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Organic Matter in Rivers: The Crossroads between Climate and Water Quality

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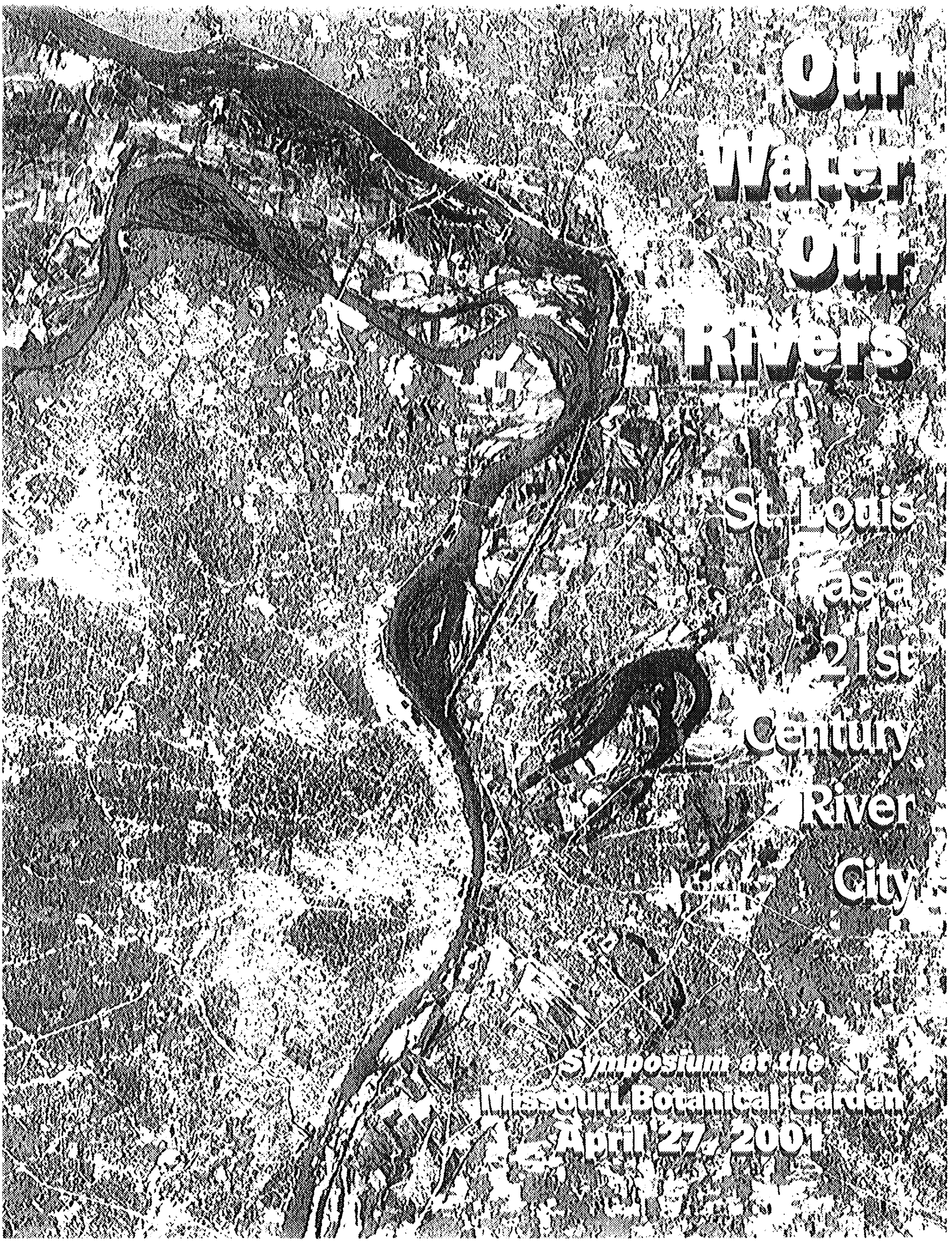

Our Water Our Rivers

St. Louis Has a 21st Century River City

Symposium at the Missouri Botanical Garden
April 27, 2001

ORGANIC MATTER IN RIVERS: THE CROSSROADS BETWEEN CLIMATE AND WATER QUALITY.

