to, and regions promoting deep percolation (44). In some areas, clay gouge present at fault surfaces prevents the transmission of groundwater (17).

Figure 3-2 is a geologic cross-section through a portion of the southern Los Angeles basin (reproduced from reference #38). The primary water producing strata in the Huntington Beach/Santa Ana area are in the San Pedro Formation,

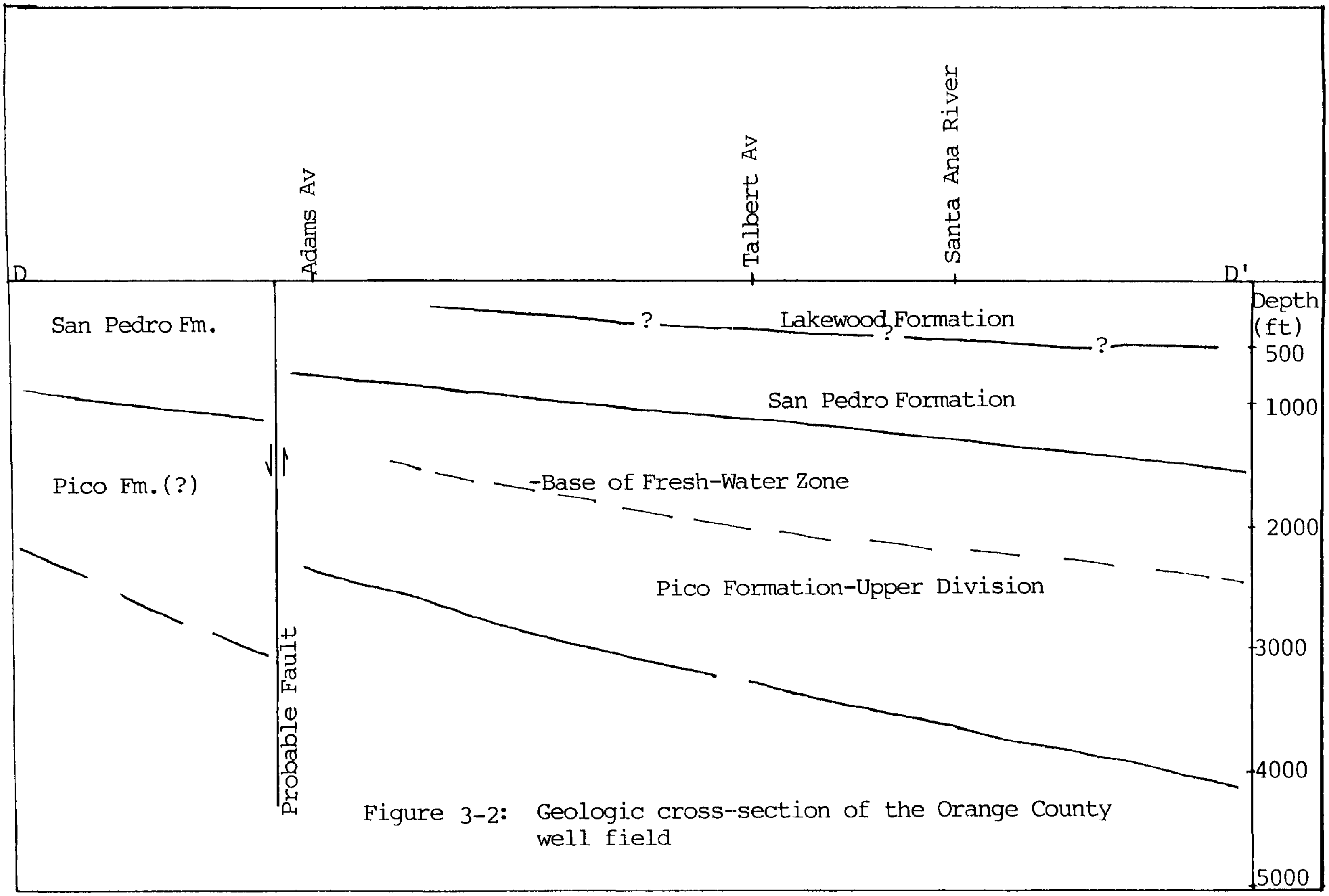


Figure 3-2: Geologic cross-section of the Orange County well field

Lakewood Formation and Recent fluvial deposits (44).

Current groundwater occurrence and chemistry in the San Pedro formation is strongly influenced by the original depositional sedimentary environment (38). Sediments present in the formation were transported largely by streams and deposited either on land or in the ocean. The formation consists of up to 1350 feet of sand and gravel layers; gray, yellowish or brownish clay; clayeysilt, sandy silt and marl (38). Of particular interest are fine grained strata containing fragments of carbonized wood and vegital fibers and the presence of black shales which have high organic contents (38). The high organic content of sediments deposited in the basin was preserved as a result of poor circulation and rapid burial (57). Rapid burial allows organic carbon to quickly pass from aerobic zones to sulfate reduction zones enhancing preservation (16). Significant chemical variation between aquifers in the San Pedro formation occur because each stratum of coarse sand and gravel in the formation is a distinct confined water source. There appears to be little if any natural flux of water between the units (38).

Recent deposits in the Orange County area consist of dune sands, lagoonal deposits, tidal marsh deposits, alluvial sediments and basal stream deposits. The primary water bearing zones in recently deposited material are the basal stream deposits called the Bolsa Aquifer or 80 foot gravel. Lagoonal deposits consist of peat, silt, sand and clay and reach a maximum depth of 35-40 feet (44).

Recent deposits rest uncomformably on the upper Pleistocene Lakewood formation. The Lakewood formation consists of shallow marine, littoral, and continental deposits which are subdivided into two distinct units. The upper unit is called the Semi-Perched Zone and it contains smaller permeable beds. The second unit consists of three interconnected aquifers which have confining beds separating them at various points in the valley (44). The strata which comprise the Lakewood formation appear to thin as they trend eastward.

The San Pedro formation lies conformably below the Lakewood formation. It is lower Pleistocene in age and is comprised of marine and terrestrial deposits. The formation consists of several confined aquifers separated by aquicludes. The aquifers are characterized by continuous areal extent (44).

The eleven wells sampled by Orange County personnel, are believed to draw water largely from the Lakewood and San Pedro formations. The deepest wells may penetrate the upper reaches of the Pico formation. The Pico formation is upper Pliocene in age and consists almost exclusively of marine deposits. The uppermost Pico consists largely of silt and clay however, in Orange County, strata composed of sand and gravel are common (38).

3.2.2 Description of Aquifers:

San Pedro Formation:

There are five principal aquifers in the San Pedro formation, all strata contained are lower Pleistocene in age. The uppermost unit stratigraphically is the Hollydale Aquifer below which lie sequentially the Jefferson, Lynwood, Siverado and Sunnyside Aquifers.

Hollydale Aquifer: This upper-most unit consists primarily of shallow marine deposits (75%) with the remaining portion characterized by stream deposition (36). Strata within the aquifer are separated by aquicludes and permeable beds are not known to crop-out at the surface. The aquifer has low permeability and recharge is believed to occur where Hollydale strata merge with overlying, younger aquifers (36).

Jefferson Aquifer: This aquifer lies below the Hollydale Aquifer and contains fine-grained rocks of unknown origin. Fine-grained material is frequently characteristic of marine or flood-plain deposits which are typical to the Los Angeles Basin. Natural recharge is suspected to occur where the Jefferson Aquifer merges with other aquifers. Artificial recharge occurring around the Whitter Narrows may partially support this aquifer (36).

Lynwood Aquifer: This next aquifer in the sequence is one of the more important groundwater sources (36). It consists of continental and shallow marine deposits and is characterized by a lack of continuous permeability with depth. Natural recharge is believed to occur via surface and subsurface flows through the Whitter Narrows. Artificial recharge has occurred where the aquifer contacts permeable shallow pits around Whitter Narrows (36). It is believed that the Hollydale, Jefferson and Lynwood aquifers comprise the Meadowlark aquifer present in the coastal regions of Huntington Beach. The Meadowlark aquifer is also frequently differentiated into the Omicron and Upper Rho aquifers in the Santa Ana Gap.

Silverado Aquifer: This aquifer is one of the most important groundwater producing zones in the coastal plain (36,44). It consists of continental and marine deposits which have been subjected to a great degree of folding and faulting. Based on well logs, marine deposits in this aquifer are reportedly comprised in part of peat, wood fragments and black sands. Natural recharge occurs where the Silverado merges with other aquifers and where the strata outcrop at the surface along the Coyote, Baldwin and Palos Verdes Hills (36). This aquifer is also called the Main aquifer in coastal regions (44).

Sunnyside Aquifer: The final stratigraphic unit which overlies the Pico Formation is the Sunnyside Aquifer. The aquifer consists of strata which are largely marine in origin and extend throughout the central basin. Aquifer recharge occurs at outcrops where folding has lifted beds to the surface (36). This aquifer is also called the Lower Zone in coastal reaches. It has moderate permeability and is confined (44).

Lakewood Formation:

There are four primary aquifers contained in the Lakewood formation, all strata are upper Pleistocene in age. the uppermost unit stratigraphically is called the Semiperched Zone, below which lie the Alpha, Beta and Lambda aquifers sequentially.

Semiperched Zone: This is the upper most aquifer in the Lakewood formation. The sediments of this deposit are moderately to well oxidized and typically fine-grained. Minor constituents of this aquifer include peat lenses, organic silt and bits of wood (44). The aquifer has low to moderate permeability, has high salt concentrations and is confined in some areas. Natural recharge probably occurs from the overlying Bolsa aquifer and where beds are exposed to the surface along the Newport-Inglewood structural zone.

Alpha Aquifer: The Alpha Aquifer is separated from the Semiperched Zone by a 10-45 foot thick confining bed of marine silt and clay containing wood fragments and peat. The aquifer is typically 60-80 feet in thickness and consists of coarse terrestrial and marine deposits with interbeds of silt and clay. The presence of wood fragments in this aquifer has been reported (44). The Alpha aquifer overlies a marine silt and clay confining bed in coastward areas but merges with the Bolsa and Beta aquifers in other areas (44). This aquifer is characterized by moderate to high permeability and recharge probably occurs where the strata reach the surface or where aquifer comingling occurs.

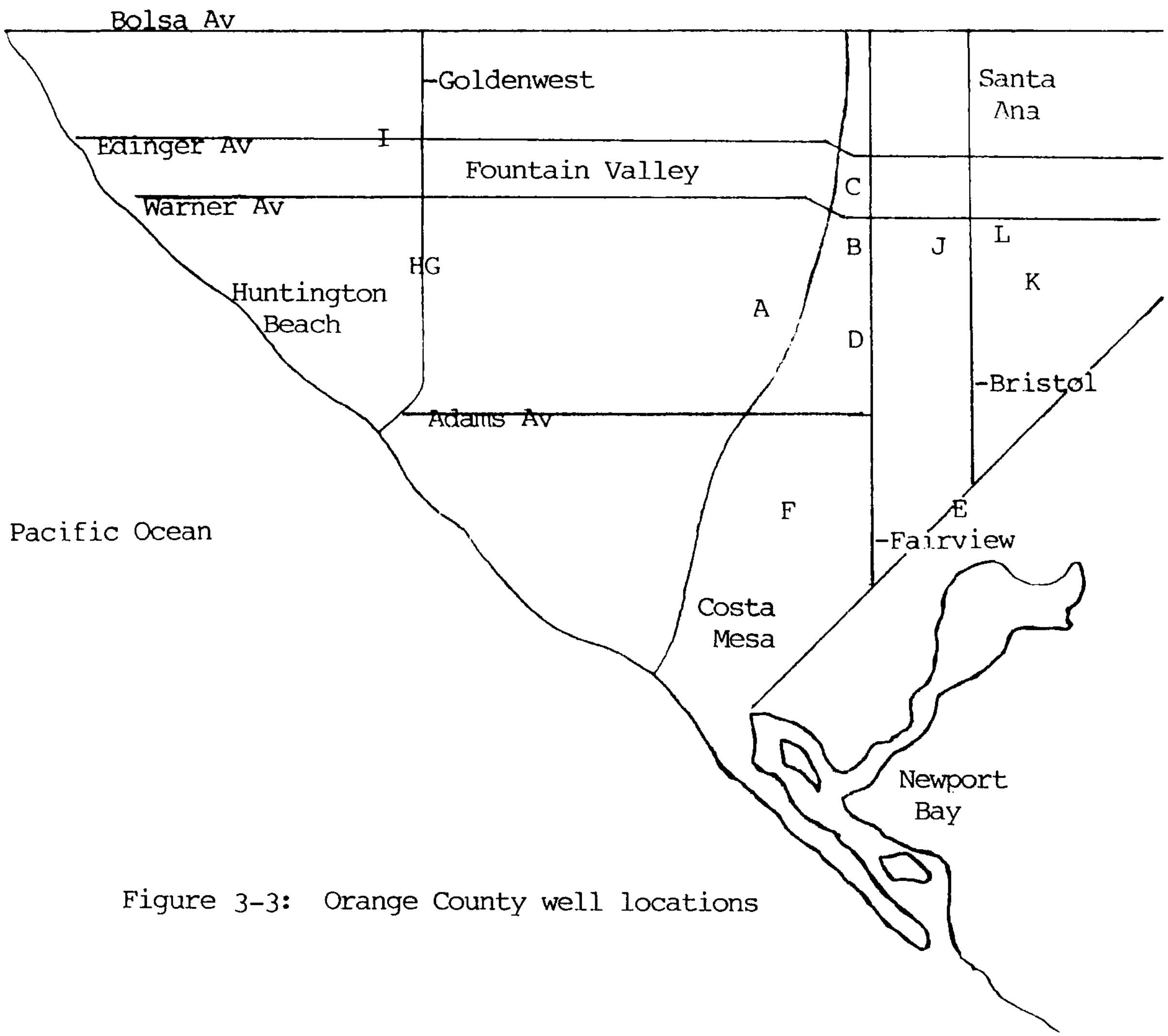
Beta Aquifer: This is the principal upper Pleistocene groundwater zone. The aquifer is typically 40-50 feet in thickness and contains abundant wood fragments (44). The Beta aquifer has moderate to high permeability and is confined in its northwestern reaches but merges with the Bolsa, Alpha and Lambda aquifers as the strata trend to the southeast. The Beta aquifer is not exposed (44) and recharge is only expected to occur through interactions with other water-bearing zones.

Lambda Aquifer: This is the deepest water bearing zone in upper Pleistocene strata. The aquifer typically ranges from 30-50 feet in thickness, contains wood fragments and has moderate to high permeability. The Lambda aquifer consists of marine deposits which conformably overlie marine silt and clay from the San Pedro formation. Recharge is expected to occur through aquifer interactions where the Lambda merges with Bolsa, Beta and water bearing zones from the San Pedro formation (44).

Wells sampled during this study draw water from many portions of these aquifers. Figure 3-3 presents the well locations used to obtain groundwater samples. Wells are identified by letter with corresponding sample numbers in the legend. Samples designated as Mesa and Carl T were part of a previous study on wells in the area. Samples designated with the prefix DR are from OCWD records and samples containing the prefix OC are part of the research which precipitated this thesis.

3.2.3 Potential Sources of Color:

Color found in Orange County groundwater is caused by the presence of dissolved humic substances (humic and fulvic acids) which are found in parts per million concentrations. This conclusion is based on the fact that removal of humic substances from Orange County groundwater corresponds to an average reduction in absorbance of visible light (wavelength = 408nm) of 97%. The following are potential sources for the humic substances found in Orange County groundwater



Legend

Well Loc.	Sample
A	OC#1 OC#15
B	OC#2 OC#6
C	OC#3
D	OC#4 Mesa
E	OC#5
F	OC#7
G	OC#8
H	OC#9
I	OC#10
J	OC#11 OC#12 OC#13 Carl T
K	DR#2
L	DR#4

Figure 3-3: Orange County well locations

samples. These candidate sources have been identified from literature, maps, and well logs:

1) Contamination from oilfield wastewaters.
2) Leaching of humic material from peat deposits located near the surface.
3) Contact contamination from oil deposits located in Pliocene and upper Miocene rocks.
4) Leaching of humic materials present in fine grained organic rich rocks.
5) Leaching of wood chips and vegetal fibers located in aquifer materials.
6) Leaching of natural organic materials contained in the vadose zone or carried with canopy drip.

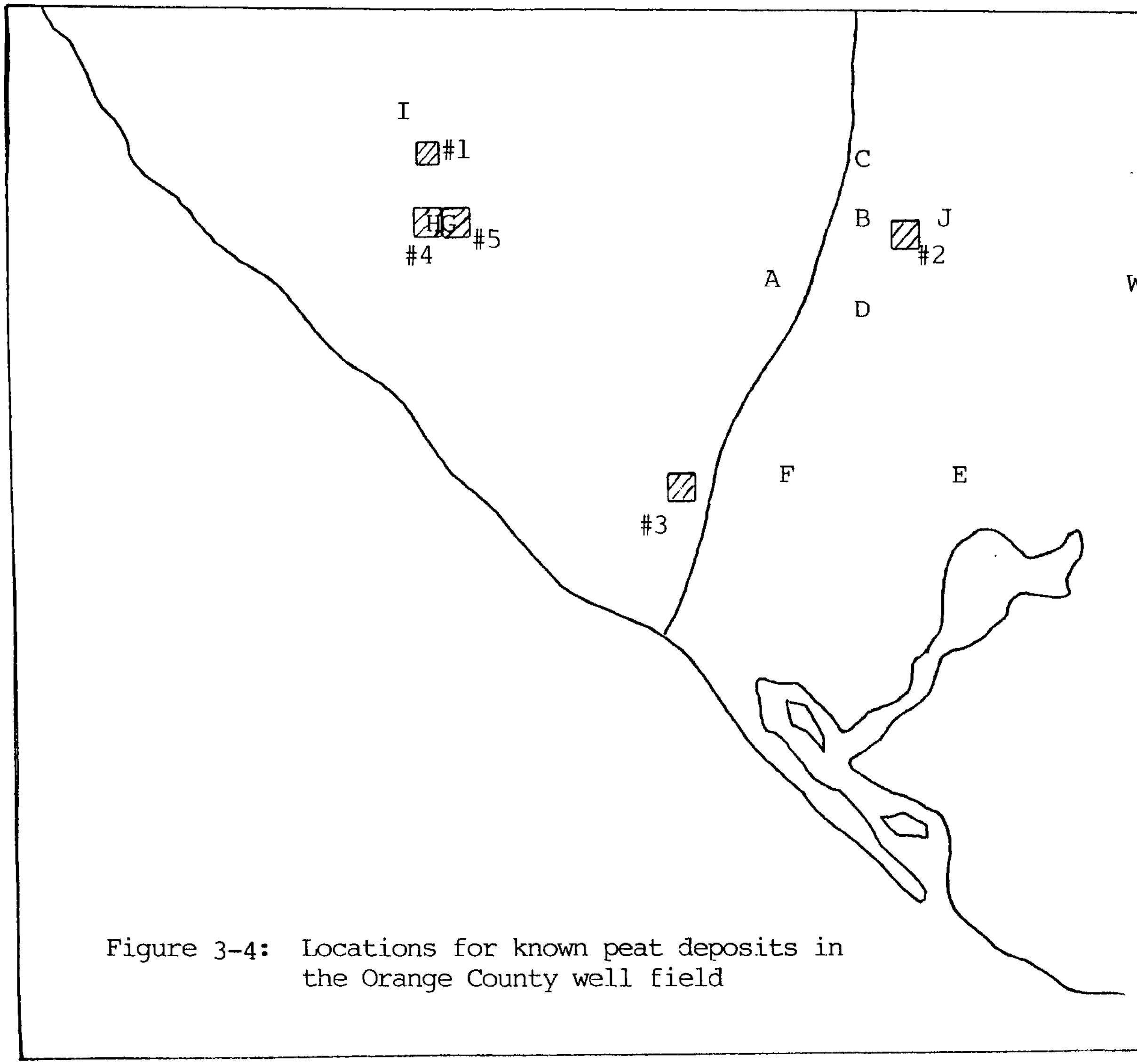
Waters responsible for the leaching of humic materials are largely contributed by percolating rainwater, streamwater and artificial recharge. Leaching occurs during migration from the surface and while waters are contained in the aquifer source rocks. The slow rates of flow, typical of groundwater, probably allow adequate contact time for the dissolution/hydrolysis of humic materials. The following discussion evaluates each of the potential sources of humic material.

<u>Oilfield Wastewater Contamination:</u> Immediately south of Orange County wells #8 and #9 (see Figure 3-3) a 14 foot bed of sand and gravel contains material that is tar stained or heavily coated with iron-oxide. Poland et al., (38) speculates that oil field wastewaters were discharged into what is described as a probable member of the San Pedro formation. Poland et al., go on to say that waste fluids discharged would doubtlessly percolate into underlying aquifers and possibly deteriorate the chemical quality of the natural waters.

While this may contribute adversely to local groundwater quality, it is doubtful that it constitutes one of the primary sources of color in Orange County groundwater. Typically, oilfield wastewaters are brines, therefore high total dissolved solids (TDS) concentrations might be expected along with the colored groundwater. This is typically not the case for Orange County groundwater except where sea-water intrusion has occurred.

Humic Materials Leached from Surficial Peat Deposits: Records from several well logs and geological maps show the presence of peat layers in recent deposits near the surface. Figure 3-4 presents the location of known peat deposits identified from well logs. Deposits range in depth from 1 foot at location #1 to 15 feet at locations #4 and #5.

Peat bog waters are typically very rich in DOC with average values around 30 mg/l (27,52) having been reported. Average color values for streams draining bog watersheds in Minnesota are approximately 300 platinum (Pt) units per liter (27). McKnight et al., (27) reported that Thoreau's Bog in Concord, Massachusetts had a hydrophobic DOC which was 77% of sample DOC. These characteristics are similar to those reported for Orange County groundwater. However, it is doubtful that peat deposits are fully responsible for the discoloration of Orange County groundwater. First of all, the deposits are fairly small and close to the surface. No mention has been made of water discoloration in the upper aquifers. Secondly, confining layers which separate the aquifers would probably prevent the migration of discolored water from the surface to depths as great as 500 to 1000 feet. Finally, the color/unit DOC ratio reported by



Legend

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G	OC#8
H	OC#9
I	OC#10
J	OC#11 OC#12 OC#13 Carl T
▨	Peat Deposits

Figure 3-4: Locations for known peat deposits in the Orange County well field

Bog in Concord, Massachusetts had a hydrophobic DOC which was 77% of sample DOC. These characteristics are similar to those reported for Orange County groundwater. However, it is doubtful that peat deposits are fully responsible for the discoloration of Orange County groundwater. First of all, the deposits are fairly small and close to the surface. No mention has been made of water discoloration in the upper aquifers. Secondly, confining layers which separate the aquifers would probably prevent the migration of discolored water from the surface to depths as great as 500 to 1000 feet. Finally, the color/unit DOC ratio reported by McKnight et al., (27) is significantly less than the color/unit DOC values measured for Orange County groundwater (7.0 vs. 16.5).

Contact Contamination from Oil Deposits: There are abundant oil deposits located in lower Pliocene and upper Miocene age rocks (57) in the Orange County area. Many of the oil fields are in or near accumulations of marine or deltaic sediments (17) which are typical of confining layers separating aquifers in Orange County.

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Although contact contamination is a potential source of organic carbon, it is doubtful that oil deposits are responsible for the color causing humic materials found in Orange County groundwater. Petroleum typically consists of abundant low molecular weight (C_5-C_{36}) hydrocarbons (5). Orange County DOC consists of high average molecular weight (1000-15,000) organic macro molecules. Additionally, thermal degradation, which is characteristic of hydrocarbon production, results in loss of functional groups (22). Orange County humic materials are rich in functional groups. Finally, most oil deposits lie stratigraphically below producing groundwater zones. Only the deepest wells (those which tap the Pico formation) are likely to contact oil bearing strata. The deepest, highly colored waters in Orange County are expected to draw water from the San Pedro formation and not the Pico formation.

Conversely, weak organic acids are the dominant species in oil field waters at temperatures higher than 80 degrees celsius (16). It is possible that migration of these waters has created some of the contamination found in Orange County.

Leaching of Humic Materials from Organic Sediments: In many ancient southern California depositional environments, poor circulation and rapid burial in restricted basins resulted in the preservation of the organic material contained in sediments (57). Many of the aquifers in the Orange County area are separated by confining zones of silt and clay (44). These confining zones (or aquicludes) are capable of slowly absorbing and transmitting water and during this process may contribute to the organic content of the groundwater. The long contact times and slow transmissibility typical of aquicludes may allow the establishment of pseudo-equilibrium between pore waters and lithologic surfaces.

Leaching of humic materials from organic rich strata is a likely source for groundwater DOC and color. The abundance of organic matter, slow rates of groundwater transmission and high groundwater pH values (7.9-8.7) create a favorable environment for the leaching of humic materials. Fluctuations in strata transmissivity (based on pumping demands and changes in infiltration) may account for variations in color values reported for specific wells.

Wood Chips and Vegital Fibers as a Source of Humic Materials: Lithologic well logs for Orange County wells frequently refer to the presence of wood chips, plant remains, minor organics and root hairs in the description of materials from core samples. The presence of wood chips or fragments has been reported for groundwaters contained in the Semi-Perched Zone, Alpha, Beta, Beta-Lambda, Silverado (or Main) and the Meadowlark aquifers. These materials are reportedly found in strata dominated by clay, sand or gravel as well as layers with varying grain sizes. However, the distribution or woody materials appears random at best, with many well borings reporting no presence of wood chips or other similar materials even though wells are closely spaced, tap the same aquifers, and are similar in depth.