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Abstract

All surface waters in the world contain dissolved organic matter and its concentration depends on climate and vegetation. Dissolved organic carbon (DOC) is ten times higher in wetlands and swamps than in surface water of arctic, alpine, or arid climate. Climates of high ecosystem productivity (i.e., tropics) typically have soils with low organic carbon storage, but drain high dissolved organic loads to rivers. Regions with lower productivity (e.g. grasslands) typically have high soil carbon storage while adjacent rivers have high DOC contents. Most DOC in a free-flowing river is derived from leaching vegetation and soil organic matter, whereas in dammed rivers algae may comprise a significant portion.

Water chemistry and oxygen-18 abundance of river water, along with radiocarbon and carbon-13 isotope abundance measurements of DOC were used to distinguish water and water quality sources in the Missouri River watershed. Drinking water for the City of St. Louis incorporates these different sources, and its water quality depends mostly on whether runoff is derived from the upper or the lower watershed, with the lower watershed contributing water with the highest DOC. During drinking water chlorination, DOC forms carcinogenic by-products in proportion to the amount of DOC present. This has recently led the USEPA to propose federal regulation standards. Restoration of natural riparian habitat such as wetlands will likely increase DOC concentrations in river water.

Introduction

Dissolved organic carbon (DOC) is ubiquitous in the parts per million concentration throughout world water supplies. As such, concerted efforts to identify, characterize, and determine the formation pathways of DOC began nearly a hundred years ago (Stevenson, 1985; Thurman, 1985; Malcolm, 1985). In general, it originates from photosynthetic fixation of carbon by land plants and aquatic organisms, which directly and indirectly produce particulate organic residue, the precursor of DOC, whose fate is either through consumption in aquatic food chains or deep burial and thermal degradation over geologic time.

The concentration of DOC has been a longstanding concern where industrial effluents or raw sewage are discharged directly into rivers and lakes because high concentration can lead to high biological oxygen demand and suffocation of fish. More recently, added concern over DOC has arisen because of its association with drinking water chlorination and the formation potential of carcinogenic disinfection by-products such as trihalomethanes and haloacetic acids (e.g. Rook, 1977, Larson and Webber, 1994, Singer, 1999). This has led to the promulgation of the Information Collection Rule, and ultimately the implementation of the Disinfectants-Disinfection By-Product Rule by the USEPA. The extent of pathogen occurrence combined with the dissolved organic carbon (DOC) concentration and its reactivity during disinfection determines the extent of regulation and the required preventive treatment.

Ecological and climate research of DOC has focused on its role in aquatic systems as a base nutrient in food chains (e.g. Munster and Chrost, 1990), its transport to and fate in oceans, its rate of change in terrestrial ecosystems (e.g. Hedges et al., 1986), and its contribution to the global carbon cycle (see Schlesinger, 1994). Ecological and climate research on DOC pursue answers to many questions commonly shared by water quality researchers, yet these two fields have no traditional overlap.

Most of the drinking water used by the City of St. Louis originates in the Missouri River watershed. Due to large variability in discharge and runoff sources, DOC concentrations in river water vary nearly a factor of three within a single season (Criss, Davisson and Kopp, 2001). With increasing landuse development and restoration of natural habitat in the watershed, combined with implementation of USEPA regulations, DOC predictability becomes critical for drinking water quality management. This paper will show how water chemistry and isotope measurements used together lead to a method of predicting DOC concentration from the complex mixture of sources represented in the Missouri River pumped and treated at the City of St. Louis Howard Bend Water Works Plant. This paper will also show how isotope measurements of the DOC itself can elucidate its source region within the watershed.

DOC in the Environment

Thurman (1985) summarized the DOC concentration in world rivers, showing the highest concentrations were in wetlands and swamps (avg. 25 mg/L), the lowest in arctic, alpine, and arid regions (avg. 2-3 mg/L), and temperate to tropical climates were in between (avg. 3-7 mg/L). Climate is one of the most important factors controlling DOC concentration in rivers (Thurman, 1985). Annual precipitation and temperature independently control terrestrial climate and vegetation in a watershed. Their correlation to net primary productivity (NPP) of vegetation has long been established (see e.g. Schlesinger, 1996). Areas of high precipitation, temperatures, and NPP (i.e. tropics) typically have extensively weathered soils somewhat poor in organic matter and soluble minerals, while their associated rivers typically have high DOC and low dissolved minerals. In contrast, regions with lower NPP (e.g. prairies) typically have less weathered soil with a high organic carbon storage and higher mineral content. Consequently, rivers in arid and semi-arid climates tend to have low DOC and high dissolved solids, whereas high DOC and low dissolved solids are common in temperate woodland, alpine, and tropical rivers (e.g. Hayes and Swift, 1978; Aiken and Malcolm, 1987).

Within river systems, different vegetation types and microclimates can control DOC concentrations. For example, in the southeastern US lowland areas comprising wetland settings produce significantly higher DOC than upland forested areas (e.g. Mulholland and Kuenzler, 1979). Wetlands typically have high NPP and are known to discharge water with high DOC concentrations (e.g. Mann and Wetzel, 1995). In the Missouri River, annual precipitation is twice as high in the lower river area than in the upper watershed, and similar DOC differences are expected (see below).

During storm flow, DOC concentration in a river typically rises. Studies attribute this rise to flushing of DOC-rich soil water, leaching of leaf litter from runoff, and flow of shallow groundwater through the soil (e.g. Brinson, 1976; Thurman, 1985; Fiebig et al., 1990).

Lastly, storage of river water in large reservoirs, effluent from agricultural irrigation and confined animal feeding operations, and treatment through artificial wetlands all have significant effects on the DOC concentration, including increased particulate organic carbon from algae, and higher disinfection byproduct formation (e.g. Amy et al., 1990; Parks and Baker, 1997). The amount of algae production in surface water can vary depending on latitude, climate, lake depths, clarity and nutrient levels. For example, mid-latitude lakes (39-55°N) have photosynthetic fixation rates up to 2gC/m^2-day in mid-summer, whereas they will be nearly 10 times lower in winter, while equatorial lakes show little seasonal variation but have high photosynthetic fixation rates (e.g. 5gC/m^2-day; Tilzer, 1987). The distribution of plant-derived sources versus autrophic (algae) sources of DOC in rivers will in general be dictated by the amount of algal productivity within the flowing water, the number and character of surface water impoundments contributing to the flow, latitude, and the season.

The most rigorous attempts to identify chemical compounds comprising DOC have resulted in identification of only 10-20% of its total mass (e.g. Ding et al., 1996). In natural waters identifiable compounds typically are mono- and polysaccharides, amino acids, pigments such as chlorophyll a, and short-chained carboxylic acids (Lytle and Perdue, 1981; Sweet and Perdue, 1982; Thurman, 1985; Leenheer, 1994). The remaining is large molecular weight compounds that are generally referred to as hydrophobic and hydrophilic substances. These compounds are derived from recalcitrant plant and bacterial residues. They can be separated and isolated based on their propensity to adsorb or remain dissolved using specific resin methods (Thurman and Malcolm, 1981).

Hydrophobic substances extracted from water can be separated into humic and fulvic acid by acidification. Humic acids are typically in low abundance in river water, but are more common in soil organic matter. The hydrophobic substances tend to be aromatic rich, with aliphatic linkages (Malcolm, 1985). Hydrophobic substances are precursors for most of the trihalomethane production occurring during water disinfection (e.g. Rook, 1977). Hydrophilic substances tend to be more carbohydrate rich, and have a higher density of oxidized functional groups (Aiken et al., 1992), hence their higher solubility.