Several well logs report the presence of black wood chips or describe wood fragments as charcoal. These wood chips probably represent an alteration of original material. It is probable that wood chips described as charcoal represent material burned prior to transport and sedimentation. It is also possible that these materials reflect post-depositional alteration of original woody material. The greater the degree of alteration or progression in organic maturation, the less likely that the material will release humics (or color) into solution (22).

Woody materials may represent an important source of DOC and color where they are locally very concentrated. It is doubtful that they constitute the primary source of DOC and color found in Orange County groundwater. Well logs for a highly colored water at Carl Thornton Park present no evidence of woody material. Conversely, well logs for low color wells (Dyer Road Wells #2 (DR#2) and #4 (DR#4) and IRWD #13 (OC#2,OC#6)) describe the presence of wood chips and other organic materials. It is important to note however, that screening intervals for these low color wells are typically very large which may promote successful dilution of local highly colored waters.

Leaching of Natural Organic Materials from the Surface and Vadose Zone: Thurman (52) describes various waters and characteristic DOC concentrations for those waters and states that precipitation is poor in DOC while canopy drip and interstitial waters are DOC rich. Additionally, Thurman points out that lake and river waters contain moderate to high DOC concentrations, but groundwater is DOC poor.

Precipitation leaches DOC from the canopy and organic material contained at the surface and in the soil. A portion of this DOC finds its way into streams and lakes where additional contributions from lake flora and micro fauna are added. At some point during migration to the groundwater zone a majority of this DOC is lost.

It is doubtful that DOC from canopy drip and the vadose zone contributes to color in Orange County groundwater. The shallowest aquifers (Bolsa, Talbert and Gaspur) are reportedly color free (41) and literature from research in the area neglects to mention the presence of shallow, color-bearing waters. Additionally, Thurman's scenario points out that DOC is lost with depth not gained as we would expect to see based on data from Orange County wells especially those located at Carl Thornton Park.

CHAPTER 4

DESCRIPTION OF WELL SAMPLE POINTS:

During the twelve month period May 1988-May 1989, eight separate Orange County wells were sampled on once and four wells were sampled twice. Figure 3-3 shows the horizontal well distribution at the surface and Table 4-1 provides a listing of well depths and casing perforation intervals. Figures 3-2, 4-1 and 4-2 are geologic cross-sections constructed from information provided in reference 38 and based on lithologic well logs.

Based on data presented in Table 4-1, water producing strata are found at depths as shallow as 105 feet and as deep as 1320 feet. Additionally, perforation intervals are as large as 570 feet and as small as 50 feet. Wells with large perforation intervals may draw from several aquifers and receive varying water qualities from each while wells with small perforation intervals may be drawing groundwater from only one aquifer.

TABLE 4-1: Summary of Orange County Wells

Sample	State Well #	Well Depth (ft)	Perforation Interval(s)(ft)
OC #1	5S/10W-32K3	926	780-880
OC #2	5S/10W-27G1	1015	410-980
OC #3	5S/10W-22Q1	1055	580-1055
OC #4	5S/10W-34Q3	650	105-?
OC #5	6S/10W-11G3	518	205-401
OC #6	5S/10W-27G1	1015	410-980
OC #7	6S/10W-9E3	225	?
OC #8	5S/11W-26M7	515	342-353 400-446 462-470
OC #9	5S/11W-26M8	515	342-353 402-463 482-486
OC #10	5S/11W-16RI	820	359-390 607-625 672-705
OC #11	5S/10W-26K3	1320	1260-1320
OC #12	5S/10W-26K2	1020	780-830 850-1020
OC #13	5S/10W-26K1	660	410-430 450-500 520-620 640-660
OC #15	5S/10W-32K3	926	780-880
MESA	5S/10W-34Q3	650	105-?
CARL T	5S/10W-26K3	1320	1260-1320

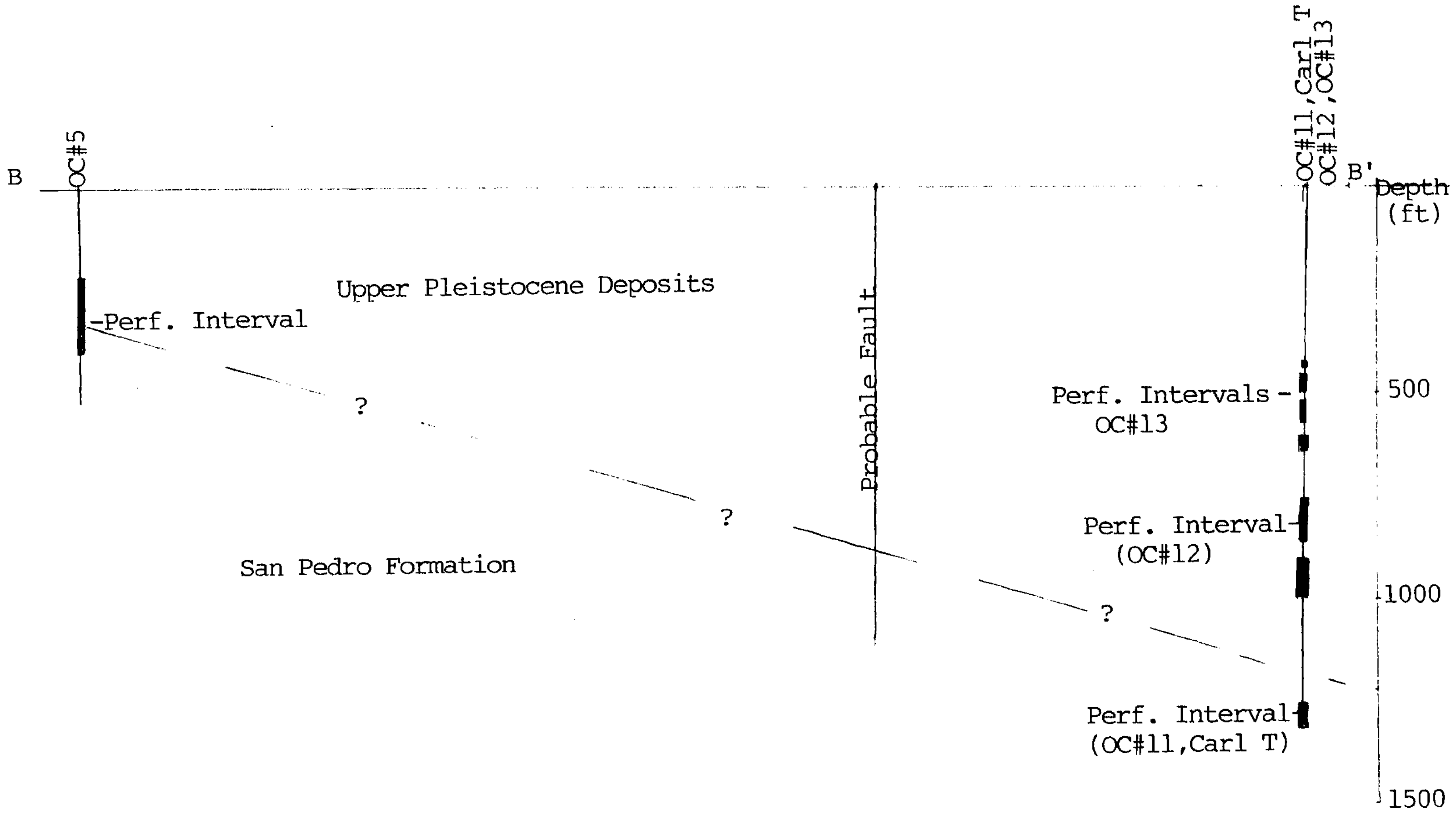


Figure 4-1: Geologic cross-section of the Orange County well field, OC#5 to Carl Thornton Park

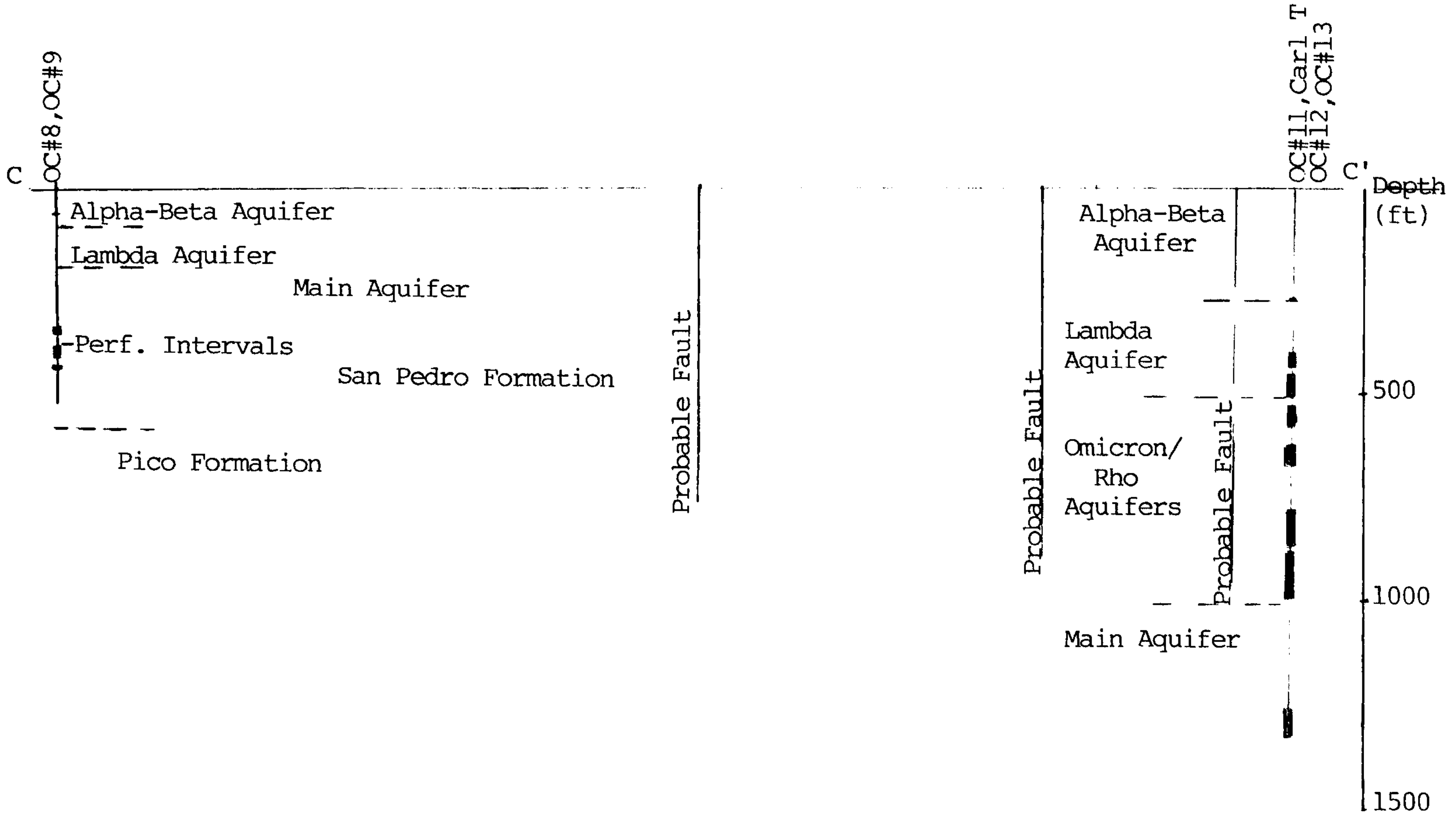


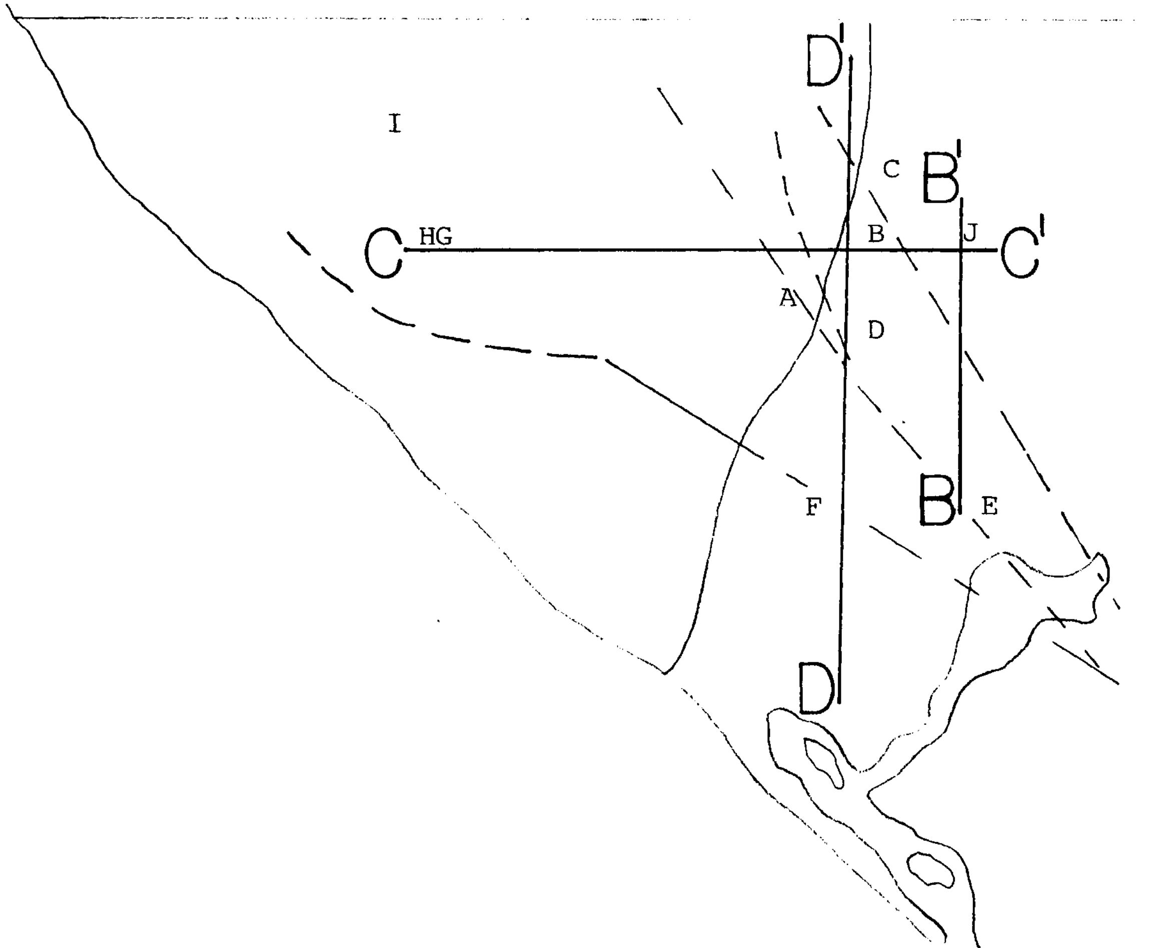
Figure 4-2: Geologic cross-section of the Orange County well field, OC#8, OC#9 to Carl Thornton Park

Several of the well sample points (OC#8-OC#10) are less than 3 miles from the ocean, while others are slightly more than 7 miles away. The entire well field is contained within a 35 square mile area lying between the cities of Huntington Beach, Newport Beach, Irvine, Santa Ana and Westminster.

Samples OC#11-OC#13 represent the change in water characteristics with depth at a single well. Groundwater characteristics for this well vary significantly as deeper screening intervals are employed. Each screening interval draws water from a different aquifer.

Geologically, the well field sits within a north dipping syncline and is transected by numerous faults including; the Bolsa-Fairview, Pelican Hill, Shady Canyon and other unnamed faults.

Figure 4-3 shows the position of faults with respect to well sampling points. Typically the faults are buried and their positions are inferred from subsurface geologic and hydrologic data, or extensions of where they appear at the surface. Figure 4-3 also shows the surface trace of geologic cross-sections from Figures 3-2, 4-1, and 4-2.



Legend

Well Loc.	Sample
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B	OC#2 OC#6
C	OC#3
D	OC#4 Mesa
E	OC#5
F	OC#7
G	OC#8
H	OC#9
I	OC#10
J	OC#11 OC#12 OC#13 Carl T
B-B'	Fig. 5-1
C-C'	Fig. 5-2
D-D'	Fig. 4-2
---	Fault Trace

Figure 4-3: Map of the Orange County well field showing the surface trace of faults and geologic cross-sections

CHAPTER 5

EXPERIMENTAL METHODS

5.1 Apparent Molecular Weight Fractionation:

The apparent molecular weight (AMW) distribution of dissolved organic carbon in Orange County groundwater samples was evaluated via ultrafiltration using Amicon stirred cells with Amicon YC and YM series hydrophilic membranes. Raw water and post-treatment samples were analyzed after ultrafiltration at molecular weight cutoffs of 500, 1000, 5000, 10000 and 30000 (YC05, YM2, YM5, YM10 and YM30 respectively).

Prior to initial use, each membrane was conditioned by soaking in distilled water for a minimum of 2 hours. The soak water was replaced and the filters were rinsed 4-5 times during the conditioning period. The membranes were then installed in the stirred cells (rejection surface up) followed by filtration with 150 ml of Milli-Q grade water. After filter preparation, 180 ml sample aliquots were processed using 50 psig nitrogen gas as a driving force. Processing involved the collection and disposal of the first

5 ml of filter permeate. This portion may have contained trapped pore water and also allowed flushing of the tygon exit tube. The following 130 ml of sample was collected and stored for analysis of DOC, absorbance at 254nm (UV abs.) and 408nm (visible) and THMFP (ug/L).

After filtration, the membranes and filter apparatus were washed using Milli-Q water and stored wet at 4 degrees Celsius. Membranes were used a maximum of 10 times prior to disposal. Sample contamination and analytical reproducibility were evaluated by successive filtration/analysis of three identical samples and by the use of experimental blanks. Blanks consisting of Milli-Q water were used to evaluate organic carbon contamination of the filtration apparatus.

Tables 5-1a and 5-1b present results of statistical analysis for ultrafiltered samples.

5.2 Humic Substances Content: Hydrophobic DOC vs. Hydrophilic DOC:

Table 5-1a: Replicate Series and Statistical Analysis for OC#4.

Parameter Measurements:

Fraction	n	DOC (mg/L) +/- C.V.(%)	UV abs (1/cm) +/- C.V.(%)	THMFP (ug/L) +/- C.V.(%)
<0.45 um	3	3.31+/- 2.1%	.185+/- 2.8%	196+/- 13%
<30K	3	3.00+/- 7.3%	.138+/- 3.3%	162+/- 6%
<10K	3	1.75+/- 8.8%	.079+/- 8.2%	117+/- 6%
<5K	3	1.31+/-16.0%	.049+/-26.0%	104+/- 12%
<1K	3	0.68+/-25.0%	.015+/-10%	67+/- 13%
<0.5K	3	0.58+/- 1.7%	.088+/-33%	47+/- 11%

Paired t-test Results

Fractions	Significance Levels* DOC	UV Abs	THMFP
<0.5K vs <1K	P<.20	P<.005	P<.01
<1K vs <5K	P<.025	P<.05	P<.01
<5K vs <10K	P<.05	P<.05	P<.20
<10K vs <30K	P<.005	P<.005	P<.01
<30K vs <0.45um	P<.05	P<.005	P<.10

*A 95% confidence level corresponds to p = .05

Table 5-1b: Replicate Series and Statistical Analysis for OC#8.

Parameter Measurements:

Fraction	n	DOC (mg/L) +/- C.V.(%)	UV Abs (cm-1) +/- C.V.(%)	THMFP (ug/L) +/- C.V.(%)
<0.45 um	3	3.44+/- 5.2%	.166+/- 0.0%	144+/- 9.0%
<30K	3	2.41+/- 2.6%	.118+/- 1.2%	120+/-16.0%
<10K	3	1.74+/- 0.6%	.072+/- 3.6%	95+/- 8.2%
< 5K	3	1.17+/- 3.8%	.038+/- 3.2%	83+/-15.0%
< 1K	3	1.01+/- 7.3%	.013+/-16.9%	55+/-12.0%
<0.5K	3	0.57+/- 3.9%	.003+/-15.7%	39+/-22.0%

Paired t-test Results:

	Significance Levels*		
Fractions:	DOC	UV Abs	THMFP
<0.5K vs <1K	P<.01	P<.01	P<.025
<1K vs <5K	P<.025	P<.005	P<.10
<5K vs <10K	P<.001	P<.005	P<.20
<10K vs <30K	P<.005	P<.0005	P<.01
<30K vs <0.45um	P<.01	P<.0005	P<.10

*A 95% confidence level corresponds to p = .05

Dissolved organic matter was separated into humic (hydrophobic) and non-humic (hydrophilic) fractions using a XAD-8 macroreticular resin (Rohm and Haas, Philadelphia, PA). The isolation of humic and non-humic fractions followed the procedure described by Thurman and Malcolm (1981).

One liter of groundwater was filtered through a 0.45 um Millipore membrane filter followed by sample acidification to pH 2.0 using concentrated HCl. The sample was applied at a flow rate of 5 ml/min to a 1 inch inside diameter pyrex column. The hydrophilic portion was collected as column effluent throughout the adsorption process and retained for analysis. Following sample application, the hydrophobic portion was eluted from the column using 0.1 N NaOH. A column mass balance based on DOC was performed to determine whether or not contamination had occurred and to insure successful desorption of the hydrophobic portion. Average carbon recovery from column mass balances was 98%.

Prior to column use resin bleed was evaluated by UV analysis at 254 nm. Sample application was initiated when effluent UV absorbance was non-detectable. UV analyses were also performed throughout adsorption to ensure that hydrophobic breakthrough did not occur. UV values throughout column operation remained constant for all samples evaluated.

5.3 Potentiometric Titration

Potentiometric titrations were performed on the hydrophobic (humic) portion of the samples after XAD-8 separation. The procedure employed was that described by Collins et al., (11). Carboxylic acidities of the hydrophobic acids were analyzed using a 100 ml three neck flask while maintaining a positive nitrogen atmosphere. After sample and blank (Milli-Q system water) pH adjustment to 3.0, 50 ml aliquots were titrated using 0.065 N NaOH. A filtration endpoint of pH 8.0 was used to operationally define carboxylic acidity. Titration curves (Figure 5-1) were developed by noting incremental NaOH additions and the corresponding pH change. The horizontal difference between the two curves at pH 8.0 can be used to calculate the carboxylic acidity using the following equation:

$$\text{Carboxylic Acidity} = \frac{\text{meq. of base for Hydrophobic sample} - \text{meq. of base for blank}}{\text{Hydrophobic sample organic carbon concentration}}$$

Analytical precision and accuracy were defined statistically and operationally by determining:

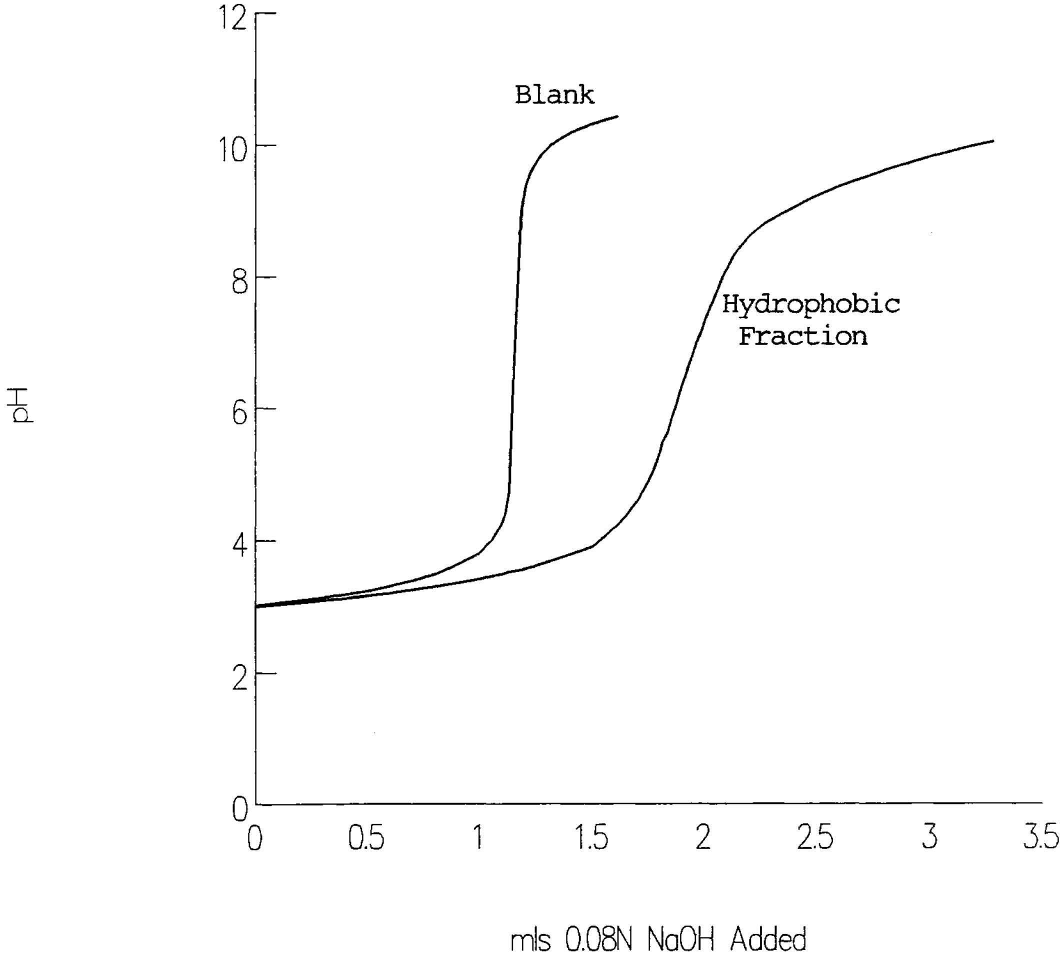


Figure 5-1: Carboxylic acidity titration curve for Carl T hydrophobic DOC fraction

1) Sample coefficient of variation.
2) Titration of a known concentration of salicyclic acid, and
3) Via third person potentiometric titration using a pH stat.

Values for statistical analyses can be found in Table 5-2. Single analyst accuracy was greater than 95% for the titrations while sample hydrophobicity varied by only 3.6%.

5.4 Dissolved Organic Carbon

Dissolved organic carbon (DOC) content was evaluated for all Orange County groundwater samples. Sample DOC was isolated by filtration through a 0.45 um membrane filter (Millipore Inc.). New filters were cleaned by passing a minimum of 500 mls of Milli-Q grade water through prior to sample filtration. The first 5-10 mls of filtrate was collected and discarded to prevent dilution affects from trapped pore water. Filters were used until noticeable changes in sample flux were observed, subsequently, a new filter was conditioned and filtration resumed.

TABLE 5-2: REPLICATE SERIES AND STATISTICAL ANALYSIS FOR XAD-8*

SAMPLE	N	DOC (mg/L) +/-CV(%)	UV@254 (1/cm) +/-CV(%)	CARB.ACID. +/-CV(%)	%PHOBIC +/-CV(%)
Phobic	3	6.9+/- 6%	0.409+/- 2%	14.4+/- 5%	90+/- 4%
Philic	3	0.8+/- 30%	0.014+/- 9%		

t-test Results:

SIGNIFICANCE LEVELS:

SAMPLE	DOC	UV@254	CARBOX. ACIDITY	%PHOBIC
Phobic	P<.002	P<.001	P<.001	P<.001
Philic	P<.05	P<.01		

*Analysis performed on samples from Carl Thornton Park

Following filtration, the pH of sample aliquots was adjusted to approximately 2.0 using 15% HCl solution. After pH adjustments samples were sparged with high purity air (<1ppm CO_2 , CO and hydrocarbons) to strip inorganic carbon from solution. After 5 minutes of sparging, 50 microliter injections were made into a Shimadzu TOC-500 Analyzer. Analyses were made by combustion using the non-dispersive infrared gas analysis method. Analytical results were compared to standards made using known concentrations of KHP in solution.

5.5 Absorption of Visible and Ultra-Violet Light

Optical properties of Orange County groundwater were evaluated using two techniques. The first involved measuring light absorption at visible and ultraviolet wavelengths. The second technique involved analyst perception of color and will be discussed later.

Sample absorbance at wavelengths of 254 nm and 408 nm was measured for groundwater aliquots after filtration through a 0.45 um filter. A Shimadzu Recording Spectrophotometer (UV-160A) was used for all measurements. A one centimeter cell was employed for sample analysis after standardizing the instrument using Milli-Q grade water.

5.6 Fluorescence

The parameter Fluorescence was measured using a St. John Associates, Fluoro-Tec Filter Fluorometer. The procedure involved continuous application of Milli-Q grade water (0.5 ml/min) past a mercury vapor excitation lamp to establish a baseline fluorescence. Sample detection was achieved using a side window cage-dynode multiplier phototube (PMT).

Filtered (<0.45um) samples were syringe introduced and pumped at a continuous rate of 0.5 ml/min. The emission wavelength selected was 320 nm while the excitation wavelength was 254 nm. Instrument accuracy was evaluated by measuring samples with known responses and correlating against UV values measured at 254 nm. Sample values required adjustment only after changing of the mercury vapor excitation lamp. Samples were analyzed in triplicate, mean values are reported.

5.7 Trihalomethane Formation Potential:

The trihalomethane formation potential (THMFP) was evaluated for treated and untreated Orange County groundwaters. Formation potential was determined by applying a 5:1 Cl_2:DOC (mass basis) ratio to water samples at pH=7. Samples were subsequently incubated at 20 degrees C for 168 hours prior to dechlorination and analysis by gas chromatography (GC). The presence of a positive chlorine residual was determined qualitatively before GC analysis.

The presence and concentrations of chloroform ($CHCl_3$), dichlorobromomethane ($CHCl_2Br$), dibromochloromethane ($CHClBr_2$) and bromoform ($CHBr_3$) were determined using a Hewlett Packard 5794 Gas Chromatograph with an electron capture detector (ECD). Compound separation was accomplished using a DB-1 Megabore Capillary column. A Hewlett Packard 3390 Reporting Integrator was used to process detector electrical signals and transform them into a chromatogram.

Prior to sample analysis, stock solutions containing known amounts of each THM species were extracted using 5 ml of pesticide-grade pentane. Extractions are required because the ECD cannot accept direct aqueous injections. THM extractions were effectuated through 2 minutes of sample agitation followed by syringe removal of two microliters of pentane. The two microliter sample volumes were injected and response factors calculated for each THM species. The instrument was operated at 45 degrees celsius for 3.5 minutes after which the temperature was raised to 85 degrees celsius for 4-5 minutes. Higher temperatures for lower volatility compounds provide more rapid analysis and decreased peak height to width ratios.

Following stock solution analyses calibration curves were developed for each species and used to determine the sample concentrations for THM species and total THM's. Samples were extracted and injected following the same procedure employed for stock solution analysis.

5.8 Total Organic Halide Formation Potential:

Orange County groundwater samples were evaluated for total organic halide formation potential (TOXFP) under a specific set of chemical conditions. The TOX parameter was measured using a Dohrmann DX-20 total organic halide analyzer.

TOXFP analysis is a three step procedure which includes halide generation, adsorption and quantification. The halide generation step required that samples be chlorinated at pH=7 for seven days to allow organo-halide formation. Samples were chlorinated based on a 5:1 chlorine to DOC ratio (mass basis) and incubated at 24 degrees celsius for 160 hours. Following incubation TOX samples were dechlorinated using sodium thiosulfate and the presence of a positive chlorine residual was determined qualitatively.

Adsorption of organo-chlorine compounds onto activated carbon was performed using the DX-20 adsorption module. Diluted TOX samples were acidified first using concentrated nitric acid (0.5 ml) followed by addition of one half a milliliter of sodium sulfite (0.5 M) to assist in adsorption. Two mls of sample were diluted to 50 mls to maintain the DX-20 in the optimum concentration range of 5.0-50.0 micrograms. After sample preparation, sample aliquots were passed through pyrex mini-columns containing granular activated carbon (Calgon Filtrasorb 400) and subsequently washed with 2 ml of nitrate solution (5,000 mg/L). Two carbon mini-columns were used in series for each sample to ensure that adsorbable compounds were retained.

The TOX analysis was performed after DX-20 start-up and recovery checks had been made. Recovery checks consisted of burning a standard solution of 2,4,6-trichlorophenol injected directly onto a pre-combusted piece of cerafelt in a sample boat. Both mini columns for each sample were burned separately and values were compared to ensure successful adsorption. Successful adsorption was assumed when the lower mini-column in the series had a value less than or equal to 10% of the upper column.

Analytical readouts from upper and lower mini-columns were added together and the difference between the sample and an analytical blank was calculated. Sample blanks were prepared by passing 50 ml of Milli-Q grade water through two carbon columns in series. Handling of blank extraction and analysis was identical to TOXFP samples.

5.9 Evaluation of Sample Color:

Sample color was determined by visual comparison with a Hellige Aqua Tester color disc (#611-11). Forty ml aliquots of sample were brought to room temperature and compared with a 40 ml standard of Milli-Q grade water viewed through wheel color designations. Samples were placed in a closed container and a light source was passed through the sample and simultaneously through the blank and color wheel. A side by side comparison was made and color values read directly from the wheel.

The Hellige color wheel is graduated into 10 pcu designations. Color values which appeared in between various graduations were assigned a value equidistant between adjacent wheel values. Analytical accuracy was confirmed by second and third party analysis. Analytical results from additional tests were averaged with initial results to provide the final color value.

Prior to initial use, Hellige color wheel accuracy was evaluated by preparing color standards in accordance with the procedure outlined in Standard Methods 204A, "Visual Comparison Methods". Complete agreement between the Hellige color wheel and color standards was realized.

5.10 Bromide Analysis:

The concentration of bromide ion in solution was measured using an Orion Ion analyzer #94-35. The bromide ion-specific electrode was used with a Corning pH meter #125 which processed electrical signals and provided digital millivolt readouts.

Prior to sample analysis, a calibration curve was prepared by successive analysis of five bromide standards. Bromide standards were prepared using stock solutions provided by Orion. Standards consisted of successive dilutions resulting in bromide ion concentrations of 100, 180, 260, 340 and 420 mg/L. A constant ionic strength was maintained by addition of one milliliter of low-level ionic strength adjuster (1.0 M NaCl) to both samples and standards.

After preparation of the calibration curve, 100 ml sample aliquots were analyzed for a millivolt reading following ten minutes of stabilization. A teflon stirbar was used to keep a constant flow of solution past the electrode sensor. The stabilization period was required for most samples because readout drift towards higher values occurred initially after sample introduction.

Millivolt readouts for groundwater samples were plotted on the calibration curve and bromide ion concentrations were subsequently read directly off the opposing axis. Following sample analysis, standards were re-analyzed to ensure that calibration had remained constant throughout the sample run.

CHAPTER 6

Analytical Results and Discussion:

6.1 Organic and Inorganic Data:

Samples of groundwater obtained from Orange County were subjected to a battery of analytical tests to determine water characteristics. The analytical tools used fall into three different categories. The first category consists of surrogate parameters used to define the waters from a non-specific standpoint. These techniques include analysis for DOC content, apparent molecular weight (AMW), color, absorbance (UV and visible), fluorescence, carboxylic acidity and humic substances content. Analytical results can be found in Table 6-1a and Table 6-1b.

The second analytical category focused on determining sample reactivity. Samples are subjected to a predetermined chemical environment and the response of sample constituents to that environment are quantified. This category includes analyses performed to determine THMFP and TOXFP. THMFP represents an estimation of the quantity of trihalomethanes

Table 6-1a: Analytical Data For Orange County Groundwater:

Sample	DOC (mg/L)	UV@254 (1/cm)	UV@408 (1/cm)	COLOR (pcu)	BROMIDE (ug/L)	Rel. Fluor (%)
OC#1	3.43	0.218	0.035	60	250	33
OC#2	1.29	0.062	0.012	15	230	11
OC#3	1.36	0.072	0.012	25	120	11
OC#4	3.21	0.183	0.036	55	160	24
OC#5	4.92	0.266	0.058	100	450	36
OC#6	1.35	0.060	0.013	20	184	10
OC#7	14.40	0.758	0.160	210	450	100
OC#8	3.44	0.166	0.031	55	392	28
OC#9	2.32	0.121	0.022	45	310	18
OC#10	1.19	0.046	0.008	13	319	10
OC#11	8.56	0.460	0.085	150	475	60
OC#12	1.20	0.059	0.011	15	291	8
OC#13	0.30	0.001	--	5	198	2
OC#15	3.15	0.188	0.032	60	318	28
MESA	2.63	0.154	0.031	53	460	22
CARL T	7.72	0.435	0.075	135	460	40

TABLE 6-1b: Analytical Data For Orange County Groundwater--cont.

SAMPLE:	THMFP (ug/L)	TOXFP (ug/L)	AVG AMW	% PHOBIC	CARBOX. ACIDITY (meq/g-c)
OC#1	254	1830	8,800	78	21.0
OC#2	137	1310	600	71	25.6
OC#3	117	590	3,600	63	22.7
OC#4	196	2630	9,300	78	17.8
OC#5	209	2420	12,000	94	16.4
OC#6	126	505	900	65	22.2
OC#7	389	3195	15,000	88	5.6
OC#8	144	1410	9,400	78	15.6
OC#9	160	890	8,700	78	21.5
OC#10	61	210	3,300	57	26.0
OC#11	206	1500	8,100	90	8.9
OC#12	87	835	11,000	65	23.7
OC#13	24	170	---	--	--
OC#15	180	1300	10,600	84	19.3
MESA	151	2175	9,800	85	22.2
CARL T	388	3345	12,200	90	14.4

which will be created during chlorination under a worst-case scenario. THM analyses are specific and each THM species is qualified and quantified. TOXFP operates under the same set of assumptions but represents a surrogate parameter. TOX values constitute a measurement of the totality of chloroorganic compounds created during chlorination which can be adsorbed by activated carbon. Values for THMFP and TOXFP can be found in Table 6-1a.

The final analytical category includes analyses which were performed by OCWD personnel. All analytical tests for these parameters were performed by OCWD personnel. Table 6-2a and 6-2b present results for all inorganic parameters evaluated. Background concentrations for VOC's were also determined but are not provided because all results were below the method detection limit (MDL) of 0.5 ug/L.

Tables 6-1a and 6-1b present analytical results listed chronologically. Samples OC#1-OC#15 were obtained during the period September 1988-April 1989. Mesa and Carl T samples were collected during July and May of 1988, respectively, and were part of a previous study.

Table 6-2a: Inorganic Analysis Results for Orange County Groundwater

Sample Number	TDS (mg/L)	Na (mg/L)	Ca (mg/L)	Mg (mg/L)	Fe (ug/L)	Mn (ug/L)	Al (ug/L)
OC#1	230	84	6.4	0.7	29.0	7.4	22.0
OC#2	232	64	17.0	3.0	15.0	0.5	14.0
OC#3	234	78	6.4	0.3	64.0	1.9	16.0
OC#4	208	68	12.0	2.0	22.0	5.1	18.0
OC#5	310	106	8.1	0.3	34.0	0.4	44.0
OC#6	256	63	16.0	3.1	11.0	2.2	60.0
OC#7	652	228	7.3	1.1	56.0	27.0	49.0
OC#8	204	69	6.5	0.3	ND	2.5	41.0
OC#9	246	73	7.4	0.3	17.0	1.0	27.0
OC#10	242	48	32.0	4.4	15.0	18.0	8.6
OC#11	272	86	2.5	1.0	77.0	4.0	63.0
OC#15	262	40	32.0	3.9	3.5	19.0	7.8

ND=Non Detectable

Table 6-2b: Inorganic Analysis Results for Orange County Groundwater.

Sample Number	NH3 (mg/L)	TKN (mg/L)	HDN* (mg/L)	ALK** (mg/L)	SO4 (mg/L)	EC (umho/cm)	COD (mg/L)
OC#1	0.5	0.7	18.9	174	4.4	382	12
OC#2	ND	ND	56.0	143	30.0	393	5
OC#3	ND	ND	17.2	144	29.0	379	3
OC#4	ND	0.1	38.0	157	17.0	371	9
OC#5	ND	0.2	21.5	177	8.8	514	13
OC#6	ND	0.1	52.7	148	29.0	354	58
OC#7	1.0	1.4	22.8	152	ND	1110	41
OC#8	0.4	0.4	17.5	126	7.5	339	10
OC#9	0.2	0.6	19.7	144	17.0	358	7
OC#10	1.0	1.0	98.0	150	35.0	399	3
OC#11	ND	0.3	10.4	174	0.9	382	26
OC#15	ND	ND	96.0	163	35.0	403	9

*Hardness
**mg/L as Calcium Carbonate
ND=Non-Detectable
EC=Electrical Conductivity at 25 degrees C.

Many of the results presented in Tables 6-1a and 6-1b are atypical when compared to much of the published data. It is generally accepted that aquatic humic substances account for roughly 50% of the DOC in natural waters (9) and that carboxylic acidities are generally around 10 meq/g-c (32,52,55). Thurman (15) reports that AMW ranges for humic materials in groundwater are approximately 500-10,000.

Much of the data in Tables 6-1a and 6-1b are unusual because values appear to be extreme in nature. For example, samples contain up to 94% hydrophobic material with an average value of 78%. Carboxylic acidities are frequently over 20 meq/g-carbon, and only the most extreme samples approach typically reported values. Orange County groundwater is also unique in its content of high AMW materials. Samples with average AMW up to 15,000 were analyzed and the colloidal organic carbon content (material >0.1 um in size) of four groundwater samples analyzed represented an average of 14% of DOC present in the sample. In addition, Orange County groundwaters appear to have high color/DOC ratios.

Table 6-3 presents TOC/DOC/COC relationships for various Orange County groundwaters. As this table demonstrates, there is a large amount of organic material which is greater

TABLE 6-3 : Relationship between TOC, DOC and COC for Orange County groundwater.

SAMPLE NUMBER	TOC (mg/L)	DOC (mg/L)	COC (mg/L)
OC#1	3.81	3.43	--
OC#2	1.37	1.29	--
OC#3	1.44	1.36	--
OC#4	3.50	3.21	--
OC#5	5.04	4.96	--
OC#6	1.41	1.35	--
OC#7	14.50	14.40	13.12
OC#8	3.61	3.44	2.68
OC#9	2.55	2.32	2.03
OC#10	1.19	1.19	--
OC#11	9.00	8.56	7.48
OC#12	1.20	1.20	1.06
OC#15	3.24	3.15	--

than 0.1 um in size. The 0.1 um cutoff represents the lower limit for colloidal organic carbon (COC).

DOC values for Orange County groundwater ranged from 14.40 mg/l to 1.19 mg/l. A direct linear relationship exists between DOC and absorbance (254 and 408) fluorescence and color. Values of r^2 for the four parameters when compared to DOC are 0.99, 0.99, 0.96 and 0.97, respectively. Figure 6-1 demonstrates the color/DOC relationship for Orange County groundwater. As a result of this strong linear relationship, basin distribution of DOC will be discussed in lieu of the other four parameters.

6.2 Well Field Divisions:

The Orange County well field can be divided into quadrants horizontally and vertically. Figure 6-2 presents the well field separated into horizontal quadrants based on DOC values. Quadrant I contains the lowest DOC (and hence lowest color) reported. Quadrant II contains the second lowest DOC values, Quadrant III and IV increasingly higher DOC and color values.

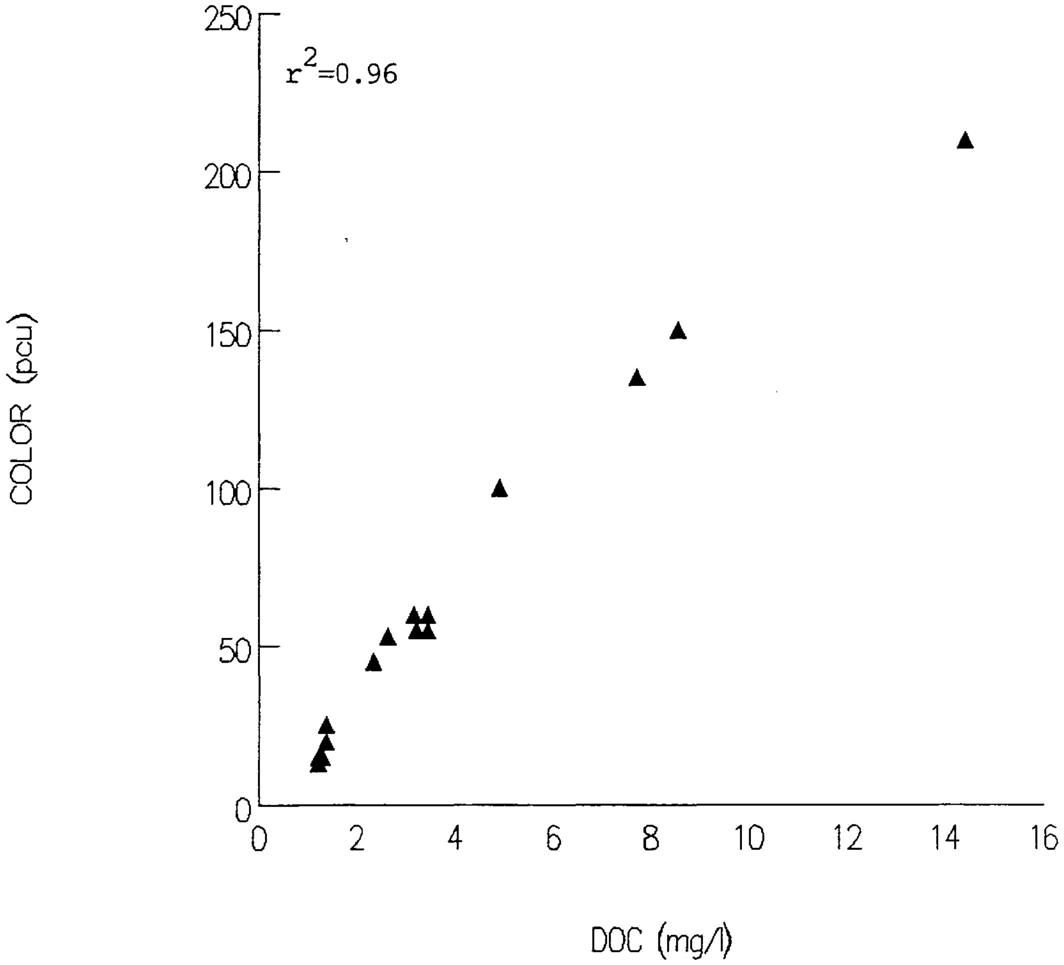
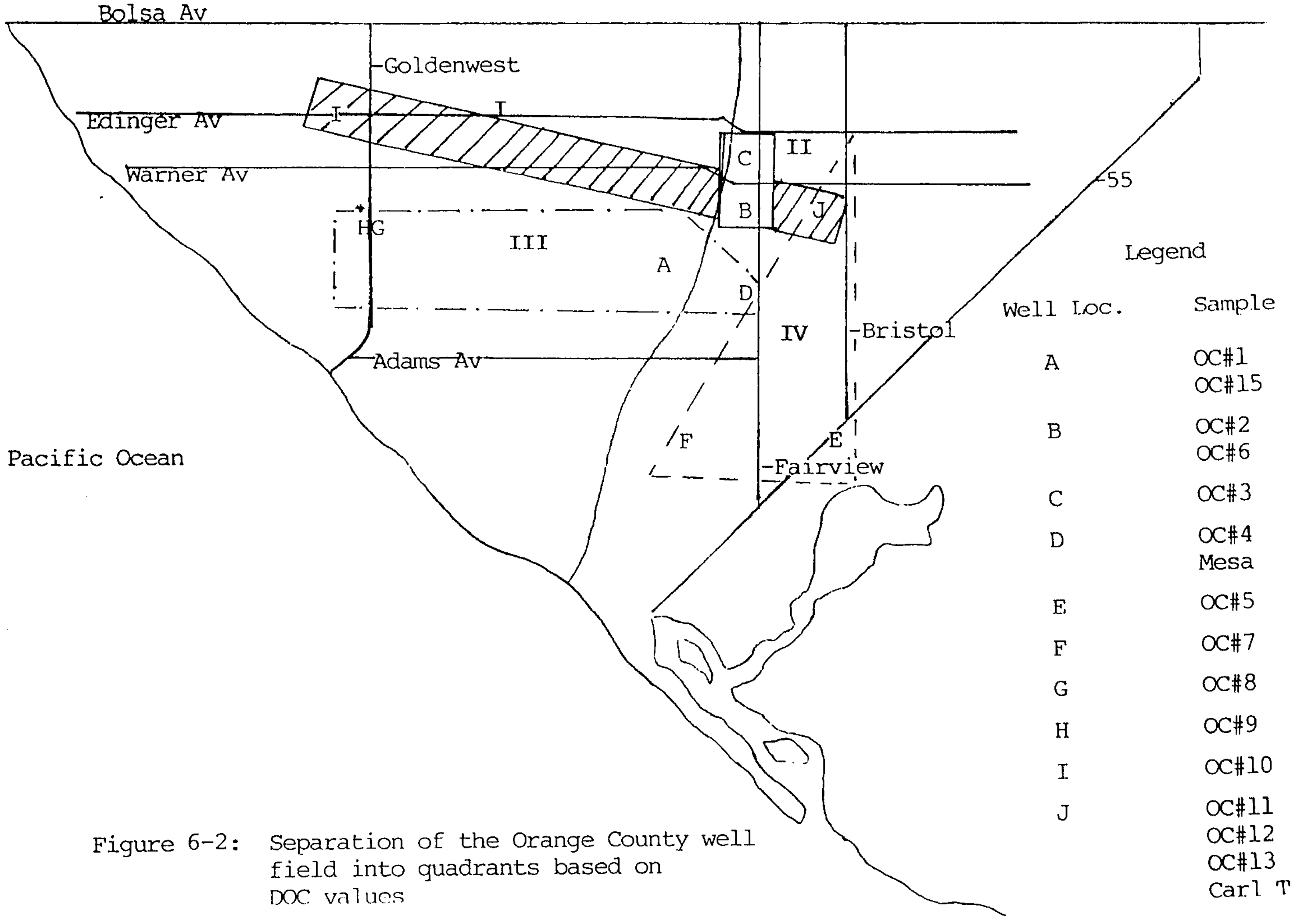


Figure 6-1: The relationship between sample color and DOC for Orange County groundwater



Legend

Well Loc.	Sample
A	OC#1 OC#15
B	OC#2 OC#6
C	OC#3
D	OC#4 Mesa
E	OC#5
F	OC#7
G	OC#8
H	OC#9
I	OC#10
J	OC#11 OC#12 OC#13 Carl T

Figure 6-2: Separation of the Orange County well field into quadrants based on DOC values

6.2.1 QUADRANT I:

Quadrant I wells are characterized by groundwater DOC values between 0.3 mg/L and 1.2 mg/L. Water, from Quadrant I wells, is of sufficient quality that extensive treatment may not be required. Color values are 5, 13, and 15 pcu which is at or slightly below the current secondary standard of 15 pcu. Worst case raw water THMFP is 24 ug/L, 60 ug/L and 87 ug/L for samples OC#13, OC#10 and OC#12 respectively. These values are close to the current primary drinking water standard for THM's of 100 ppb. Although OC#12 and OC#13 samples came from one of the Carl Thornton Park wells it is pumped from a shallower depth thereby avoiding highly colored waters.