Isotopic Studies of DOC

Isotopes are atoms of the same element that have small but measurable mass differences due to differing number of neutrons in the nuclei. Radioactive isotopes are atoms whose neutron density exceeds a region of stability and spontaneously decay into other atoms by ejecting particles from the nucleus. Radiocarbon, or carbon-14 (^{14}C), is one example in which a carbon isotope radioactively decays. The decay rate is always constant for these isotopes, lending themselves readily to age-dating methods in appropriate cases utilizing a simple exponential decay equation. The ^{14}C abundance measured in a material is typically expressed as a percent of modern carbon (pmc), where modern carbon is the ^{14}C abundance of atmospheric carbon dioxide in 1950 (Stuiver and Polach, 1977). Surface testing of atomic weapons after 1950 introduced additional radiocarbon to the atmosphere whose fallout peaked in 1963, and consequently ^{14}C abundance in recent plant matter (e.g. trees) is typically >100pmc. A ^{14}C abundance <100pmc indicates the carbon has been isolated atmospheric exchange for 100s to 1000s of years.

Stable isotopes are those atoms having neutron densities greater than simply predicted from their atomic number on the periodic table, but do not spontaneously decay. The small mass difference among isotopes of an element does not change its chemical behavior, however, stable isotopes of lighter elements in the periodic table commonly exhibit partitioning behavior or enrichment during chemical phase changes and biochemical reactions (Criss, 1999). Carbon-13 (^{13}C) is a stable isotope of carbon that often is depleted in biological systems relative to the ^{13}C abundance in atmospheric CO_2, or calcium carbonate in geologic deposits. The ^{13}C abundance is usually expressed as a ratio to the ^{12}C and normalized to a recognized standard following the common "del" notation, where $\delta = (R/R_{std} - 1)1000$, and R is the $^{13}C/^{12}C$ ratio of the sample and standard (std). The $\delta^{13}C$ values are expressed as a per mil deviation from the standard. Isotope measurements of organic matter utilizing both ^{14}C and ^{13}C have been more common in the soil sciences and used to determine carbon cycling rates (Trumbore, 1993; Harrison et al., 1993, Torn et al., 1997), rates of carbon storage (Heidmann and Scharpenseel, 1992; Wedin et al., 1995), and processes of soil aging (Natelhoffer and Fry, 1988). Isotopic studies of DOC in water have been surprisingly limited. Most isotope measurements in aquatic organic matter have been on particulate organic matter, usually in ocean settings for source indication (Williams et al., 1992), or in large river basins for understanding biogeochemical cycling (Hedges et al., 1986; Quay et al., 1992). In rivers, seasonal variation in the $\delta^{13}C$ of particulate organic matter (up to 6 per mil) has been attributed to changes in the contribution from different vegetation sources (Bird et., 1998; Goni et al., 1998), and contribution from algae production and decay (Barth et al., 1998).

The carbon isotope composition of bulk DOC in surface water has been measured in at least one study of a small watershed, where $\delta^{13}C$ and ^{14}C measurements of surface water DOC were compared to groundwater and soil water DOC (Schiff et al., 1990; Schiff et al., 1997). No seasonal variation has been measured. Isotopic analysis of groundwater DOC has been developed specifically as an age-dating tool (Wassenaar et al., 1990; Artinger et al., 1996). In these studies hydrophobic substances were isolated specifically for the measurement.