Other characteristics shared by samples OC#10 and OC#12 are a low percentage of hydrophobic organic carbon (relatively speaking) and a high carboxylic acidity. These two organic carbon characteristics do not typically result in successful DOC removal by conventional treatment processes. Removal successes will be discussed in the following sections.

One of the primary differences in organic carbon between the two samples is the average AMW. Organic carbon from OC#12 has an average AMW that is 3.3 times higher than the average AMW of OC#10. This might be explained by geographical differences between the samples. The two wells are separated by a distance of approximately 8 miles and deeper waters found in Carl Thornton Park wells are characterized by high AMW organic material.

6.2.2 QUADRANT II:

Quadrant II waters are characterized by DOC values between 1.3 and 1.5 mg/l. Waters from these wells are typically low in color(15-25 pcu), have moderate THMFP (117 ug/L-137 ug/L) but high carboxylic acidity (22.2-25.6 meq/g-carbon). The DOC of these samples is relatively low in hydrophobic material (63-71%) and as a result of this and the high charge density, organic matter in these waters is expected to be relatively stable. It is important to note that although THMFP values are moderate, samples from these wells exhibited the highest reactivity (micrograms of THM production per milligram of organic carbon present) reported. This may be due to the low average AMW for Quadrant II waters.

The two wells which comprise Quadrant II draw water from middle to deep strata. Wells (see Table 4-1) are over 1000 feet deep and screening intervals are at least 2.5 times as large as the other wells tested. Large perforation intervals may be responsible for the low observed color values because strata with highly colored water may be diluted. Conversely, permeable strata may convey low colored groundwater to Quadrant II wells.

6.2.3 QUADRANT III:

Groundwaters from Quadrant III wells are characterized by DOC concentrations which range from 2.0 mg/L to 4.0 mg/L and are highly colored (45-60 pcu). Waters from these wells are characterized by a high degree of hydrophobicity (78-85%), high average AMW and medium to high values for THMFP. Carboxylic acidities are still quite high for several of the samples (OC#1 and OC#9) but others (OC#8 and OC#4) approach lower charge densities.

Wells from Quadrant III are moderately deep (470-880 feet) and are characterized by small screening intervals (less than 100 feet). Well D, from Figure 6-2, (OC#4 and Mesa samples) is 650 feet deep but has an unknown screening interval. The presence of higher DOC concentrations, smaller well screening intervals and depths similar to Quadrant II wells may indicate that color bearing waters are narrowly defined vertically and by increasing screening intervals successful color dilution can be achieved. The complexity of the basin and poor lithologic well logs prevent accurate correlation of strata between various wells.

6.2.4 QUADRANT IV:

Quadrant IV groundwaters are the most highly colored waters analyzed during this study. DOC concentrations for these groundwaters ranged from 4.92 to 14.40 mg/l and associated color values from 100-210 pcu. Although sample reactivity was lower than other quadrants, high DOC concentrations resulted in THMFP values from 200-400 ug/L. Average molecular weights for these groundwaters were typically very high (8,000-15,000 AMW) and sample hydrophobicity averaged 91%. These groundwaters were also characterized by a low charge density and hence charge neutralization removal mechanisms proved most successful for Quadrant IV waters.

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Two separate well conditions exist for Quadrant IV wells in terms of depth from which waters are drawn. The southern most wells (samples OC#5 and OC#7) are drawn from shallow aquifers (200-400 feet) while the northern well (Samples OC#11 and Carl T) is drawn from 1260-1320 feet. It is probable that each well pumps water from a similar stratigraphic sequence. Poland and Piper (38) indicate that in the vicinity of the southern wells, (locations F and E on Figure 6-2), the San Pedro formation (which is found at a depth of 280-300 feet) dips northward approximately, 300 feet per mile. At this rate, similar strata would be found at a depth of 1100-1300 feet in the wells at Carl Thornton Park, 3 miles to the north.

Of similar interest is the location of these strata in Quadrant III wells which lie between the southern and northern Quadrant IV wells. Samples OC#1, OC#15, OC#4 and Mesa, come from wells located 2-2.25 miles north of wells F and E. This would place the suspected color bearing strata at a depth of roughly 800-1000 feet. While perforation intervals for well A (samples OC#1 and OC#15) achieve a depth of 880 feet, partial contamination from upper strata in the contaminated area is possible. The depth of well D is 650 feet and is not expected to be influenced by these same strata.

Other Quadrant III wells draw water from shallower depths (samples OC#8 and OC#9) and are located slightly farther north and west. As a result of their location, the presence of faults, and unknown synclinal dips in the westward direction, stratigraphic correlations between Quadrant IV wells and western Quadrant III wells is difficult.

6.3 OTHER PARAMETERS:

Other parameters evaluated during this study are Total Organic Halide Formation Potential (TOXFP) and ionic bromide concentrations. Analytical results for these parameters are also found in Table 6-1a and Table 6-1b. The relationship between TOXFP and THMFP is poor with $r^2 = 0.76$, and the TOXFP:THMFP ratio is approximately 8.2:1 with extreme values of 14.4:1 and 3.4:1.

Bromide values can either be used as an indication of salt water encroachment or a technique for prediction of brominated THM species formation. Bromide concentrations in Orange County groundwater show no direct relationship to the concentration of brominated THM's formed after chlorination. The r^2 values for percent bromide content of THM's verses bromide ion concentration (ug/L) is less than 0.10. In addition, the percent chlorine as a hydrogen substitutent for THM species was 90%. In other words, 90% of the halogens on THM molecules was chlorine. As an indicator of salt water encroachment, bromide concentrations also showed poor agreement with TDS values ($r^2 = 0.25$), therefore, bromide ion concentration probably is a poor indication of salt water intrusion for this portion of Orange County.

Bromide analyses were duplicated by Orange County Water District (OCWD). OCWD employed ion-chromatography to quantify bromide ion concentrations and the OCWD results correlated very poorly with those obtained during this study. A comparison of analysis results can be found in Table 6-4 for those samples analyzed by both techniques. The data presented in Table 6-4 suggests two possibilities; 1) analytical errors were committed during analysis by one or both techniques, or 2) sample constituents interfered with ionic bromide quantification. The second scenario seems more likely for the following reasons:

Table 6-4: Comparison of Bromide Ion Concentrations by Two Separate Analytical Techniques:

Sample:	Concentration (ug/L) ISE*	IC**
OC#4	160	<100
OC#5	450	300
OC#6	184	<100
OC#7	450	1,800
OC#8	392	<100
OC#9	310	<100
OC#11	475	<100
OC#13	198	200
OC#15	318	<100
OC#16	243	<100

* Ion-Specific Electrode Technique
** Ion-Chromatographic Technique

1. Using the ion-specific electrode technique, standards reached equilibrium rapidly while groundwater samples often took 5-10 minutes.

2. Highly ionic humic and fulvic acids may have interfered with millivolt readings displayed by the electrode meter.

3. The only sample where agreement exists for both techniques has virtually no dissolved organic carbon present (<0.3 mg/L) and hence mitigates the potential for humic and fulvic acid interference.

To circumvent these analytical problems, it may be advantageous to lower sample pH to 3.0 or less thus preventing humic and fulvic acid ionization.

6.4 Comparison of Treatment Techniques:

Bench scale testing was conducted on Orange County groundwater to identify treatment technologies successful in removing color, DOC and THM/TOX precursors. An additional goal was the recognition of sample characteristics which will allow the prediction of the most viable treatment technology.

Alum coagulation, ozone oxidation, activated carbon adsorption and membrane separation were the treatment technologies employed for DOC, color and THM/TOX precursor removal. Table 6-5 presents the fractional reduction in DOC and UV absorbance for each mass of treatment chemical added. This table can be used to compare DOC and UV removal success on a sample by sample basis. Those samples with the highest values for each column were most successfully treated by the specific treatment technique.

Values from columns 1 and 2, represent the removal of DOC by 5 mg/L Alum (as Al^{3+}) and 500 mg/L PAC (Calgon Filtrasorb 300), respectively. Column 3 provides DOC removal data for PAC doses between 25 and 100 mg/L, and column 4 demonstrates the reduction in light absorbance (at wavelength 254 nm) after application of 5.0 mg/L of ozone (applied dose). The final column is a listing of percent DOC removal by a Desalination Systems Inc., Desal 5 nanofiltration membrane operated at 200 psi. Removal success by the various treatment processes appears to be strongly related to the chemical characteristics of the organic carbon present in each groundwater sample.

TABLE 6-5: Treatment Success for Orange County Groundwater:

Sample	DELTA DOC/ Alum*	DELTA DOC/ PAC**	Delta DOC/ PAC***	DELTA UV/ 03****	%Removal by NF
OC#1	0.288	0.0051	0.018	0.015	-
OC#2	0.066	0.0012	0.008	0.006	-
OC#3	0.106	0.0019	0.010	0.007	-
OC#4	0.374	0.0050	0.019	0.021	-
OC#5	0.540	0.0061	0.030	0.012	-
OC#6	0.142	0.0016	0.010	0.008	-
OC#7	1.018	0.0156	0.041	0.013^	90.6
OC#8	0.39	0.0045	0.035	0.017	-
OC#9	0.27	0.0031	--	0.008	52.6
OC#10	0.092	0.0016	--	0.005	-
OC#11	0.852	0.0113	--	0.028	75.5
OC#12	0.072	0.0022	--	0.004	0
OC#15	0.306	0.0050	--	0.015	42.5
AVG.=	0.347	0.0049	0.021	0.012	52.3

* Alum dose = 5 mg/L
** PAC dose = 500 mg/L
*** PAC dose = 25-100 mg/L
**** Ozone dose ~5.0 mg/L applied
NF Nanofiltration
^ 20 mg/L applied

6.4.1 Organic Carbon Removal by Alum Coagulation:

The primary mechanisms by which alum removes organic material from solution are adsorption/destabilization, interparticle bridging and enmeshment. The removal mechanism which occurs is largely a function of solution pH and aluminum concentration. At the pH values found in Orange County groundwater with an aluminum concentration of 5 mg/L, sweep flocculation (enmeshment) conditions are expected to prevail (58).

Alum coagulation was fairly successful in removing DOC from solution under ambient pH conditions. Average DOC removal was 46% with values ranging between 25% and 57%. Treatment success may have been aided by the high average AMW typical of Orange County DOC. This is because coagulation/precipitation relies upon the growth of particles. The largest particles are the most likely to grow and be removed.

6.4.2 Organic Carbon Removal by PAC Adsorption:

The primary mechanisms by which activated carbon removes organic material from solution are physical, chemical, and exchange adsorption. Successful DOC removal requires that organic carbon molecules diffuse through the laminar liquid film surrounding PAC particles and accumulate at the PAC surface or continue to diffuse into internal carbon pores prior to attachment. The majority of available binding sites are located in carbon pore spaces.

Organic carbon removal by PAC is expected to be the greatest where charge densities are the lowest, molecular weights are high, and where pH values are reduced. This is because, hydrophobicity increases with increasing MW, decreasing charge density and decreasing pH.

DOC removal by PAC at ambient pH values was typically quite good although high PAC doses were employed. Average DOC removal was 66% with extreme values of 79% and 45% for PAC concentrations of 500 mg/L and four hour contact times. Even where DOC removal per mass PAC was good, an unfavorable adsorption isotherm existed. A favorable isotherm is concave downward while an unfavorable isotherm, as demonstrated in Figure 6-3, is concave upward.

6.4.3 Color Destruction using Ozone Oxidation:

Ozone oxidation is an entirely different removal mechanism from alum coagulation or PAC adsorption. Alum and PAC remove particles intact and represent accumulation at a surface or incorporation into a solid phase. Ozone oxidation is a destructive process which changes chemical characteristics. At the ozone doses employed (approximately 5 mg ozone per liter) very little organic carbon is oxidized completely to carbon dioxide and water. However, during the process of molecule oxidation, groundwater color (in the form of UV absorbance) is often substantially reduced.

At low pH values ozone directly attacks humic materials. At higher pH values or in the presence of catalysts like hydrogen peroxide and UV light, ozone is decomposed to a hydroxyl radical. The hydroxyl radical reacts more rapidly and is less selective than direct ozone oxidation.

Removal of UV 254 absorbing compounds by ozone oxidation averaged 49%. Values ranged from 30% and 64%. The relationship between percent reduction in absorbance verses

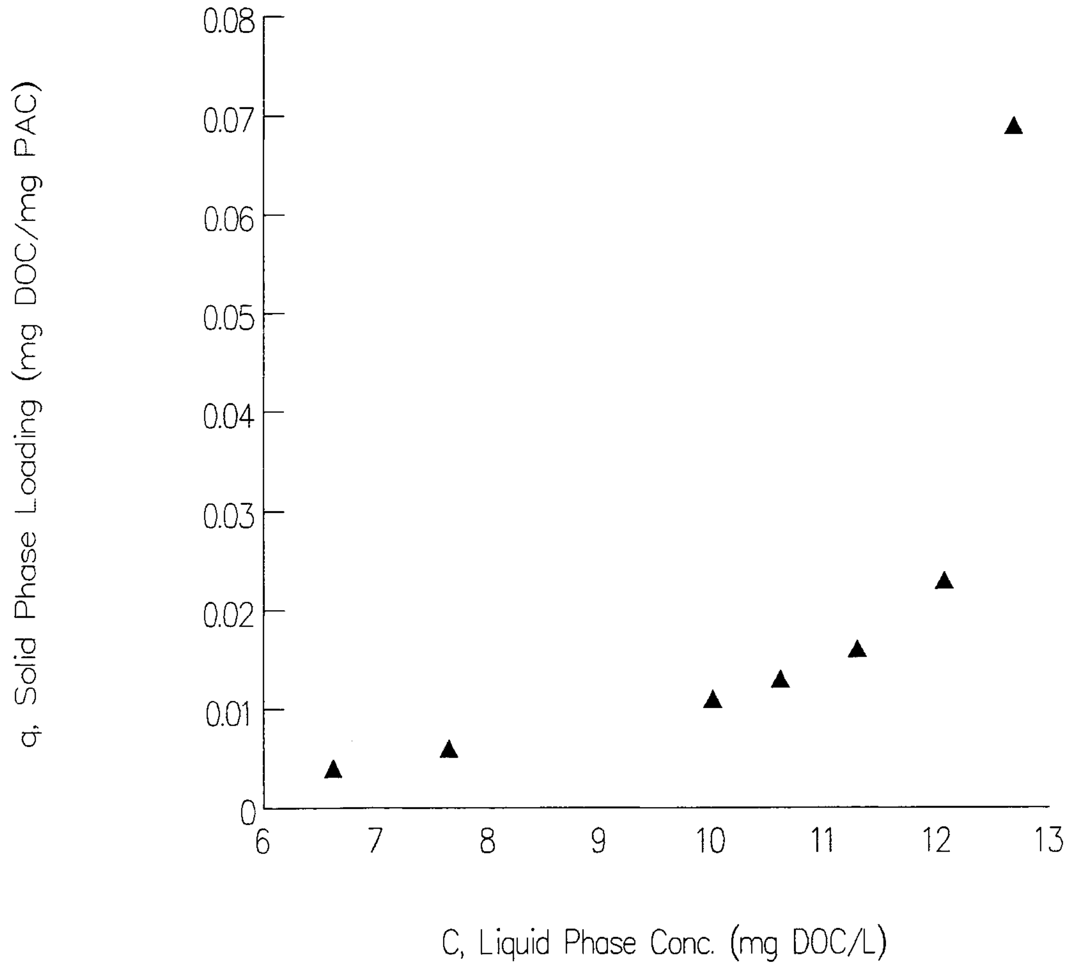

Figure 6-3: PAC adsorption isotherm for Orange County sample OC#7

ozone dose applied is best seen in Table 6-5. The largest values for delta UV/ozone dose applied represent the most successful removal. Sample characteristics which lend themselves to ozone destruction will be discussed in the following pages.

6.4.4 Organic Carbon Removal by Nanofiltration Membranes:

The removal of DOC by nanofiltration (NF) membranes is accomplished by applying feedwater under pressure to a membrane surface. A certain percentage of the feedwater is recovered as permeate while the remainder exits as a brine stream. The membrane is designed to reject all materials which exceed a specific molecular size.

A Desal 5 membrane with an approximate molecular weight cutoff of 100-150 was employed to evaluate DOC removal from Orange County groundwater. Permeate recovery was 1-2% of the original sample volume. The system was run in a closed loop where brine streams were recovered and reapplied to membrane surfaces.

Five groundwater samples were evaluated to determine DOC removal success by the Desal 5 membrane. Average DOC removal was 52% with extreme values of 91% and 0%. The 0% value can be explained in two ways; first, all DOC present had AMW less than the design membrane pore diameter; second, analytical error, membrane failure or sample contamination occurred. The second scenario is more likely because the average AMW for that specific sample was roughly 10 times the design pore diameter.

Disregarding the value of 0% removal seen in Table 6-5, membrane processes were quite successful in removing DOC from solution. This is especially true where high AMW organic carbon is present. Sample OC#7 had an AMW of 15,000, 91% of which was removed by the Desal 5 membrane.

6.5 Relationships Between Treatment Success and Various Surrogate Analytical Parameters:

One of the primary goals of this research was to define a relationship between removal success and various surrogate analytical parameters. By approximately defining these relationships, the ideal treatment scheme could potentially be determined simply by analyzing a groundwater sample for the appropriate parameter.

The principal surrogate parameters selected for use were carboxylic acidity, average AMW, Color/DOC ratio, and hydrophobicity (or percent hydrophobic organic material). The evaluation of each surrogate parameter allows a comparison to be made between expected results (based on theory) and experimental results.

6.5.1 Carboxylic Acidity and Removal Success:

Figure 6-4 is a graphical representation of DOC removal by alum as a function of carboxylic acidity. The graph demonstrates that a linear relationship exists between removal success and charge density. The correlation coefficient (r) for this relationship is 0.98 and the results agree well with predicted values.

Carboxylic acidity is an operational definition of the number of functional groups present on a humic molecule which undergo ionization between pH 3 and pH 8. High values for carboxylic acidity represent a high charge density and hence correspond to a more stable molecule in water. Increased stability generally results in poorer removal efficiencies, or greater chemical coagulant requirements. At a constant coagulant dose, such as that which is

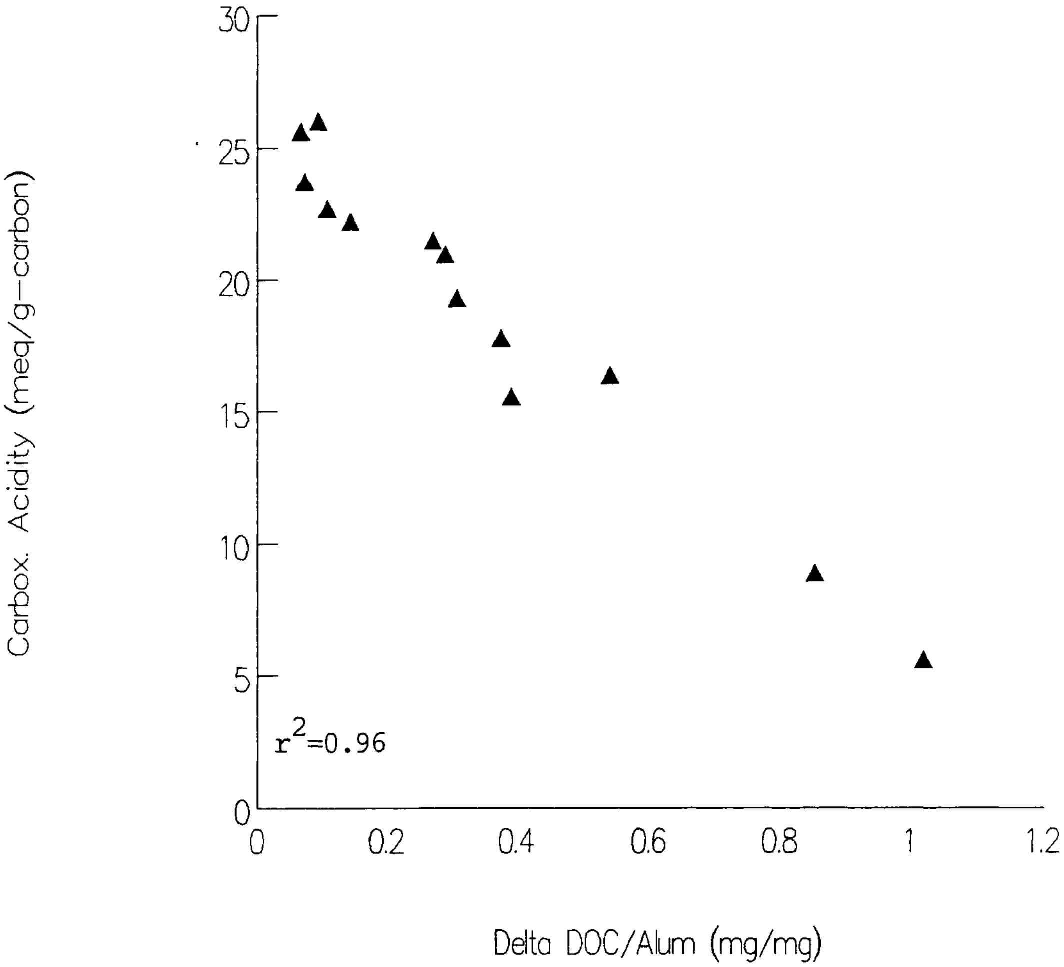

Figure 6-4: DOC removal by alum as a function of humic carboxylic acidity for Orange County groundwater

represented in Figure 6-4, one would expect organic carbon removal to be inversely proportional to carboxylic acidity.

A similar relationship is expected for organic carbon removal by activated carbon. Highly ionic materials are more soluble and thus tend to partition more favorably in the liquid phase. Activated carbon adsorption of organic carbon from Orange County groundwater increases with decreasing charge density. Figure 6-5 demonstrates this inverse linear relationship ($r^2 = 0.92$).

Ozone oxidation of Orange County groundwater organic carbon does not appear to be affected by charge density. In fact, a very poor inverse relationship exists between color removal by ozone (measured by light absorbance) and sample carboxylic acidity, ($r^2 = 0.44$).

A linear regression of the carboxylic acidity verses DOC removal by NF resulted in an r^2 value of 0.79. The small sample size may have biased this value, however, ignoring other factors, it appears that a strong inverse relationship exists between DOC removal by nanofiltration and carboxylic acidity.

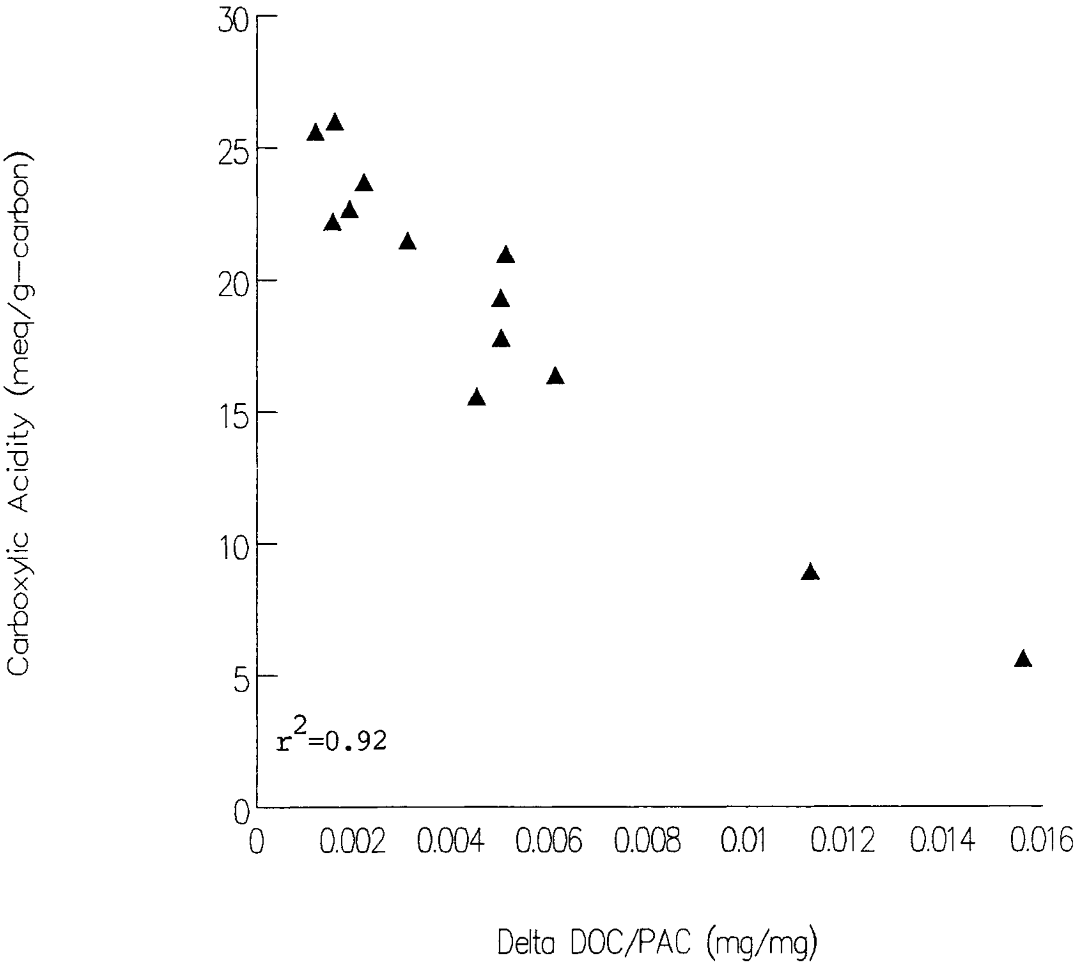

Figure 6-5: DOC removal by PAC as a function of carboxylic acidity for Orange County groundwater

6.5.2 Average AMW and Removal Success:

Organic carbon removal by various treatment techniques was evaluated as a function of average AMW. Average molecular weight was determined graphically on log-log probability paper by plotting percent organic carbon less than a specified MW cutoff verses the AMW of the membrane. Graphical results were confirmed numerically by assuming a linear distribution of organic carbon between each MW cut off and calculating the 50% value.

A typical AMW distribution for Orange County groundwater is shown in Figure 6-6. 70% of the organic carbon for this sample is contained in the greater than 10,000 AMW range and the less than 500 AMW range. As a result of this bimodal distribution of organic carbon, the average AMW is approximately 3,300. It is important to note that roughly 15% of the organic material is in the 1,000-5,000 AMW range, therefore sample response to treatment is not only a function of the average AMW but largely dependent on actual carbon AMW distribution.

Chadik and Amy (6) report that alum coagulation more successfully removes higher molecular weight organic

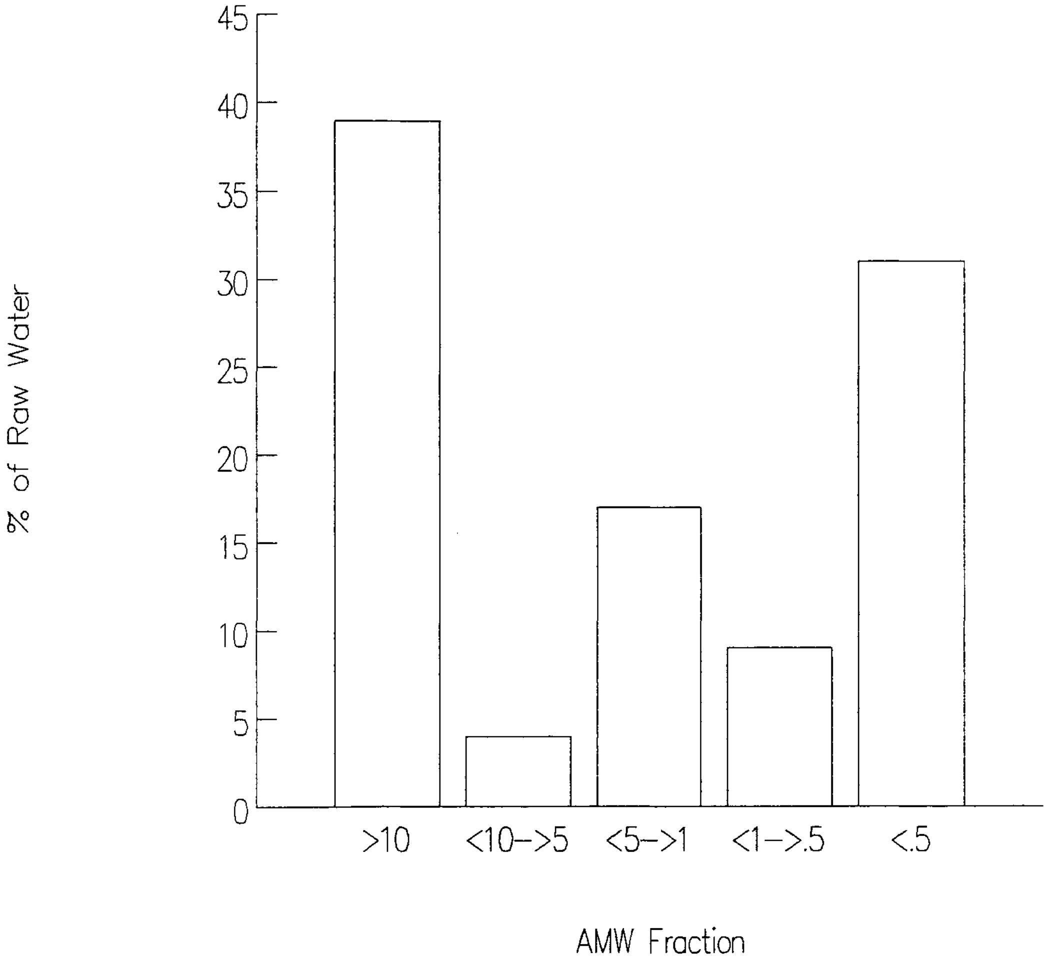

Figure 6-6: Organic carbon molecular weight distribution for OC#10

material. This is expected because higher MW material is typically less soluble and has been reported to have lower charge densities. In spite of this, a poor relationship exists ($r^2 = 0.43$) between organic carbon removal by alum and average AMW. This may be explained by the distribution of organic carbon for each sample. By reevaluating r^2 using 9 data points the correlation changes from 0.43 to 0.87.

The samples which were responsible for the variation in r^2 values do not correlate because their distributions of organic carbon are unusual. For example, Figure 6-7 depicts DOC removal by coagulation verses average AMW. Specific data points have been circled and the rationale for their positions is explained below. These data points do not represent erroneous values, rather they provide insight into chemical characteristics responsible for their positions.

Point #1: This sample (OC#7) has a very high AMW (15,000) with only 13% in the <1,000 range. Typically for Orange County groundwater, 29% of the DOC present is less than 1,000 in size, this means that almost 1/3 of normal groundwater samples consists of DOC which is difficult to remove. Because OC#7 has less than half the normal amount

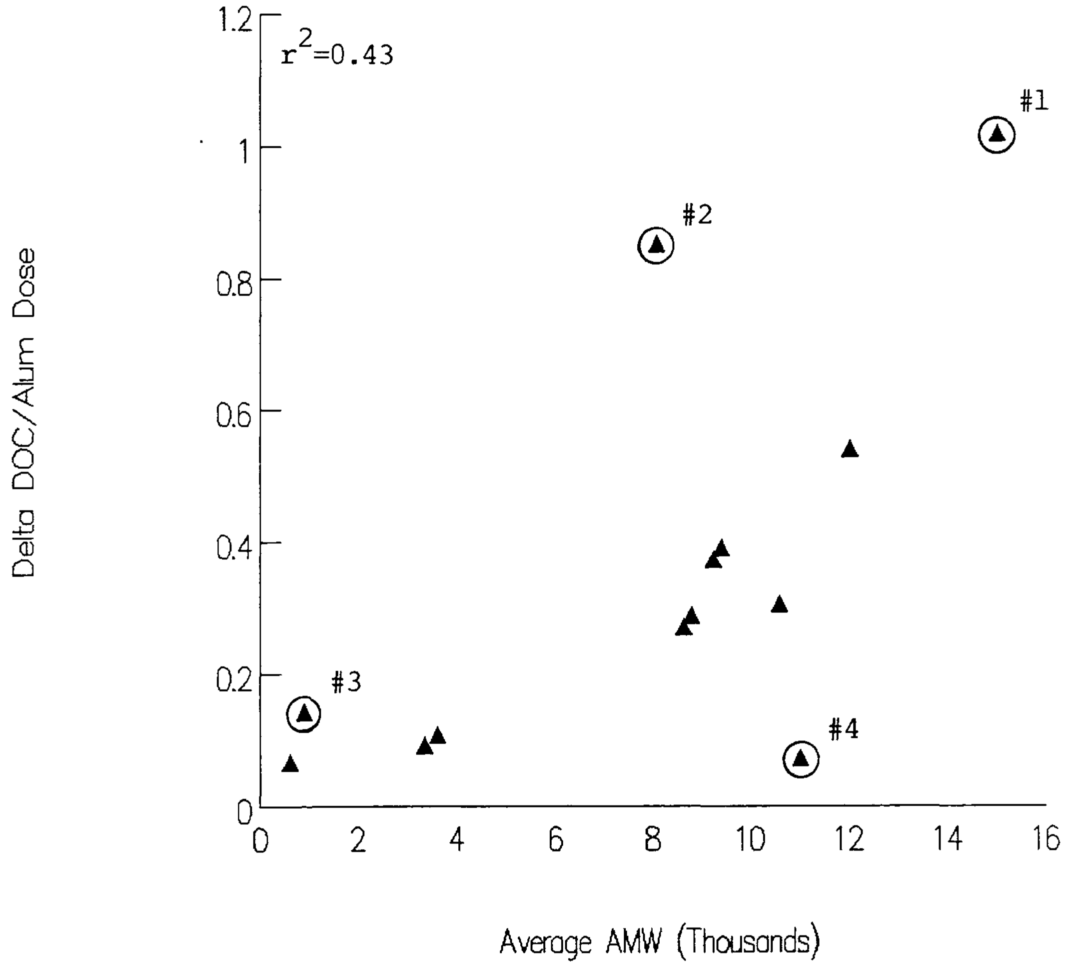

Figure 6-7: The effect of organic carbon average AMW on DOC removal by alum coagulation

of low AMW material, final removal success was greater.

Point #2: This is a similar scenario to #1. 14% of the DOC in OC#11 is <1,000 AMW while a great deal of DOC is in the 1,000-5,000 and 10,000-20,000 range. Because 86% of the DOC is greater than 1,000 in size, excellent DOC removal was expected, and occurred.

Point #3: This sample (OC#6) contains almost 40% of its DOC in the <500 range but 26% of the DOC is greater than 10,000 in size. As a result, a low average molecular weight is reported while almost 30% of sample DOC is large and amenable to removal by alum coagulation.

Point #4: The position for this sample (OC#12) has no rational explanation. 57% of sample DOC is greater than 10,000 in size and therefore should be amenable to alum coagulation. The sample carboxylic acidity is high which may be responsible for the poor removal noted. The highest carboxylic acidities are, however, generally associated with the lower AMW's. It is possible that the DOC result for the <10,000 fraction is erroneously high resulting in an overstated average AMW.

DOC removal by PAC is also expected to vary with AMW although Chadik and Amy (6) point out that MW has a smaller effect on PAC removal success than it does on alum coagulation. A poor correlation exists (r^2= 0.46) between average AMW and DOC removal by PAC. Figure 6-8 demonstrates the removal success of PAC compared with average AMW. With the exception of three values, a linear relationship (r^2 = 0.88) exists for Orange County groundwater.

Three data points, which are circled, have possible explanations as to their positions. The mechanisms which are probably responsible for ineffective adsorption are; 1) pore size exclusion and 2) increased solubility of organic molecules. In pore size exclusion, organic molecules are too large to migrate into PAC pore spaces. As a result, the only available attachment sites are on the molecules exterior thus reducing the total available attachment sites significantly. Increased solubility of humic materials is generally a function of charge density, molecular size and pH. There appears to be a direct relationship between AMW and charge density (smaller molecules being more densely charged) and in addition, pH effects the degree of ionization of humic materials.

Organic carbon removal from Orange County groundwater appears to benefit from increased molecular size. This is demonstrated in Figure 6-8 and therefore it is possible that charge density and/or pH control removal by PAC to a large extent. The cause of positions for circled data points are explained below:

Point #1: This sample (OC#7) has a low charge density (5.6 meq/g-carbon), high molecular weight and the relative absence of material <1,000 in size creates a favorable adsorption situation (relative to the other samples).

Point #2: This sample (OC#11) was successfully treated with PAC for similar reasons as Outlier #1. A low charge density (8.9 meq/g-carbon) and high hydrophobicity (90%) probably contribute to successful organic carbon removal.

Point #3: This sample (OC#12) has a high charge density (23.7 meq/g-carbon) which may be responsible for the poor unit removal by PAC. OC#12 is also characterized by a lower hydrophobicity (65%) and a high MW. The opposing forces of MW and charge density seem to have resulted in poor carbon removal, thus demonstrating that charge density probably controls organic carbon removal by PAC.

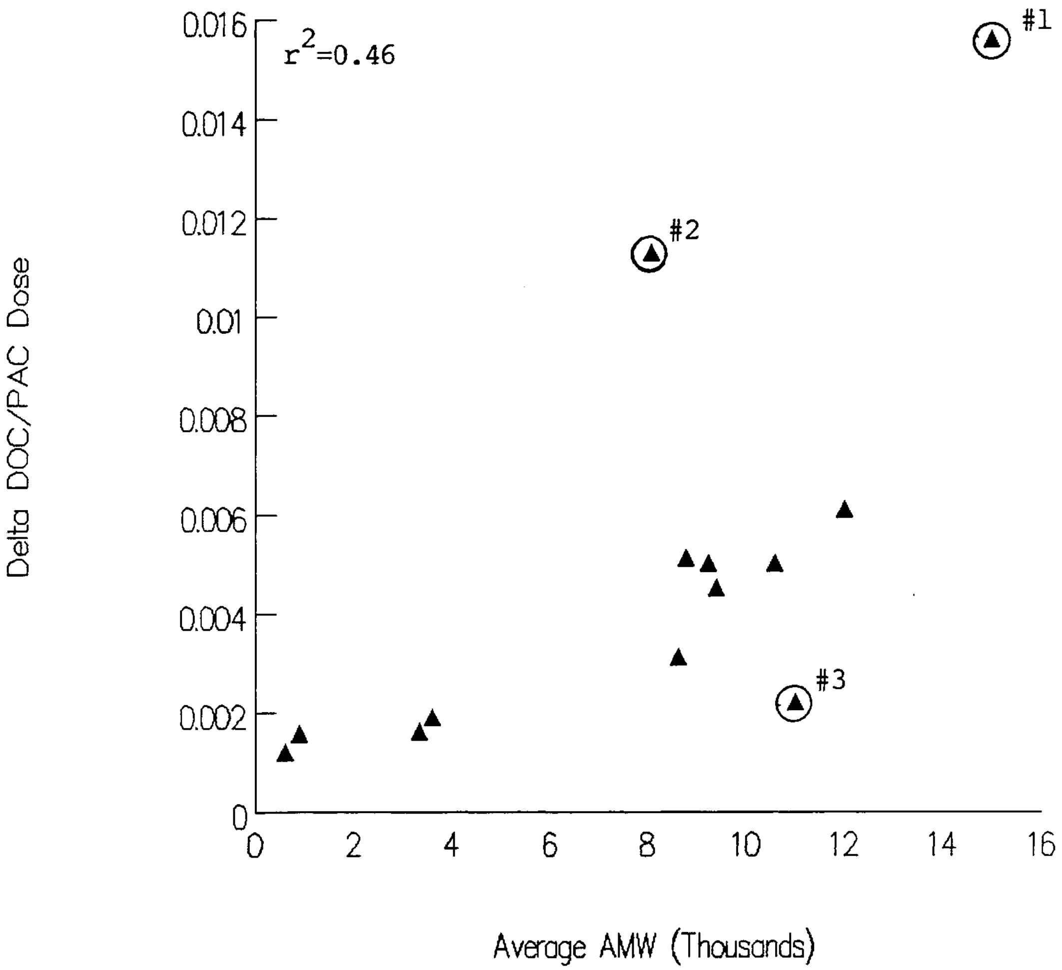

Figure 6-8: The effect of organic carbon average AMW on DOC removal by PAC

Removal of DOC by processes such as nanofiltration are expected to be influenced greatly by molecular weight. Nanofiltration membranes are designed based on the pore size exclusion of particular molecular weights.

Figure 6-9 is a graphical representation of the effect of average AMW on percent removal by nanofiltration (r^2 = 0.05). As seen in Figure 6-9, no apparent relationship exists. The sparse number of data points makes interpretation of this figure difficult, however a few statements can be made.

Data point #1 (see Figure 6-9) is sample OC#12. OC#12 has a very low DOC concentration (1.20 mg/L) and a very low color (15 pcu). Sample OC#12 does, however, contain high AMW organic material (Average AMW = 11,000). Analysis of nanofiltration permeate resulted in a DOC value of 1.6 mg/L. It appears therefore that sample contamination may have occurred to bias results towards the left side of the X-axis. Alternately, this data point, inconjunction with anomalous results for Figures 6-7 and 6-8, may demonstrate that analytical error in the DOC measurement for the <10,000 fraction has resulted in an overstated average AMW.

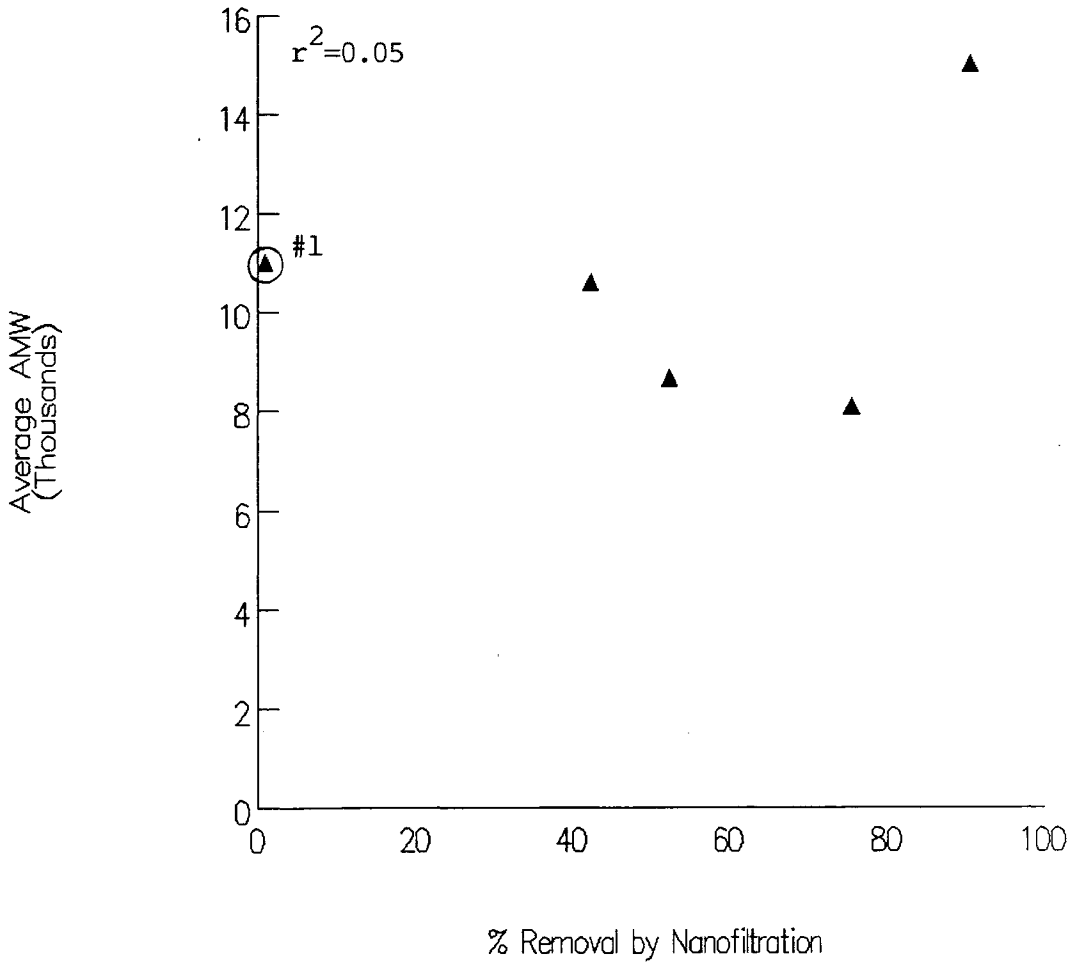

Figure 6-9: The effect of organic carbon average AMW on DOC removal by nanofiltration

Adjustment of the values employing a UV:DOC correlation (r^2 = 0.99) for other <10,000 fractions predicts a DOC value of 1.07 mg/L as opposed to the reported 0.54 mg/L value. This change alters the average AMW from 11,000 to 6,600.

Ozone oxidation of Orange County groundwater does not appear to be impacted by variations in the molecular weight of organic material. Figure 6-10 demonstrates the relationship between ozone destruction of UV absorbing compounds as a function of AMW. Poor linearity exists (r^2=0.14) between the two parameters which suggests that effective ozone destruction is independent of molecular weight.

6.5.3 Hydrophobicity and Removal Success:

The effect of hydrophobicity on removal success by various treatment techniques is expected to be good. Hydrophobic molecules typically partition at solid surfaces given the opportunity. Therefore, DOC removal by alum and PAC should increase with the degree of hydrophobicity. Figures 6-11 and 6-12 demonstrate the relationship between hydrophobicity and DOC removal by alum and PAC, respectively. From Figures 6-11 and 6-12 it can be seen that a good direct relationship exists between the various parameters. The majority of the

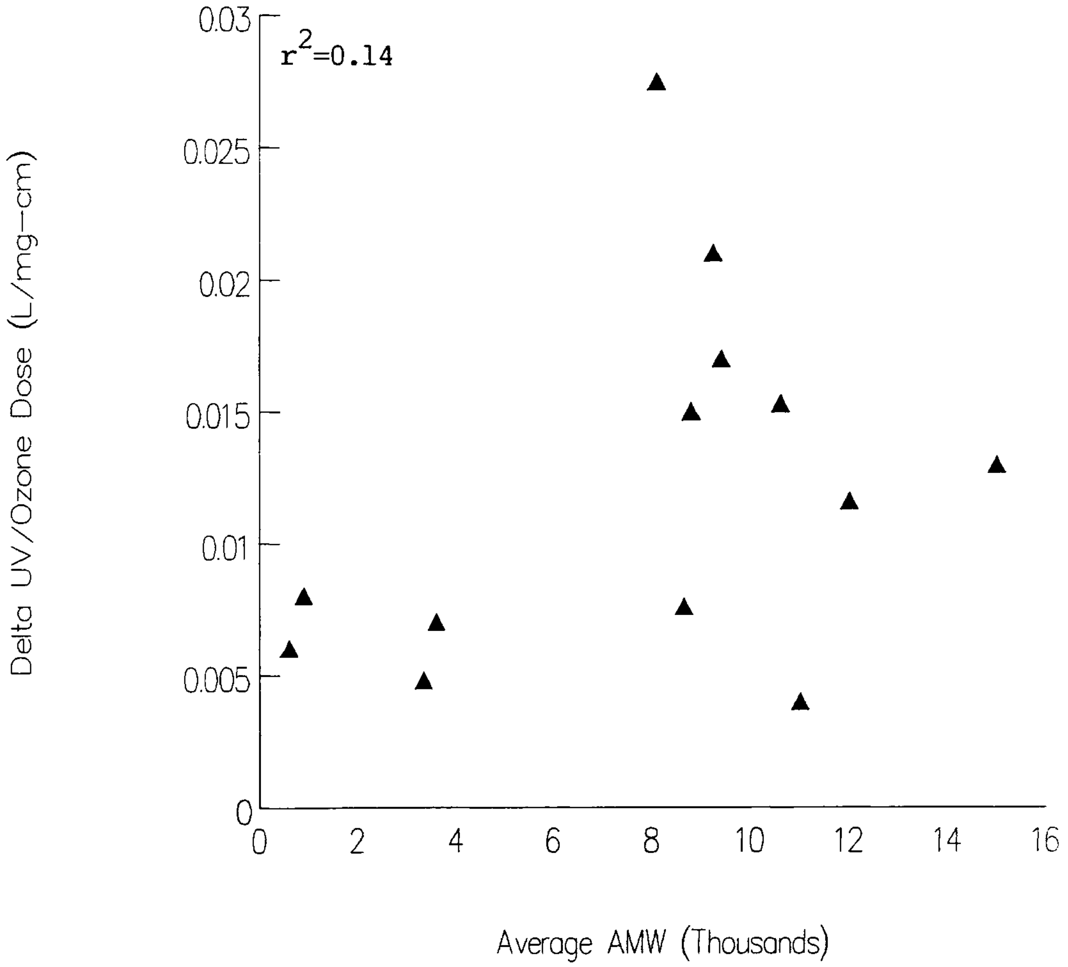

Figure 6-10: The effect of organic carbon average AMW on ozone destruction of UV254 absorbing compounds

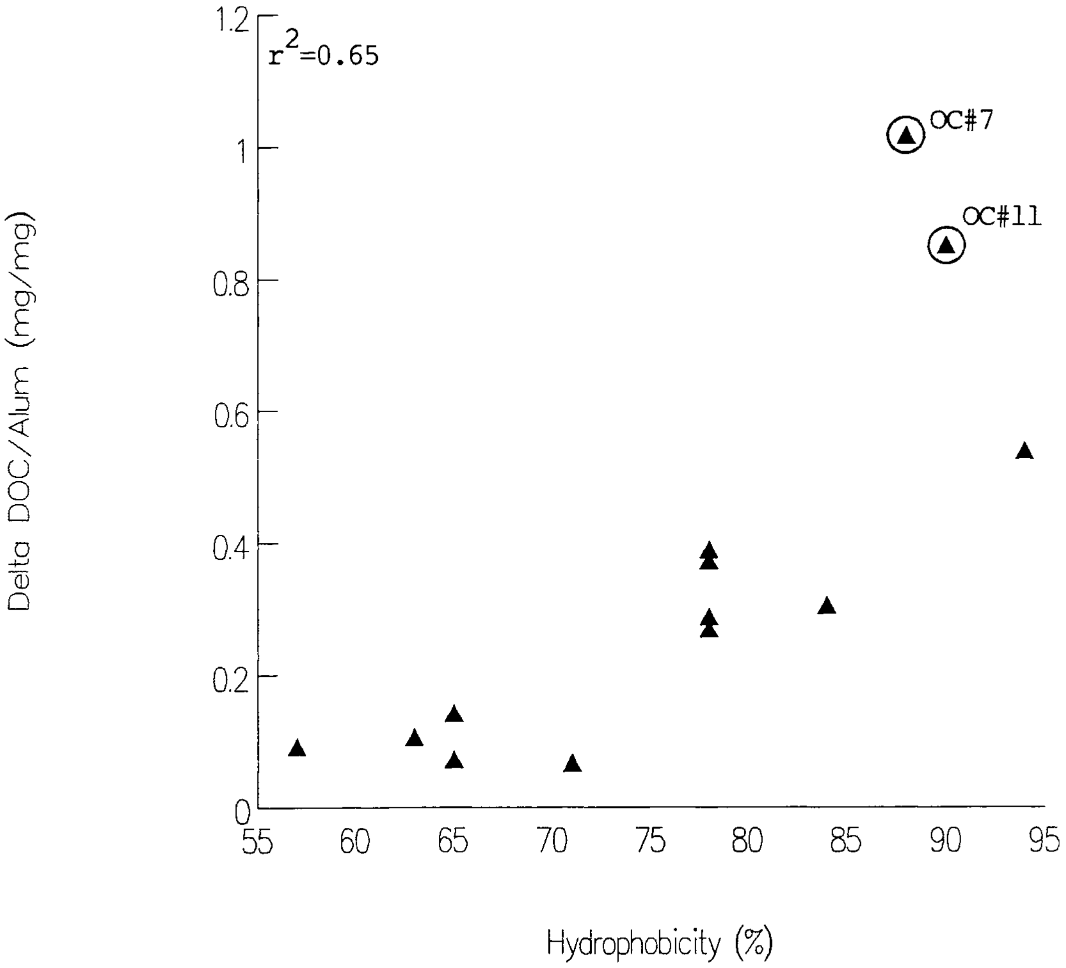

Figure 6-11: DOC removal by alum as a function of hydrophobic organic carbon content for Orange County groundwater