Missouri River System

The 1.4 million km^2 watershed of the Missouri River system terminates and joins the Mississippi River at St. Louis after transcending nine US states for a total length of over 4000km (Criss and Wilson, this vol.). Even though its drainage area is large, its average discharge is only about 78,500 cfs (van der Leeden, 1975). The river originates in alpine regions of the continental divide of Montana, drains much of the Great Plains, and acquires nearly half of its flow in the state of Missouri. Annual precipitation in the prairie-dominated Great Plains (avg. ~ 20in/yr) is much lower than in the woodland-dominated lower river area of Missouri (avg. ~ 40in/yr). Streamflow of the Missouri River can vary dramatically over the course of one season, with peak flows and historical flooding occurring during the late spring. During high discharge periods, turbidity and DOC concentration is typically high.

The City of St. Louis operates and maintains two surface water treatment plants that combined produce 140 million gallons of drinking water per day for the St. Louis area. One plant is located at the Howard Bend Station (Fig. 1) along the lower end of the Missouri River. The second plant is the Chain of Rocks Station located on the west-bank of the Mississippi River just below the confluence of the Missouri and Mississippi

Rivers. However, based on historical water quality data, the Chain of Rocks plant draws 100% Missouri River water, since the rivers have not mixed appreciably at the plant's intake point (Dave Visintainer, per. comm.). This has been verified by comparative ^{18}O measurements between the two rivers collected at the same time (Robert Criss, pers. comm.). The plants use standard practices of settling, coagulation, sand filtration, and chlorination for water treatment.

Analytical Methods

This study utilized daily water measurements of electrical conductivity, temperature, and river stage generated by the City of St. Louis at the Howard Bend Plant. Daily stage measurements were converted to discharge by comparing them to discharge records at the US Geological Survey gauging station at Hermann, Missouri, approximately 60 miles upstream (Criss et al., 2001).

Details of the methods for isolation, purification, and measurement of DOC concentration and measurement of its isotope abundance can be found in Davisson (in review). Briefly, DOC concentration was measured by high temperature combustion methods. Isolation of hydrophobic fractions of DOC was by standard resins techniques (Thurman and Malcolm, 1981), and samples for isotope measurements were prepared using sealed tube combustion and cryogenic purification. The ^{14}C was measured by accelerator mass spectrometry, and the ^{13}C by isotope ratio mass spectrometry.

Geographic Separation of Discharge and Water Quality in the Missouri River

Discharge in the Missouri River has a seasonal cycle, with maximum annual flows typically occurring between March and May (Niebur et al, this vol.). Seasonal changes in river discharge cause an inverse proportional change in the electrical conductivity (EC) from as low as ~200µS during high flow to greater than 900µS during low flow. Criss, Davisson and Kopp (2001) developed a method to trace the source of water quality parameters, including DOC, in the Missouri River. They correlated water quality parameters to the ratio of discharge measurements collected at two different gauging stations. This procedure allows the fraction of water contributed in the intermediate reach of the river to be calculated. The electrical conductivity (Fig. 1a), DOC concentration (Fig. 1b), and the concentrations of major ions were shown to exhibit a linear correlation with this "within reach" source fraction. The EC is primarily controlled on average by two different salt sources. The higher EC source is an upper watershed component, where the climate is semi-arid to temperate, and the lower EC source is the lower watershed, which is temperate to humid. The mean daily discharge nearly doubles between St. Joseph in northwest Missouri and Howard Bend in southeastern Missouri.

In detail, the discharge measured at Howard Bend can be separated into an upstream and downstream component by recognizing

$$X_{Her} = \frac{D_{Her} - D_{SJ}}{D_{Her}}$$

where D_{SJ} is the measured discharge at St. Joseph, in northwest Missouri, D_{Her} is the measured discharge downstream at Hermann, MO, and X_{Her} is the fractional amount of discharge, or "within reach" fraction, contributed between those two points (Criss et al., 2001). If a simple two end-member model for water quality is valid, then a comparison between a water quality parameter and the fraction of discharge (X) from either upstream or downstream should result in a linear relationship.