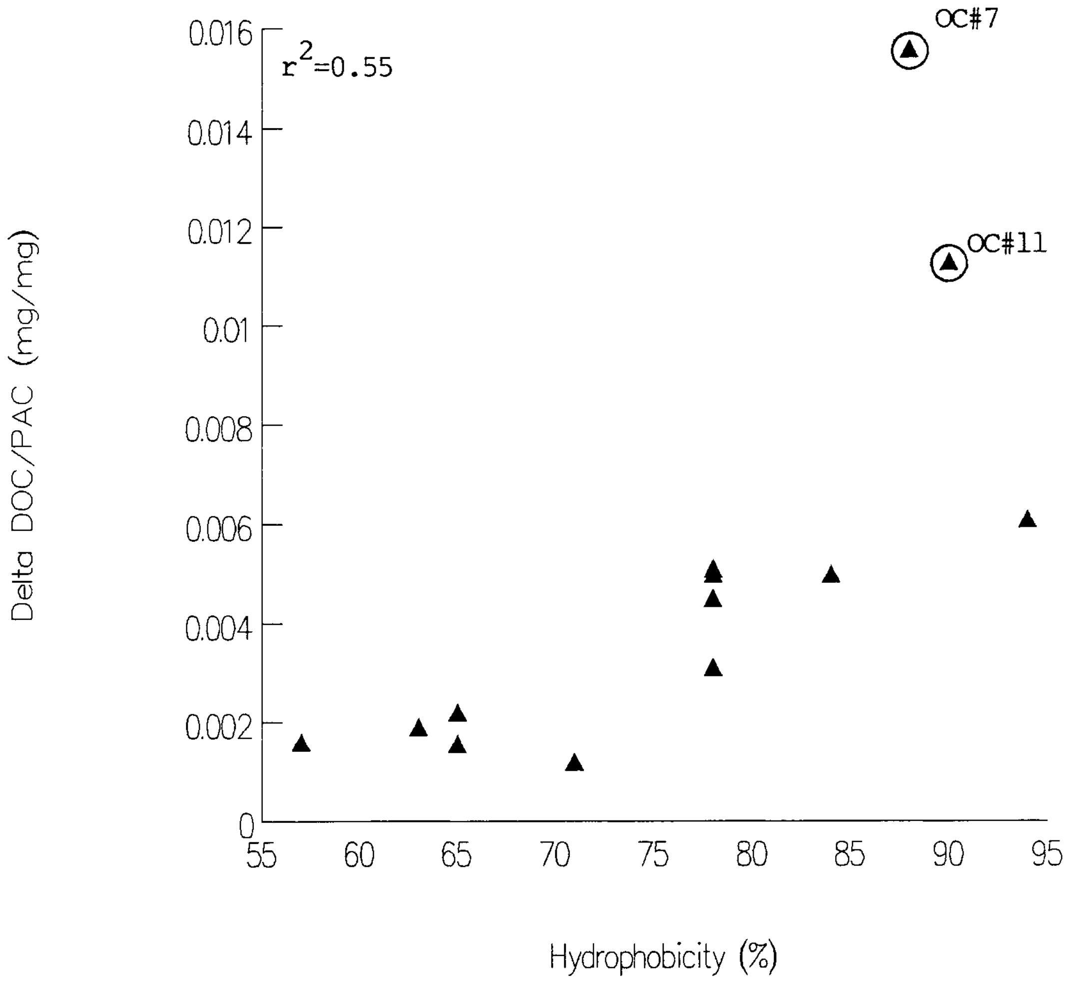

Figure 6-12: DOC removal by PAC as a function of hydrophobic organic carbon content for Orange County groundwater

variation in linearity is caused by 2 data points for the wells OC#7 and OC#11.

The primary difference between OC#7, OC#11 and the remaining samples, may be the abundance of high AMW materials present in the samples. Hydrophobicity is an operational definition of percent organic carbon made up of humic and fulvic acids. The basic assumption in Figures 6-11 and 6-12 is that all molecules are equally hydrophobic, which is erroneous. There is a general relationship between average AMW and charge density which can be seen in Figure 6-13. As Figure 6-13 weakly demonstrates, an inverse relationship exists whereby high AMW humic materials are more hydrophobic than low AMW humic materials. The reason that OC#7 and OC#11 are more successfully removed by PAC and alum coagulation is due to their relative abundance of low charge density humic materials.

An interesting relationship exists between ozone destruction of UV254 absorbing substances and hydrophobicity. Figure 6-14 shows how these two parameters are interrelated. It appears that there is a general increase in the destruction of UV254 absorbing substances per unit ozone applied with increasing hydrophobicity. As hydrophobicity increases,

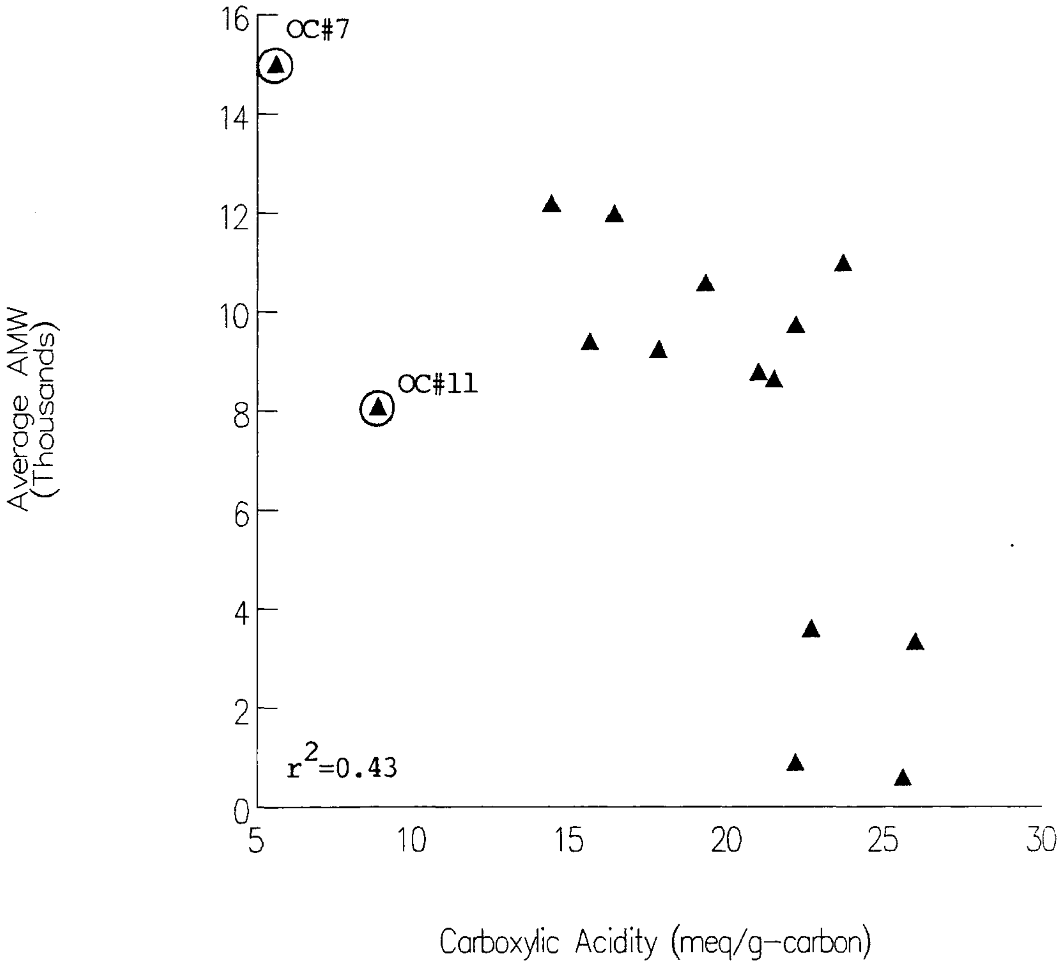

Figure 6-13: The variation of carboxylic acidity with changing average AMW for Orange County groundwater

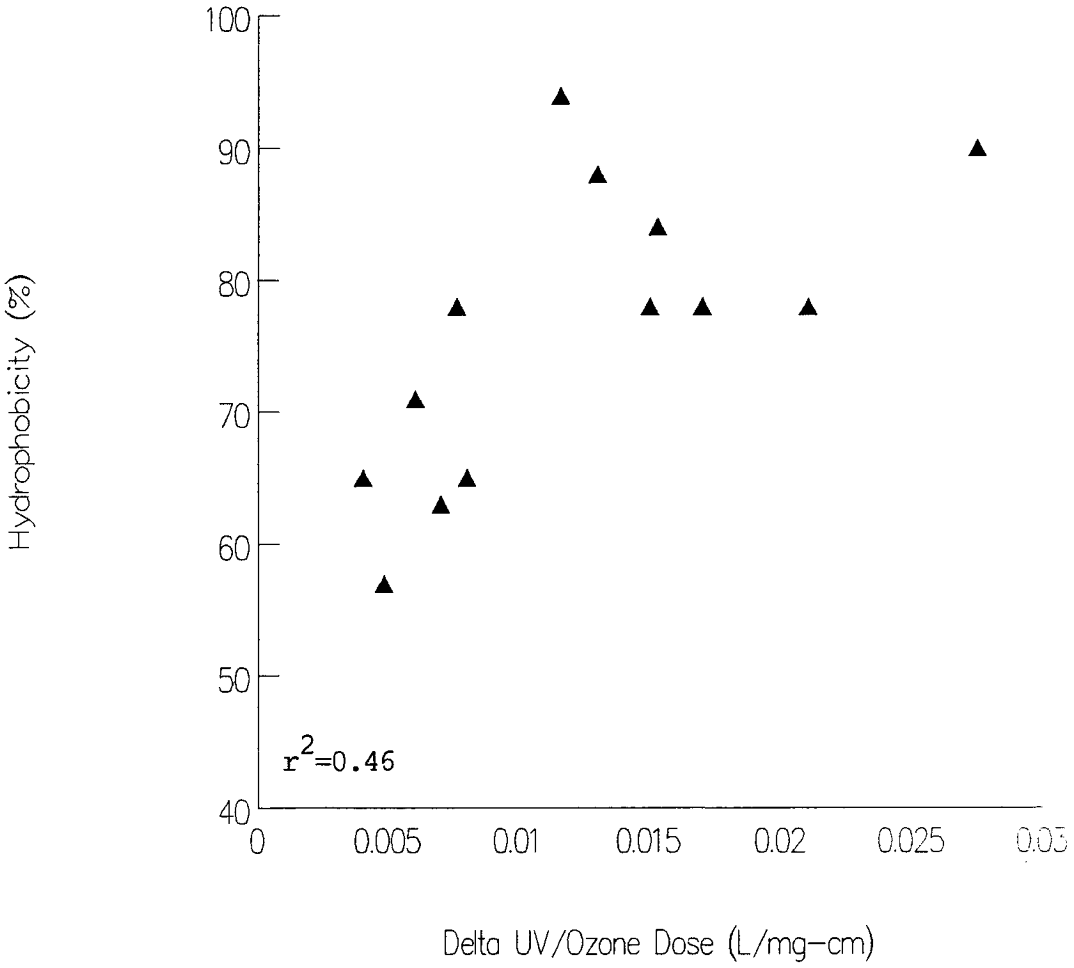

Figure 6-14: The effect of hydrophobic organic carbon on UV254 destruction by ozone for Orange County groundwater

specific absorbance increases, therefore, ozone is expected to lower the specific absorbance of a sample. Unfortunately, the data set is too small and the scatter too great to draw definitive conclusions in this regard.

6.5.4 DOC/408 and Removal Success:

The final group of correlations was selected to determine the effect of raw water combinational parameters (DOC/Abs.@408) on DOC removal. The DOC/408 parameter embodies the normalization of DOC values using a less subjective surrogate for color. High DOC/408 ratios are indicative of low color to DOC ratios. This in effect, is another method for evaluating sample hydrophobicity against DOC removal.

Figures 6-15 and 6-16 show the relationship between DOC removal by alum and PAC verses the DOC/408 parameter. Each case shows a poor correlation which tends to indicate that color causing properties are unrelated to removal success. Another way of interpreting this is that carboxylic acidity appears to be unrelated to color and hence chromophores are not centralized in functional groups such as carboxylic acids.

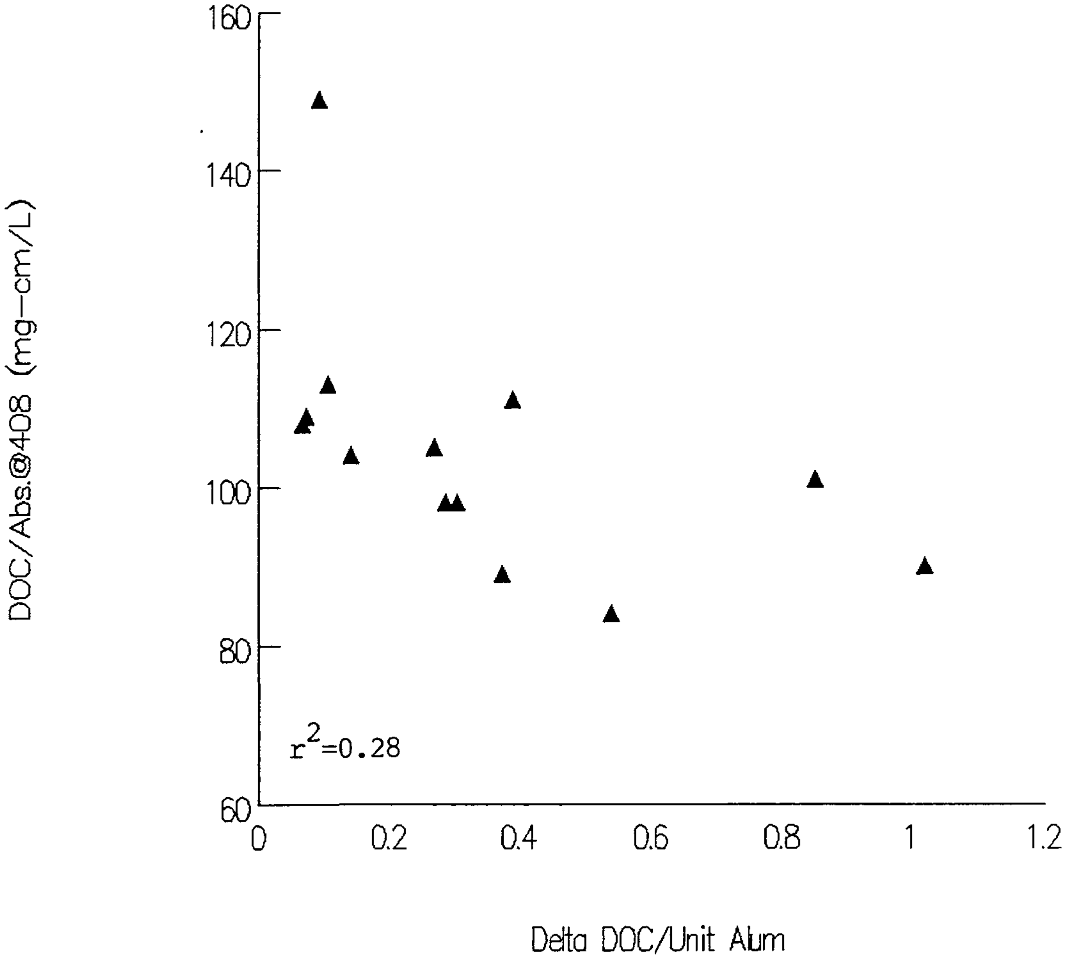

Figure 6-15: DOC removal by alum as a function of the DOC:408 ratio for Orange County groundwater

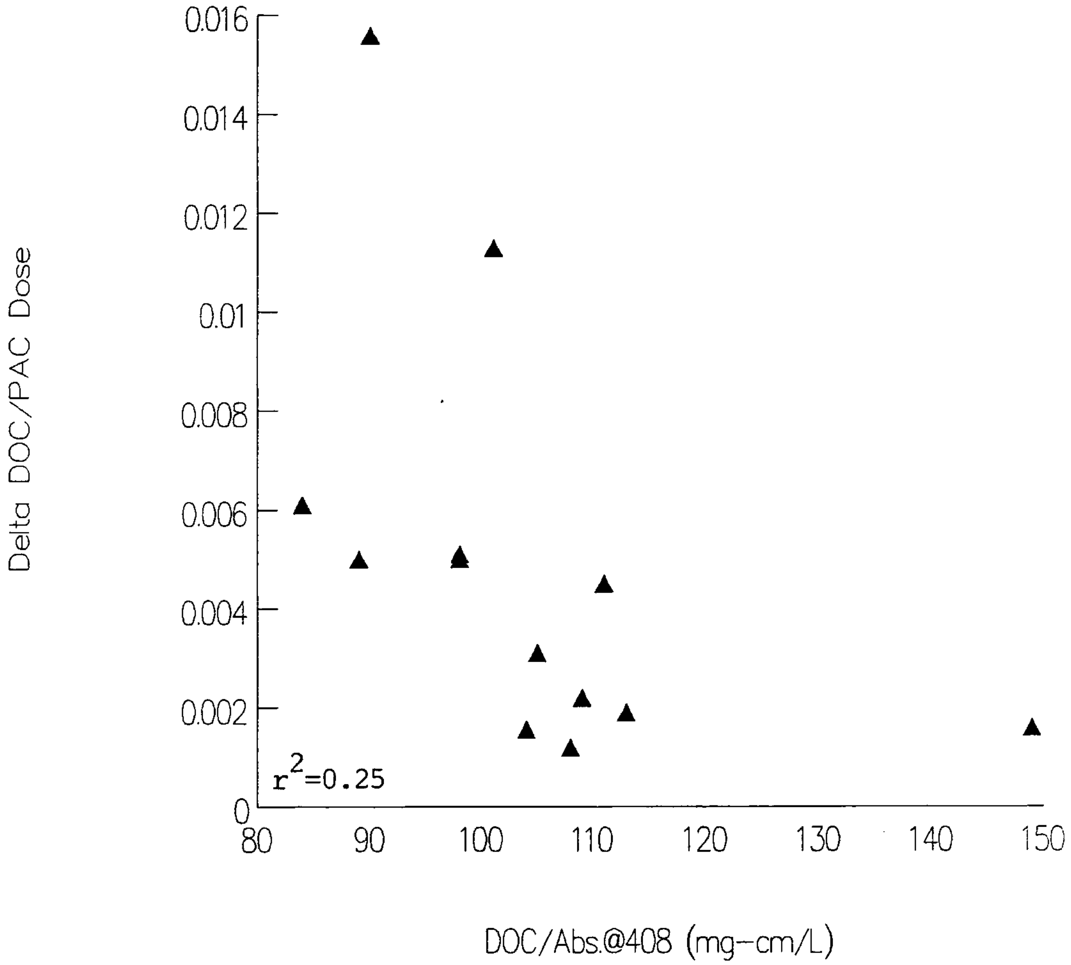

Figure 6-16: DOC removal by PAC as a function of the DOC:408 ratio for Orange County groundwater

Figure 6-17 presents the effect of DOC/408 verses ozone destruction of UV254 absorbing substances. The graph shows a general trend towards greater destruction of UV254 absorbing materials per unit ozone dose with decreasing DOC/408 ratios. This seems to imply that ozone preferentially attacks color causing compounds and hence lowers specific absorbance.

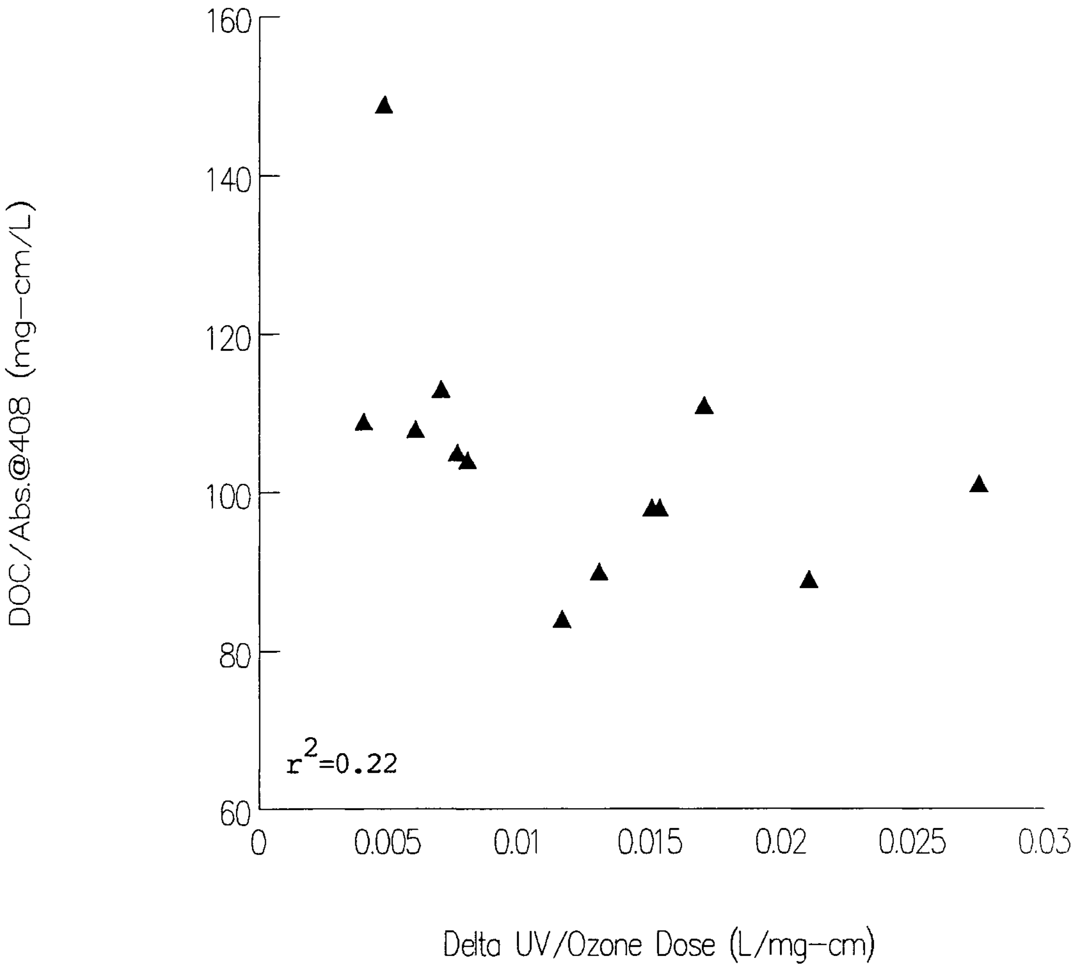

Figure 6-17: Comparison of the DOC:408 ratio with UV254 destruction by ozone for Orange County groundwater

CHAPTER 7

Statistical Analysis of Orange County Groundwater

Analytical results for Orange County groundwater were evaluated statistically by performing simple linear regressions between components to determine r^2 values, and through the use of a Principal Components Analysis (PCA) (12). The simple linear regression model was used to determine how closely parameters were related on a one to one basis. The PCA transforms uncorrelated surrogate and inorganic parameters into orthogonal parameters (or principal components) which are interrelated.

PCA attempts to explain sample variation in terms of those parameters which weigh most heavily into the principal components.

7.1 Results of Simple Linear Regression:

Simple linear regression analysis was broken up into two separate categories. The first category evaluated relationships between DOC removal and sample characteristics and the second category looked at the interrelationships between analytical parameters.

7.1.1 DOC and UV Removal Verses Surrogate Parameters:

Table 7-1 presents the relationships between DOC removal and surrogate parameters. Graphical representations of much of this data have been introduced in the previous chapter.

In Table 7-1, n represents the number of individual analyses or bench scale tests which were used to compute the r^2 value. Also shown in Table 7-1 are the significance levels (p) for each regression and regression constants for slope (m) and y-intercept (b).