For example, the correlation between daily EC measurements and the fraction of downstream flow is linear ($R^2 = 0.62$), indicating that EC is strongly driven by the fraction of upstream flow (Fig. 1a). The linear extrapolation through the data suggest that an end-member EC ($X_{Her} = 0$) is 838μS, whereas the downstream "within reach" source ($X_{Her} = 1$) is 219μS. Using monthly average EC and discharge values improve the linear correlation ($R^2 = 0.82$), which can facilitate reliable salt load calculations (Criss et al., 2001). The daily and monthly EC values are far better constrained by separating discharge into geographically controlled flow components rather than simple comparisons with discharge at a single point.

Criss et al. (2001) showed that monthly average concentrations of water quality parameters collected at Howard Bend also show linear correlation with the fraction of downstream flow. These include cations of Ca, Mg, and Na (R = 0.70, 0.65, 0.89 respectively), anions of HCO_3, SO_4, and F (R = 0.67, 0.87, 0.84 respectively), and DOC ($R^2 = 0.63$; Fig. 1b). The correlation between the fraction of discharge and DOC (Fig 1b) is a key result in this study and several details of this correlation need clarification. For example, DOC concentrations for the El Nino period of 1998 were unusually low and were not included in the linear regression. It is still unclear why the DOC was low during this period, although an unusually steady baseflow period persisted from June, 1997 to March, 1998, and the spring runoff pulse in 1998 was fragmented and not persistent. However, the total discharge over the year, and also from March through July of each year, was similar between El Nino and non-El Nino years. In addition, the spring growing season of 1997 was dry and cold, which could have lead to a reduced fall leaf litter available for DOC leaching in the following spring 1998 runoff season.

The monthly average DOC values from before El Nino (1995-1997) show a stronger correlation with X_{Her} ($R^2 = 0.78$), and an equally strong inverse correlation with EC ($R^2 = 0.80$). Typically, the DOC concentration is higher on average during the spring to early summer corresponding to seasonal snow melt and rain storms (Fig. 2). Even though monthly average DOC correlates to fraction of discharge, the daily values show a poor correlation. This suggests local effects control the instantaneous DOC concentration, which may include 1) various local geographic sources contributing short-term DOC loads, 2) algal blooms, 3) rainfall and runoff intensity, and 4) season. Given these as additional variables contributing to DOC on a daily basis, they still represent second-order variables in regards to major sources of DOC (Fig. 1b). In particular, since the DOC monthly averages correlate to the fraction of downstream discharge, regional geography represents the first-order control on DOC source and concentration. Also separated from the linear regression of Figure 1b are DOC values for January of each year. This month is always marked by a minimum baseflow in the river, and DOC values unpredictably vary probably due to groundwater contributions.

Results and Discussion

^{14}C Measurements of DOC

Ten samples of Missouri River were collected at Howard Bend over the course of one year for ^{14}C and ^{13}C isotopic analysis of DOC, and on their hydrophobic fractions. The DOC concentrations varied from <3 mg/L to >5 mg/L among the ten samples. The lowest concentration was in late summer of 1997 during a long baseflow period. Highest concentration was during spring runoff in 1998. The DOC concentrations of these ten samples did not correlate to daily discharge in the Missouri River. DOC in the Missouri River was unusually low during the El Nino period in 1998.

The hydrophobic content was determined on 6 of the ten DOC samples collected. The hydrophobic content ranged between 43% and 61% of the DOC. The lowest values were during September, 1997 and February, 1998 during low flow periods. The percent hydrophobic content did not correlate with the fraction of downstream discharge (X_{Her}). The hydrophobic fraction was dominated by fulvic acids, as indicated by low humic acid yields after acidification. Low concentrations of humic acids are typical for river and stream hydrophobic substances (Malcolm, 1985), whereas humic acid is the dominant hydrophobic substance in soil organic matter.