Table 7-1 shows that a strong direct correlation exists for DOC removal based on raw water DOC or color. In other words, those samples which exhibit the greatest contamination (by color or DOC) are the most successfully treated. Since hydrophobics (or humics) are most successfully removed, typically the percent reduction in color is greater than the percent reduction in DOC (this correlates well with the XAD-8 demonstration of color removal with humic disappearance).

TABLE 7-1 : Analysis of DOC and Absorbance Removal by Various Treatment Techniques.

Parameter	n	r^2	Signif. Interval p	Regression Constants m	b
DOC Removal by Alum vs:					
Carboxylic Acidity	13	0.96	<0.0005	-0.05	1.26
Average AMW	13	0.43	<0.05	0.0001	-0.002
Hydrophobicity	13	0.65	<0.005	0.02	-1.27
DOC	13	0.92	<0.0005	0.08	0.06
Color	13	0.97	<0.0005	0.005	0.03
THMFP	13	0.68	<0.0005	0.003	-0.17
DOC Removal by PAC vs:					
Carboxylic Acidity	13	0.92	<0.0005	-0.0007	0.02
Average AMW	13	0.46	<0.005	0.0001	-0.001
Hydrophobicity	13	0.55	<0.005	0.003	-0.016
DOC	13	0.97	<0.001	0.001	0.001
Color	13	0.98	<0.0005	0.0001	0.001
THMFP	13	0.77	<0.005	0.0001	-0.003
UV@254 Removal by Ozone vs:					
Carboxylic Acidity	13	0.44	<0.05	-0.0008	0.027
Average AMW	13	0.14	<0.005	0.0001	0.007
Hydrophobicity	13	0.46	<0.025	0.0004	-0.02
DOC	13	0.25	<0.10	0.0009	0.009
Color	13	0.33	<0.005	0.0001	0.008
THMFP	13	0.20	<0.05	0.0001	0.005
DOC Removal by Nanofiltration vs:					
Carboxylic Acidity	5	0.79	<0.20	-3.85	113.08
Average AMW	5	0.05	<0.30	0.003	20.09
Hydrophobicity	5	0.84	<0.025	3.18	-205.08
DOC	5	0.74	<0.20	5.36	20.69
Color	5	0.81	<0.20	0.39	15.13

The one unusual set of correlations in Table 7-1 are those listed for UV@254 removal by ozone. Removal success by ozone appears random suggesting that unevaluated parameters may control ozone treatment success. The affect of ozone scavengers (such as alkalinity) were evaluated but no relationship to removal success was noted ($r^2 = 0.07$).

Simple linear regression analyses were also performed on surrogate parameters to determine inherent interrelationships which exist between the various parameters. Table 7-2 presents the data divided into the three categories, DOC verses surrogate parameters, THMFP verses surrogate parameters and miscellaneous surrogate parameters. Interrelationships between absorbance, color and fluorescence were not evaluated against other parameters because of the close correlation which exists between DOC and absorbance, color and fluorescence.

7.1.2 Linear Regression of DOC vs. Surrogate Parameters:

As Table 7-2 demonstrates, absorbance, color and fluorescence values can be used to predict DOC concentrations for Orange County groundwater. The correlation of the color:DOC relationship is slightly less

TABLE 7-2: Analysis of Interrelationships Between Surrogate Parameters.

Parameter	n	r^2	Signif. Interval	Regression Constants	
			p	m	b
DOC Relationship with:					
Absorbance @ 254	15	0.99	<0.0005	18.5	0.002
Absorbance @ 408	15	0.99	<0.0005	90.4	0.27
Color	15	0.97	<0.0005	0.06	-0.21
Fluorescence	15	0.97	<0.0005	0.15	-0.36
Hydrophobicity	15	0.46	<0.005	0.22	-13.08
Carboxylic Acidity	15	0.88	<0.0005	-0.58	15.01
Average AMW	15	0.41	<0.005	0.001	-0.55
THMFP	15	0.72	<0.0005	0.032	-2.07
TOXFP	15	0.51	<0.0005	0.003	-0.34
THMFP Relationships with:					
Absorbance @ 254	15	0.77	<0.0005	424.5	95.08
Absorbance @ 408	15	0.71	<0.0005	1997.8	104.29
Color	15	0.74	<0.0005	1.4	94.80
Fluorescence	15	0.64	<0.005	3.16	94.39
TOXFP	15	0.76	<0.0005	0.09	49.31
Hydrophobicity	15	0.51	<0.005	6.10	-286.42
Carboxylic Acidity	15	0.57	<0.005	-12.32	419.42
Average AMW	15	0.45	<0.10	0.01	67.82
Specific Absorbance	15	0.17	<0.10	6315.01	-147.87
DOC/Abs. @ 408	15	0.26	<0.05	-3.04	502.69
DOC*Abs. @ 254	15	0.61	<0.005	25.06	149.52
Miscellaneous Relationships:					
DOC/408 vs %Phobic	15	0.56	<0.001	-1.04	184.03
Color/DOC vs %Phobic	15	0.41	<0.01	0.17	3.25
Abs.@254 vs CA*	15	0.87	<0.0005	-0.03	0.81
Avg. AMW vs CA*	15	0.43	<0.005	-471.82	17110.93
React. vs Avg. AMW	15	0.53	<0.30	-0.001	93.95
DOC/408 vs Sp. Abs.	15	0.37	<0.10	-1573.1	187.03
TOXFP vs. CA*	15	0.46	<0.01	-110.39	3691.63
Color vs. %Phobic	15	0.61	<0.001	3.96	-239.90
Color vs. Avg. AMW	15	0.46	<0.01	0.009	8.63

*Carboxylic Acidity

than absorbance:DOC correlations due to the subjective nature of the color test. However, even with the built-in error, a strong direct correlation exists.

DOC concentrations also exhibit a strong inverse correlation with carboxylic acidity. This may be the result of increasing molecular weights which are typically found in higher DOC (and hence more highly colored) waters. The DOC:average AMW relationship appears poor but, with the exception of a few data points, it is typically quite good. Figure 7-1 demonstrates this relationship. As was the case with previous AMW relationship the circled data points consist of values for OC#7, OC#11 and OC#12. An adjusted r^2 value minus these three data points is 0.63. The rationale for the location of the points is similar to that which was previously presented. An interesting condition displayed in Figure 7-1 is the weak relationship between high DOC samples (DOC>6 mg/L) and average AMW and low DOC samples which seem to correlate more closely with average AMW.

With increasing DOC, average AMW and color, the percentage of hydrophobic materials present in a sample is expected to increase. While this situation may be true, the clustering

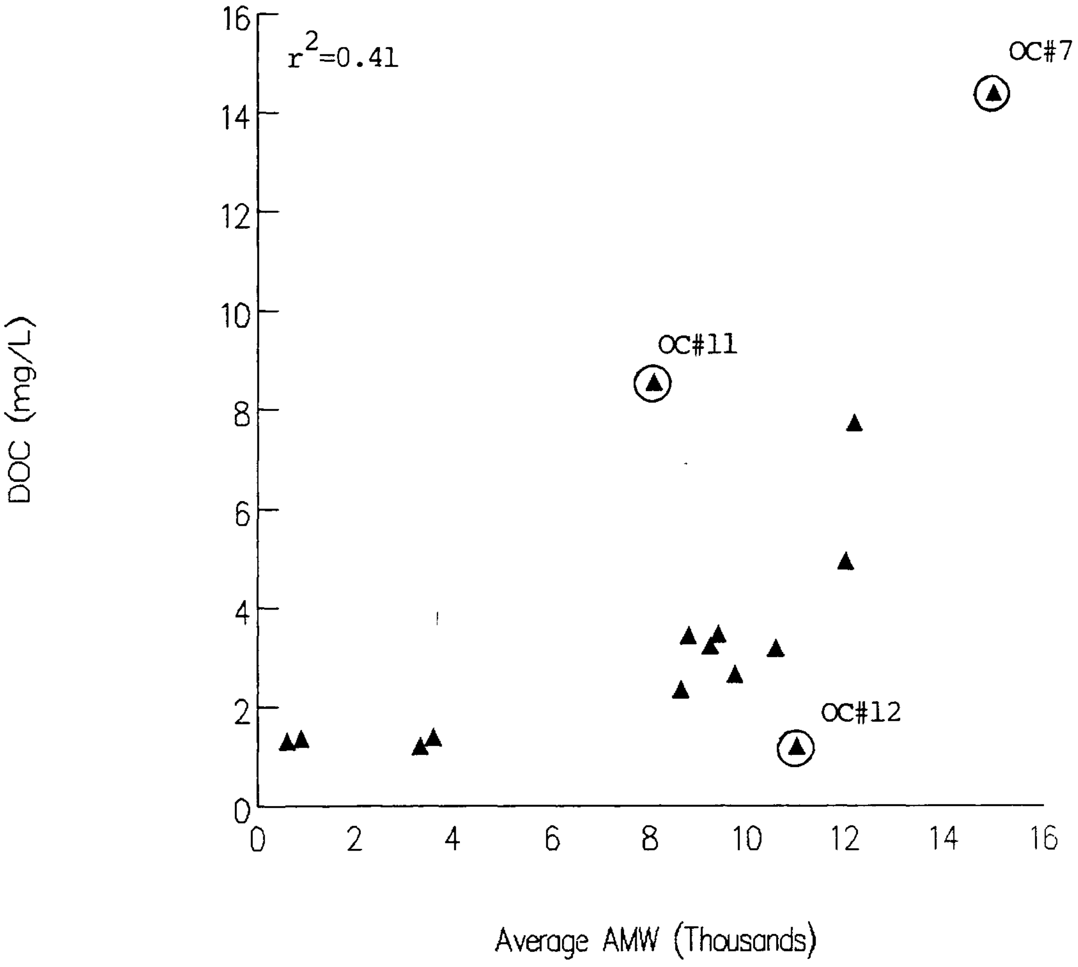

Figure 7-1: The relationship between sample DOC and average AMW for Orange County groundwater

of values between 78% and 90% prevents the establishment of a good linear relationship.

7.1.3 Linear Regression of THMFP vs. Surrogate Parameters:

Relationships between THMFP and surrogate parameters are also found in Table 7-2. The establishment of a good direct linear relationship between THMFP and simple analytical parameters like absorbance or color will allow the prediction of THMFP simply and quickly. The best THMFP relationships that exist are for absorbance at 254 nm and color. Figure 7-2 shows the relationship between UV absorbance at 254 nm and THMFP. With the exception of a few samples, accurate prediction of THMFP can be made simply by analyzing a groundwater by UV@254.

THMFP also shows a strong direct relationship with TOXFP. Although currently unregulated, TOXFP values for Orange County groundwater are larger than THMFP values by a factor of 7.2. The coefficient of variation between TOXFP and THMFP is quite large (39%) which makes prediction of TOXFP based on THMFP difficult.

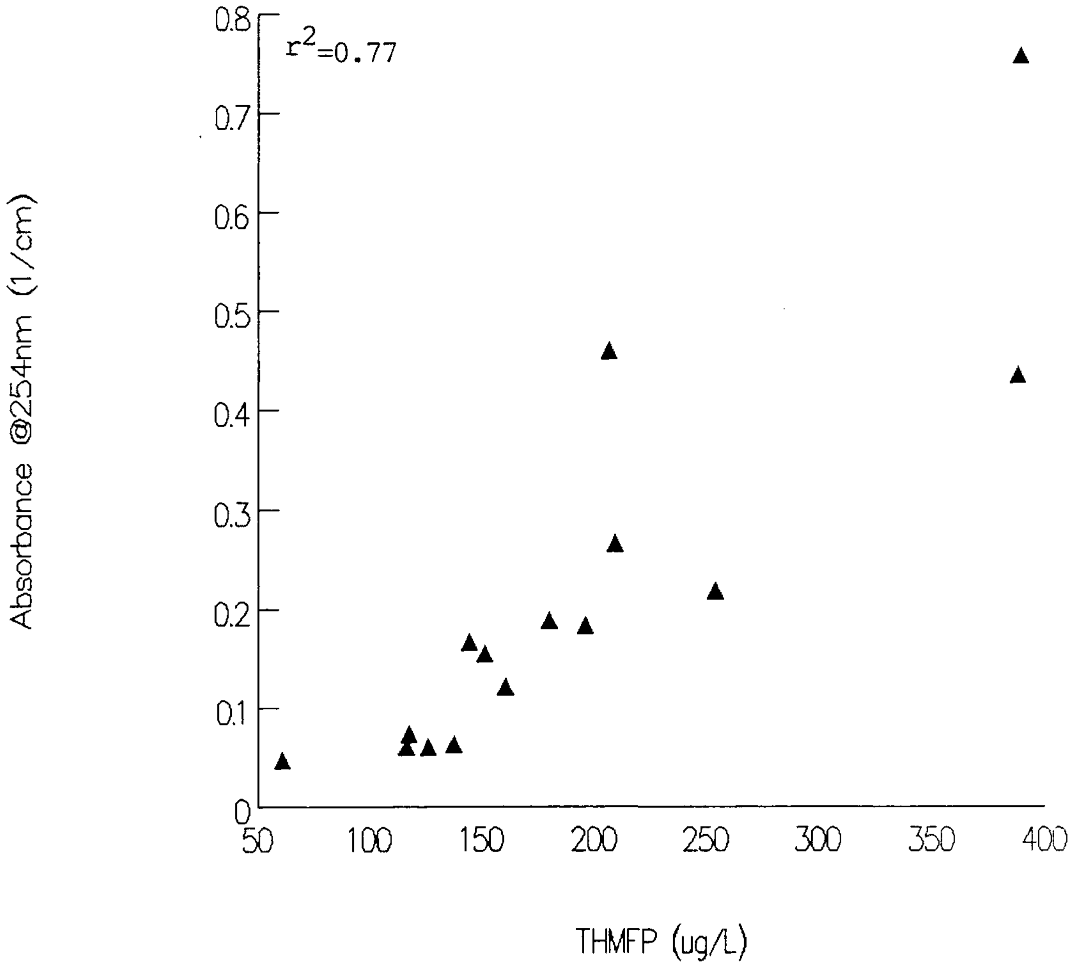

Figure 7-2: The relationship between THMFP and UV absorbance at 254 nm for Orange County groundwater

THMFP correlates fairly well with carboxylic acidity (inverse relationship) and hydrophobicity (direct relationship). This suggests that less highly condensed molecules show poorer formation potential than do highly condensed molecules. The relationship between TOXFP and carboxylic acidity is weaker ($r^2 = 0.46$). It is unknown whether the difference is due to analytical variation or structural reasons. THMFP/carboxylic acidity correlations conflict with the relationship between THMFP and hydrophobicity. Hydrophobicity increases with degree of condensation and should therefore decrease with THMFP. Figures 7-3 and 7-4 show THMFP relationships with carboxylic acidity and hydrophobicity respectively.

Ten of the data points in Figure 7-3 show excellent correlation, while five others deviate from the trend. Those samples which deviate are the two Carl Thornton Park samples (OC#11 and Carl T), OC#1, OC#8 and OC#2. The three sample coefficient of variation for carboxylic acidity analyses is 4.9% (or 0.7 meq/g-carbon). This could be responsible for the location of OC#2 (circled and designated on Figure 7-3 as #2), but other sample characteristics are probably behind the position of the remaining data points.

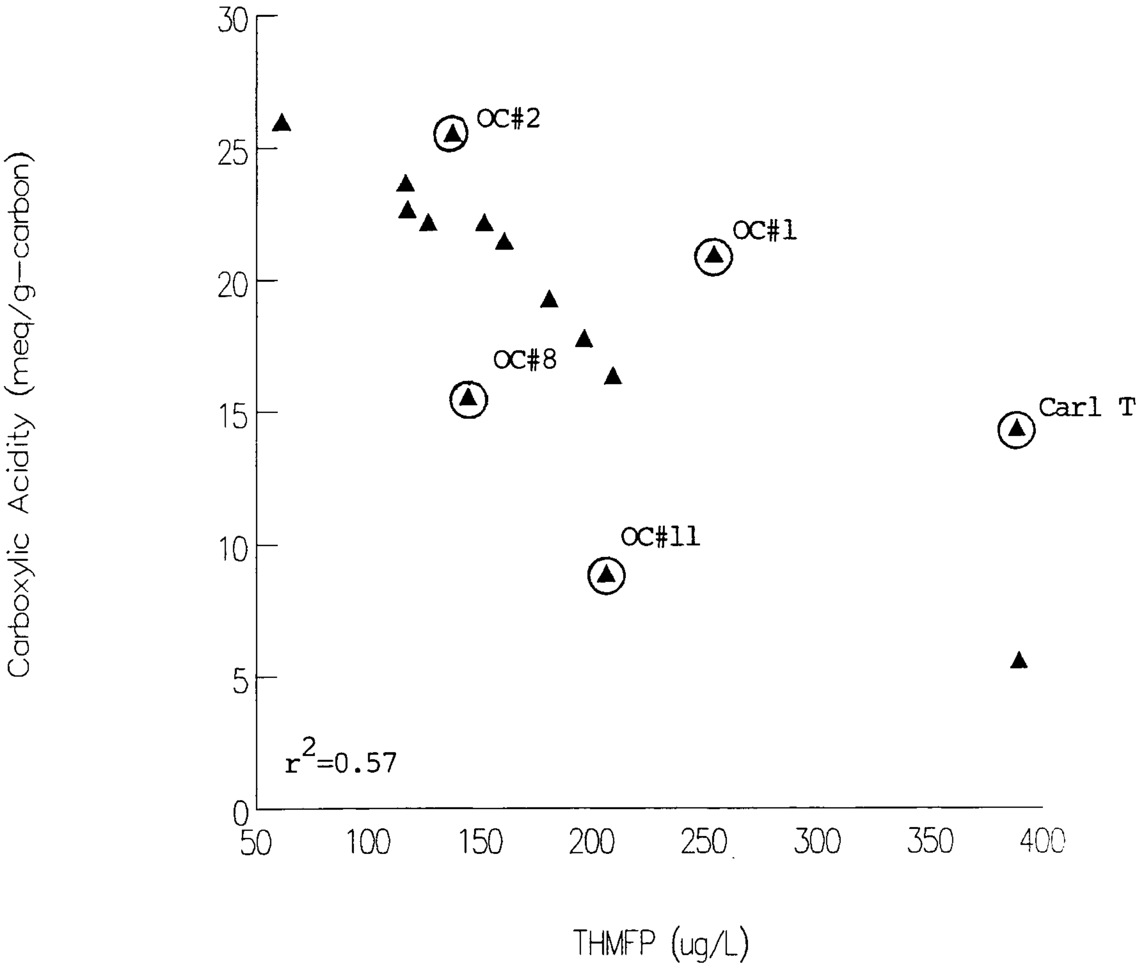

Figure 7-3: The effect of carboxylic acidity on raw water THMFP for Orange County groundwater

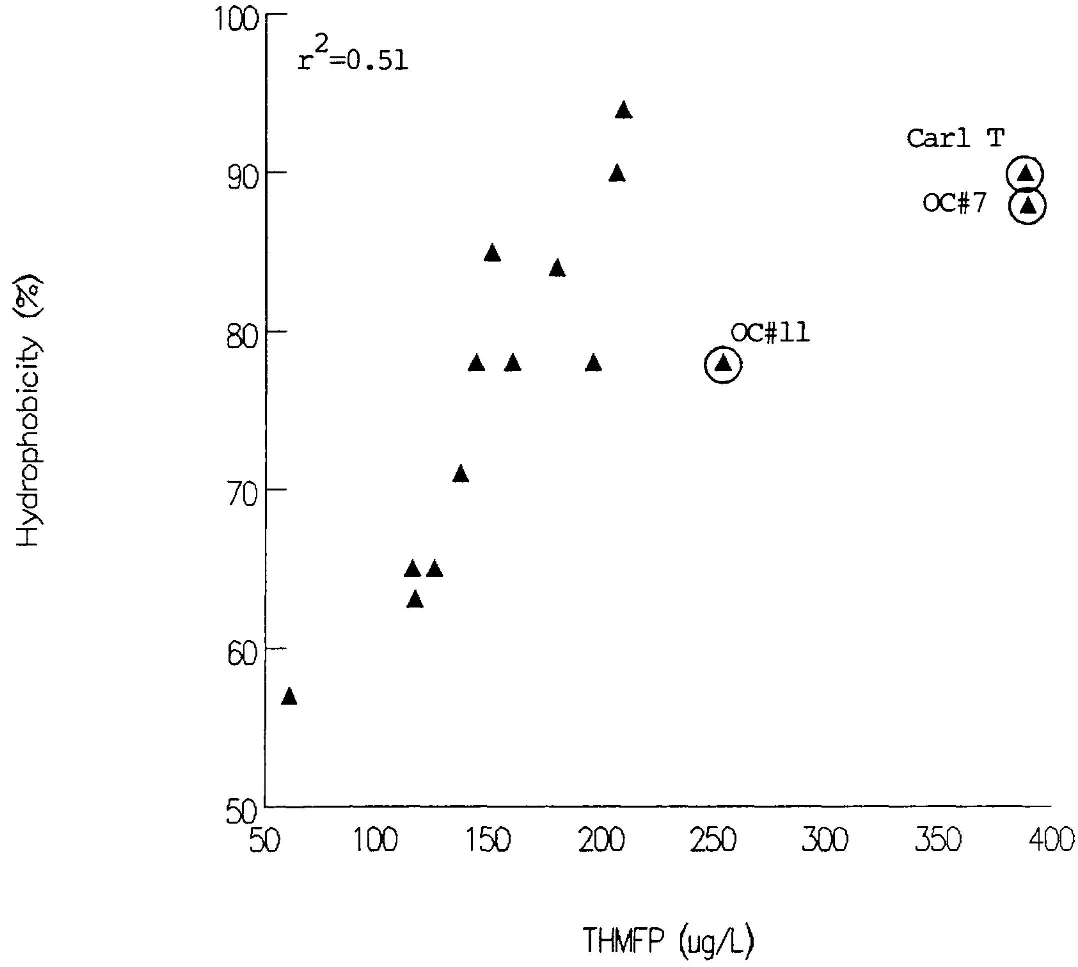

Figure 7-4: The effect of hydrophobic organic carbon on raw water THMFP for Orange County groundwater

The relationship between hydrophobicity and THMFP in Figure 7-4 is good with the exception of three specific points. The circled data points are from samples OC#1, OC#7 and Carl T. Figure 7-4 appears to indicate that THMFP increases with the percent of hydrophobic materials present in a sample.

Finally, THMFP was evaluated verses combinations of terms multiplied or divided by each other. Specific absorbance is UV absorbance at 254 nm divided by DOC. DOC divided by absorbance at 408 nm attempts to discern a relationship between visible color and DOC. The multiplicative parameter, DOC * UV@254, creates a value based on UV and DOC for correlation against THMFP. As Table 7-3 indicates, direct parameter relationships with THMFP correlate more precisely than do combinations of parameters.

7.1.4 Miscellaneous Surrogate Parameters:

Miscellaneous relationships between surrogate parameters are also found in Table 7-2. As indicated by XAD-8 experiments, color is removed along with humic materials. As a result of this, a direct relationship is expected between color and hydrophobicity. Table 7-3 shows that a quasi-linear relationship exists between visual color (subjective technique) and sample hydrophobicity.

Regardless of the relationships, the results need to be standardized to the amount of color or absorbance imparted per unit of organic carbon. Figure 7-5 demonstrates this inverse relationship. As the amount of color (as measured by absorbance at 408 nm) per unit carbon decreases, sample hydrophobicity increases. Stated another way, specific absorbance increases with hydrophobicity.

Other correlations of interest in Table 7-2 are the carboxylic acidity relationships. A strong inverse relationship exists between absorbance at 254 nm and carboxylic acidity. This appears to indicate that structures that absorb light at 254 nm are related to condensed or aromatic units and not associated with the functional groups. However, normalizing the data by dividing each absorbance value by the associated DOC concentration results in an r^2 value of 0.03. In other words, no relationship seems to exist between sample absorbance at 254 nm and the density of carboxylic acid functional groups.

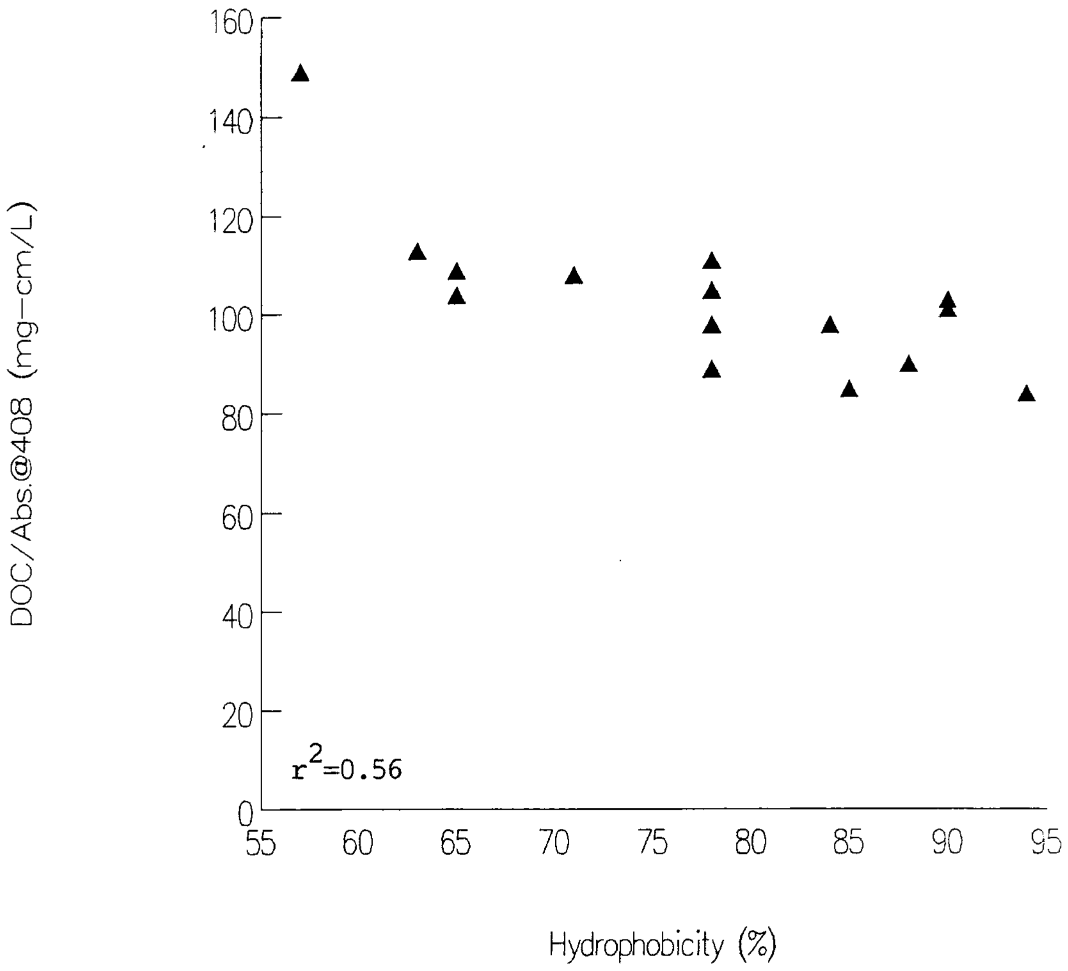

Figure 7-5: The relationship between hydrophobic organic carbon content and the DOC:408 ratio for Orange County groundwater

The relationship between average AMW and carboxylic acidity is expected to be quite good. Various authors (10,42,48,52,55) have indicated (either directly or indirectly) that carboxylic acidity increases with decreasing molecular weight. The relationship discerned for Orange County groundwater is not so precise. Figure 6-13 (previously presented) shows the relationship between average AMW and carboxylic acidity for Orange County groundwaters. Although many of the values are clustered, the overall trend is towards decreasing carboxylic acidity with increasing average AMW.

The final point from Table 7-2 may be gleaned from the relationship between DOC/abs. @ 408 versus specific absorbance. A strong relationship here would indicate that molecular structures absorbing light at 254 nm are responsible for visible color. The weak relationship between the parameters seems to imply otherwise.

7.2 Data Evaluation Using PCA:

The principal components analysis generates uncorrelated linear combinations of variables such that each successive combination has a smaller variance. Essentially, the PCA defines those members of a data set which cause greatest variation. In two dimensions (two variables), the data points can be contained by an ellipse. The longest axis of the ellipse represents the first principal component and it accounts for the greater percentage of the variance (or the area of the ellipse). The shorter axis is the second principal component which accounts for a smaller amount of sample variance. Figure 7-6 shows hypothetical data and the associated principal components which exist for a two variable system.

7.2.1 Analysis of Surrogate Parameters Using PCA:

The surrogate parameters in Tables 6-1a and 6-1b were examined using the Principal Components Analysis. PCA transforms each set of parameters into orthogonal parameters in n dimensional space. The relative importance of the original parameters to the principal components can be examined in Table 7-3. It can be stated generally that the parameters which weigh most heavily into each principal component can be called by that name. For example, in Table 7-3, component number 1 can be said to represent average AMW, component 2, consists of TOXFP, component 3, bromide and so on. Conversely, surrogate parameters with high

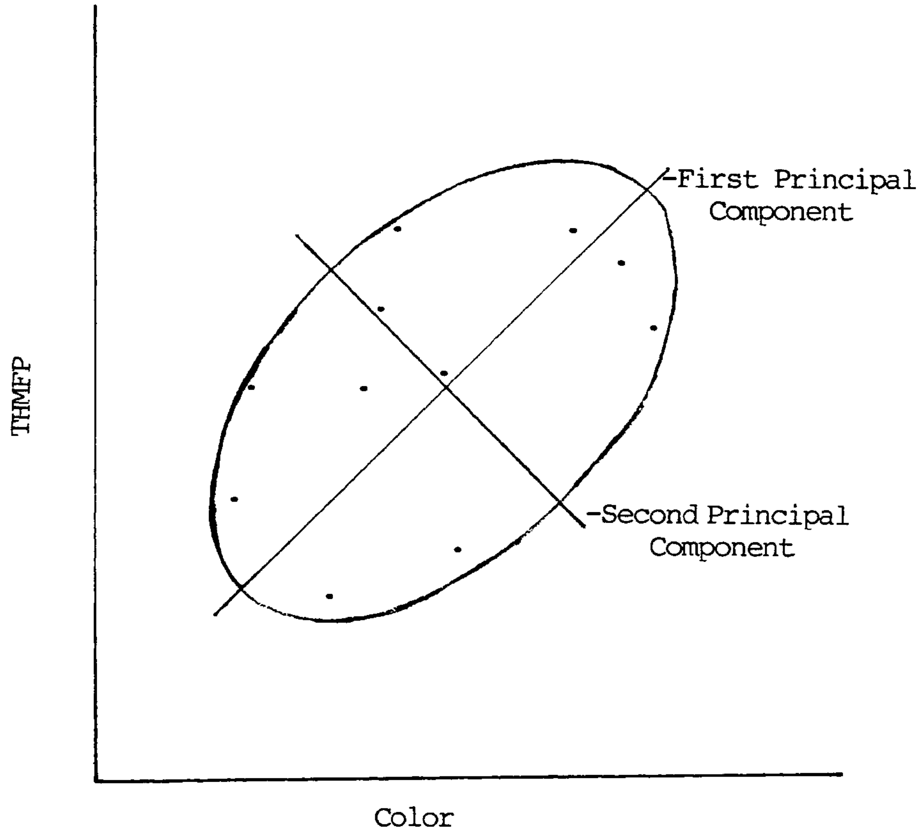

Figure 7-6: Hypothetical data for two variables showing the two principal components

TABLE 7-3: Component Loadings for the Principal Components Analysis:

	1	2	3	4	5	6	7
DOC	0.056	0.053	0.160	0.276	0.271	-0.040	-1.038
Color	0.008	0.832	2.992	5.163	2.785	0.492	0.057
Fluorescence	0.005	0.010	0.128	1.235	1.138	0.690	-0.230
Abs. @254	0.004	0.015	0.153	1.538	1.410	0.863	0.004
Abs. @408	0.002	0.021	0.261	2.753	2.529	1.576	0.102
Bromide	4.332	-0.422	21.143	-1.539	-1.338	1.037	-0.009
Hydrophobicity	1.020	-0.212	7.884	3.017	1.505	-3.003	0.021
Average AMW	121.434	-3.573	-0.910	-0.030	0.047	-0.021	0.000
Carbox. Acidity	45.540	-18.283	0.992	-4.441	4.052	-0.194	0.011
THMFP	59.583	-18.319	-0.866	3.908	-3.453	0.188	-0.010
TOXFP	59.089	34.148	0.207	-0.414	0.244	-0.024	0.001

negative loadings have a strong negative correlation to the data set.

The PCA can be used to reduce the number of variables in a data set (26) where certain variables have strong direct correlations. The first few principal components typically account for the majority of the sample variation. Table 7-4 (below) presents the percent of the total variance which is explained by each principal component.

TABLE 7-4: Percent of Total Variance Explained by Each Principal Component:

Component Number	% Variance
1	80.5
2	14.3
3	4.0
4	0.7
5	0.4
6	0.1
7	0.01

Table 7-4 demonstrates that approximately 95% of total sample variance is explained by the first two principal components. In other words, average AMW and TOXFP are responsible for 95% of the variation in sample characteristics. Stated another way, only 5% of sample variation would be lost if the first two principal components were used and the others ignored. Additionally, bromide can be said to cause 4% of the variation.

Although average AMW can be said to represent the first principal component, carboxylic acidity, THMFP and TOXFP can be said to embody some of the variation explained by the first principal component. Likewise, carboxylic acidity and THMFP, show a negative correlation with the second principal component.

There is good agreement between PCA results and data obtained from simple linear regression analyses. Tables 7-1 and 7-2 demonstrate that a strong correlation exists between DOC, color, absorbance and fluorescence. Therefore, the data set can be reduced to embody one of the previous parameters because the others create very little sample variation. Results of the PCA substantiate this and by looking at component loadings in Table 7-4, it can be seen that DOC, color, absorbance at 254 nm and 408 nm and fluorescence constitute an insignificant portion of the first and second principal components.

It may also be said that hydrophobicity plays a small role in the first two components and hence has little effect on sample variation. Hydrophobicity does however contribute to the third principal component although very little sample variation is embodied in the third component. The small role of hydrophobicity may be due in part to the small variation in values from the sample set (the coefficient of variation for hydrophobicity is small compared to the coefficient of variation in other parameters).

A final point regarding PCA is that THMFP and TOXFP, while responsible for sample variation to an important extent, are not in themselves causing the sample variation. Rather, those molecular characteristics which cause variation in THMFP or TOXFP are most probably responsible for the variation assigned to THMFP and TOXFP by the PCA.

7.2.2 Analysis of Inorganic Parameters Using PCA:

Inorganic data provided by the OCWD laboratory was subjected to a principal components analysis to determine which inorganic parameters caused the greatest sample variance.

Generally, a great deal of similarity exists between the various groundwater samples from an inorganic standpoint. This statement is consistent with the results of the PCA. The first six (6) principal components were responsible for 97% of total sample variance (compared with 99% for the first 3 principal components from surrogate parameter analysis). The specific parameters which weighed most heavily on each principal component were also more evenly distributed.

The first principal component, which explained 44% of the total variability in the data set, consisted of sodium, TDS, EC and sulfate with an approximate equal weighting for each parameter. Sodium, TDS and EC had positive correlations while sulfate correlated negatively. The second principal component accounted for 27% of the variability and consisted of positive correlations for calcium, manganese and hardness. The third component (9.5%) consisted primarily of COD and aluminum (both correlations positive), the fourth, fifth and sixth components (8.6%, 4.8%, 3.9%) were embodied by the parameters alkalinity, ammonia-TKN-sulfate-alkalinity, and iron respectively. All correlations for components 4, 5 and 6 were positive with the exception of sulfate.

The principal components analysis of these data appears to have demonstrated that sample variability is weakly affected by inorganic parameters and embodied largely by organic carbon related factors. In other words groundwater source (specifically well location and depth) change significantly in an organic sense but insignificantly, to an extent, in an inorganic sense.

CHAPTER 8

Treatment Alternatives

Orange County groundwater treatment alternatives include the three following primary scenarios:

1) Well head treatment.
2) Decentralized treatment for well clusters.
3) Centralized treatment.

Each treatment alternative has positive and negative attributes which must be compared and evaluated prior to selection of the most cost effective and successful treatment scheme. Centralized treatment will require pipeline and pumping requirements to move water from well heads to the treatment location. On the other extreme, well head treatment will reduce pumping and pipeline needs but increase treatment costs because economies of scale are not achieved. Decentralized treatment will allow a reduction in pumping and transmission, recognize minor economies of scale, and allow for individual well field designs which are site specific.

While decentralized treatment of well clusters has its merits it can also be costly from a design standpoint (design of 4 separate plants compared with design of one plant) and wells which are potential cluster candidates are separated geographically, as opposed to centralized. Figure 6-2 (presented previously) shows potential clusters based on DOC divisions.

Well field treatment needs were evaluated based on two parameters, DOC and THMFP. DOC was selected because it represents an adequate surrogate for color. THMFP was selected because of the existing and proposed limitations under the Safe Drinking Water Act (SDWA).

Table 8-1 presents a comparison of THMFP precursor removals by various bench scale treatment tests. Two very important conclusions can be drawn from Table 8-1: 1) Alum was typically the most successful treatment alternative in removing THM precursors (nanofiltration was also quite successful but limited data are available) and 2) THMFP reduction by ozonation was generally weak however, ozone reduced sample reactivity more successfully than other treatment techniques.

TABLE 8-1: THMFP Reduction and Sample Reactivity Resulting from Various Treatment Methods

	THMFP (ug/L)/Reactivity (ug/mg)				
SAMPLE	RAW	ALUM	OZONE	PAC	NF
OC#1	254/74	173/87	273/78	248/83	--
OC#2	137/105	85/87	104/77	121/138	--
OC#3	117/87	77/93	80/66	54/64	--
OC#4	196/58	102/72	131/46	120/52	--
OC#5	209/42	142/62	193/38	187/68	--
OC#6	126/93	81/127	96/69	101/122	--
OC#7	389/27	296/32	306/26	333/32	130/96
OC#8	144/42	116/78	117/43	119/70	--
OC#9	160/75	62/60	94/44	--	113/111
OC#10	61/55	44/69	49/57	--	--
OC#11	206/24	241/56	193/24	--	81/39
OC#12	87/70	63/75	71/56	--	91/61
OC#15	180/52	81/45	104/40	--	53/29

The implications of this data are significant. While alum and PAC removed a greater percent of the THM precursors, they typically remove the least reactive precursors. Since alum and PAC remove higher AMW materials most successfully, low AMW materials are probably the most reactive and hence should ideally be the targeted compounds for removal. Figure 8-1 demonstrates the relationship between reactivity and average AMW. The overall trend seen on Figure 8-1 is towards increased reactivity with decreasing values for average AMW.

Two alternatives, from a treatment standpoint, may successfully remove low AMW materials. The first possibility involves the use of ozone for microflocculation. Ideally microflocculation raises the average AMW through flocculation of smaller (and more reactive) humic materials. This would effectively create more removable particles and lower THMFP.

The second alternative requires combinational treatment using alum and ozone. Alum removes carbon through sweep flocculation dominantly reducing the larger MW material. Subsequent ozonation effectively reduces the reactivity of the remaining organic carbon thus lowering THMFP.

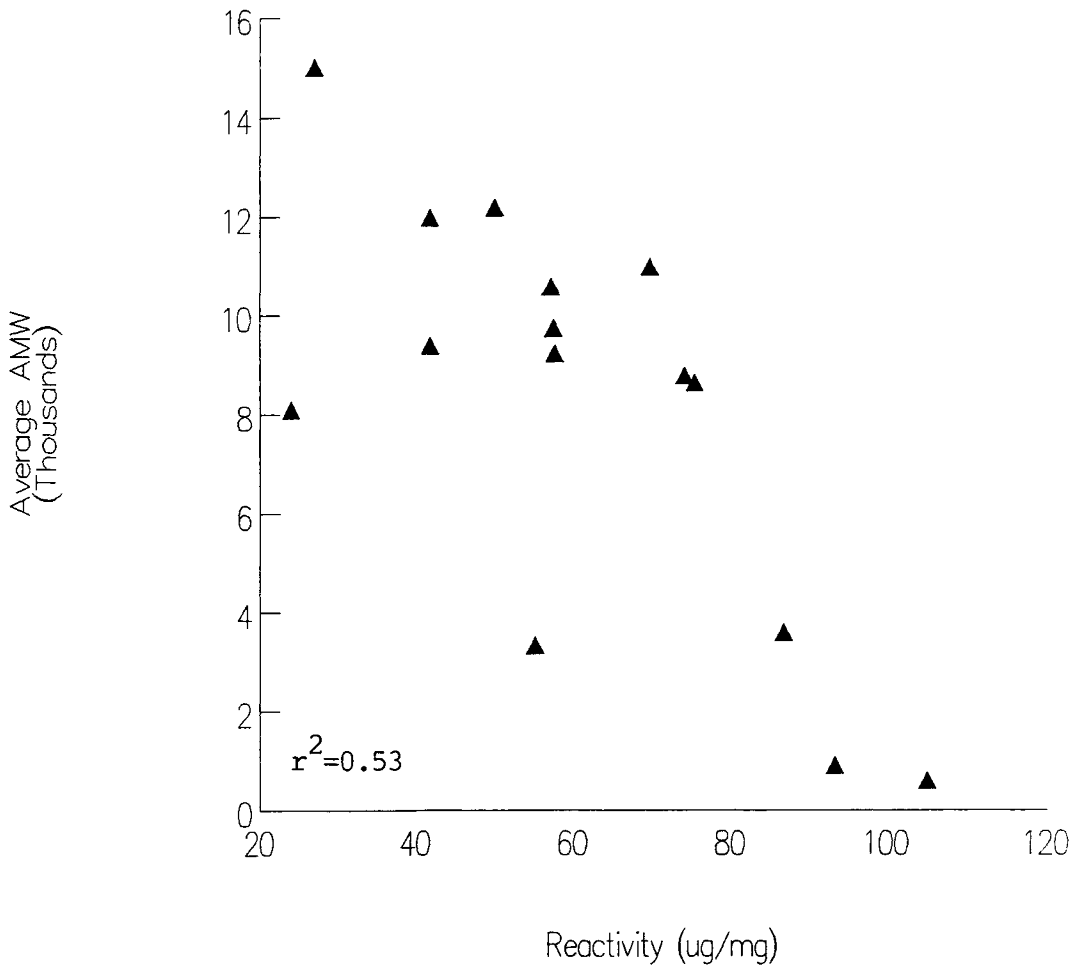

Figure 8-1: The relationship between organic carbon average AMW and sample reactivity for Orange County groundwater

A final treatment possibility is use of nanofiltration to remove higher MW materials. Nanofiltration exhibited excellent success in removal of DOC from certain waters and in THMFP reduction. Although successful removal of THM precursors was achieved, highly reactive organic carbon typically remained in solution. Reactivity values for nanofiltration permeates in Table 8-1 support the low AMW/high reactivity relationships which were alluded to earlier.

Given these potential treatment techniques, the scenario which may prove most viable would be centralized treatment. Alum coagulation proved consistently most successful in DOC removal compared with PAC and ozone. However, THMFP following alum coagulation frequently remained high (in excess of the current THM standard 46% of the time and in excess of the proposed 50 ppb standard 92% of the time). The short-term THMFP (24 hour incubation at a chlorine to DOC ratio of one) is significantly lower than the THMFP values reported previously. Typically, short-term THMFP is one-seventh of worst-case THMFP although values as low as 2.5:1 have been obtained.

Regardless of the ultimate THMFP, ozonation following alum coagulation will successfully reduce final THMFP values by lowering sample reactivity in addition to other potential benefits (e.g., disinfection). Centralized treatment is an ideal situation because varying treatment schemes appear unnecessary.

CHAPTER 9

CONCLUSIONS

The large body of groundwater lying below Orange County in the Santa Ana-Huntington Beach area can be treated. Groundwaters at various depths from 105 to 1320 feet are contaminated by naturally occurring DOC and color. The distribution of these waters, the sources of DOC and color, interrelationships between water characteristics and the impact of these factors on groundwater treatment have been evaluated as part of this research. During the course of this research, data that was generated has been compared and contrasted with information found in literature and subsequently several observations have been made regarding Orange County groundwater.

9.1 Sources of DOC and Color:

The most likely source of DOC and color in Orange County groundwaters is finely disseminated organic material which was deposited with the original strata. It is likely that while emplaced, varying degrees of diagenetic alteration occurred changing the original organic material to some extent.

The highest DOC concentration measured during this research was 14.4 mg/L which represents almost 120 lbs. of dissolved organic carbon for every million gallons of groundwater. A quantity of organic carbon this large requires a significant source. Organic rich shales or other fine grained sediments constitute a possible source of sufficient magnitude.

Diagenetic alteration of carbon bearing strata could be responsible for the abundant supply of hydrophobic materials. With increasing diagenesis, aromaticity (and hence hydrophobicity) increases. Diagenetic alteration in the narrow temperature-pressure regions needed for organic acid creation may be responsible for the observed charge densities which are uncharacteristic of surface and groundwaters.

Within specific areas of Orange County the carboxylic acidity of humic materials tends to decrease with depth. Because the degree of metamorphism (or diagenesis) also typically increases with increasing pressure, the reduced number of functional groups and the increased hydrophobicity may be signs of increased alteration (diagenetic or metamorphic) in the lower stratigraphic units. These trends are however, impossible to confirm due to the magnitude of screening intervals associated with several wells in the area.

9.2 Chemical Nature of Color:

Chemically, the majority of the DOC (78%) is humic in nature and consists of highly charged humic and fulvic acids. These humic materials are responsible for 86-100% of the color present in groundwater samples analyzed during this study.

Humic materials are defined operationally by extraction using XAD resins. When groundwaters with color concentrations of up to 210 pcu's are passed through a column containing XAD-8 resin, frequently, 100% of the visual color and light absorbing materials (408nm) are removed.

Orange County groundwater humic and fulvic acids are believed to be highly charged because of their ability to resist pH change between pH 3 and 8 when compared with

Milli-Q grade water.

9.3 Color Distribution:

Colored waters are found throughout the groundwater basin and the extent of coloration is highly variable horizontally and vertically. Color bearing strata appear to be confined vertically to smaller stratigraphic limits. This belief is based on the following circumstances:

1) Wells with the largest screening intervals typically exhibit lower color values.

2) The Carl Thornton Park wells have distinct color profiles with depth and three independent screening intervals. Collection of groundwater simultaneously from each screening interval would reduce color from the deeper interval dramatically.

3) The greatest color concentrations appear to correlate stratigraphically to a fairly well defined unit. Deeply colored waters from Carl Thornton Park could be generated by the same sequences of strata responsible for high color values in OC#5 and OC#7 samples. Geologic information

suggests that this trend is possible. The Carl Thornton deep well has a 50 foot screening interval, above which low colored waters are found. If this water producing zone correlates with OC#5 and OC#7 wells it could be responsible for all of the highly colored waters in the entire basin.

4) Aquicludes, which are frequently found in water producing areas, could be the source of DOC and successfully prevent water migration creating a narrow band of colored water.

9.4 Causes of Sample Variation:

The success of treatment techniques in removing DOC and color from Orange County groundwater samples was highly variable. Variation in treatment success was largely a function of the chemical differences in DOC from sample to sample. The behavior of individual humic molecules is controlled to an extent by the opposing forces of molecular weight and carboxylic acidity. While molecular weight tends to decrease solubility through increasing molecular size, carboxylic acid functional groups increase molecular solubility when they ionize.

Experimental data indicates that charge density has the greatest impact on DOC removal, however, statistical data analyses suggest that average AMW is responsible for the greatest percent of variation from sample to sample. Average AMW cannot be considered independent of carboxylic acidity and therefore, it is probably responsible both directly (due to size) and indirectly (as a result of size/charge density relationships) for the treatment successes observed and the reactivity of a specific groundwater.

Average AMW is a simplification of actual molecular weight distribution. Two samples may have similar average AMW values but vastly different molecular weight distributions (e.g., bimodal verses normal distribution). In actuality, it is probable that molecular weight distribution controls sample behavior and not the values assigned through average AMW determinations.

9.5 Treatment Alternatives:

The treatment alternative which appears most viable is centralized treatment employing alum coagulation with pre or post ozonation. Alum coagulation was successful in removing DOC, color and THMFP for all samples evaluated thus precluding the use of multiple treatment schemes for differing waters.

Ozonation could be used as a pre-oxidant to promote microflocculation and removal of low AMW compounds. Alternately, ozone could be employed after coagulation to assist in the reduction of THMFP and for disinfection. Bench scale testing has demonstrated ozones effectiveness in reducing reactivity and successful microflocculation has been reported (13,18) under certain conditions.

CHAPTER 10

Recommendations for Future Research

During the course of this research many questions were raised which require additional time and expertise to fully understand. Recommendations are made for future research to assist in the understanding of Orange County groundwater and, more importantly, the role of humic substances, source materials, and diagenetic processes on the characteristics and reactivity of humic molecules.

During future well drillings, lithologic samples should be thoroughly evaluated to determine organic material content of stratigraphic sequences. After drying, lithologic samples should be used subject to extraction procedures to determine leachable organic content. Extractions should occur at ambient pH using organic free water and with 0.1 N NaOH solution. The first procedure will empirically model groundwater conditions (not including pressure profiles), and the second will provide humic content. These tests will allow correlations on a more specific basis and potentially identify source materials (this protocol essentially represents a method of extracting humic and fulvic acids from soils).

The geochemical and thermodynamic relationships of carbon maturation should also be studied. Specifically, the processes which result in the formation/destruction of functional groups, require additional research. Understanding the processes which create or destroy functional groups may provide insight to their stability and removal from natural systems.

Continued research is needed into the effects of ozonation on functional group content. Recent research in ozonation has indicated the applicability of low ozone doses to promote microflocculation. In certain waters, oxidation of humic and fulvic acids may result in the formation of oxygen-containing functional groups thus making particles more stable. Conversely, ozone oxidation may destroy functional groups rendering organic materials more amenable to other removal techniques. The relationship between ozone oxidation and functional groups should be explored in further detail.

Additional research is needed to determine the degradation pathways followed by humic and fulvic acids when subjected to oxidizing environments. Assuming that THM formation is partially mediated by oxidizing conditions established during chlorination, determination of degradation pathways may allow the isolation of those molecules primarily responsible for THM generation. However, to facilitate this type of research, use of a GC/MS is recommended.

Further bench scale testing is required for nanofiltration and combinational treatment alternatives. Nanofiltration demonstrated the potential to successfully remove a large percentage of raw water DOC.

Combinational treatment has also shown success in reduction of THM precursors, color and DOC. The establishment of appropriate relationships between treatment methods can potentially achieve the greatest water quality possible. Finally, research is needed to determine the kinetics of DOC removal from groundwater by various treatment alternatives. Kinetic data would provide a vital link in the transformation of bench scale results to site specific design considerations. Corollary to this is understanding the relationship between bench scale geometry (i.e., reactor shapes, length to width ratios, etc.), and plant scale conditions.

Armed with this additional information mitigation of the Orange County groundwater color/THM problems could more successfully be achieved.

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