The ^{14}C content of DOC was measured on all ten samples collected and ranged from 115 pmc to 94 pmc (Fig. 3). The highest ^{14}C values were for samples collected in September, 1999 and February, 1998, while the lowest was for the January, 1998 sample. The variation in ^{14}C content did not correlate with river discharge, the fraction of downstream discharge, or DOC concentration.

Of particular note, however, is a correlation between the ^{14}C content of DOC and the fraction of hydrophobic substances in DOC (Fig. 4). The ^{14}C content of the DOC clearly decreases with increasing hydrophobic content. This indicates that the hydrophobic substances have an older mean age than the DOC measured as a total, as also seen in the fulvic and humic acid fractions (Fig. 3). Providing that the data relation in Figure 4 varies on a linear scale, a linear regression suggests that for a DOC with no hydrophobic content (hydrophobic/DOC = 0), the ^{14}C would be 140pmc, whereas if the DOC was 100% hydrophobic (hydrophobic/DOC = 1), then the ^{14}C would be 63pmc. These postulated end-member ^{14}C values are consistent with environmental levels of post-atomic age radiocarbon fallout, or with mean ages of soil organic matter, respectively (e.g. Trumbore, 1993).

The ^{14}C of isolated fulvic acid from the Missouri River DOC varied from 99pmc to 87pmc. Humic acids (measured on only 4 samples) ranged from 94pmc to 67pmc (Fig. 3). The ^{14}C content of the fulvic acid showed remarkably strong linear correlation with electrical conductivity and the fraction of downstream discharge (Figs. 5ab). These parameters are both indicators of water source in the lower Missouri River, and their linear correlation with fulvic acid ^{14}C indicate this part of the DOC is transported conservatively with the water. A key conclusion is that the source of fulvic acids can be distinguished by their ^{14}C variation. Recall that the fulvic acid dominates the hydrophobic fraction, and represents approximately half the DOC content. Extrapolation of the linear regressions in Figures 5a and 5b to upstream and downstream end-members suggest that these two geographic source areas contribute fulvic acids whose ^{14}C on average is, respectively, 83pmc and 122pmc. The age of hydrophobic substances derived from the upper Missouri River is much older than those derived from the lower Missouri basin.

The above results are explicable in terms of climatic variations within the Missouri River watershed. The lower Missouri is dominated by southern deciduous woodland vegetation, which has a temperate to humid climate with mean annual precipitation averaging ~40in/yr. The upper Missouri is mostly mixed prairie grassland of more arid and seasonal climate with mean annual precipitation averaging ~20in/yr. The headwaters of the Missouri River are the eastern Rocky Mountains of Wyoming and Montana. Vegetation in these areas is mixed alpine forest. Annual precipitation is mostly as snow. Most of the snowmelt is impounded annually in five large reservoirs operated by the Army Corps of Engineers on the upper Missouri River. Storage in reservoirs likely contributes to evaporation, which increases the electrical conductivity of upper river flow.

Climate and vegetation control the quantity and character of dissolved hydrophobic substances in the river water (e.g. Thurman, 1985). River fulvic and humic acids represent the most soluble fraction of soil organic matter (Malcolm, 1985; Aiken and Malcolm, 1987), and their ^{14}C content will be controlled by their total length of storage in the soil environment. The different vegetative regimes in the Missouri River watershed are controlled by the variable climate, which results in different soil types. For example, woodland forests like the lower Missouri River area have relatively high primary productivity rates. Carbon turnover in the ecosystem can be large and high precipitation rates contribute to annual soil flushing. Deep root systems contribute to appreciable weathering of soils and likely reduce their organic matter retention capacity. Annual leaf litter produced from deciduous trees also contributes to DOC and modern ^{14}C (>100pmc) in the river, which can have soluble components with hydrophobic character (i.e. hydrolyzable tannins, see Wershaw et al., 1996).

In the grassland dominated region of the Missouri River, the soil organic matter content can be significantly higher. This results mainly from the annual growth of natural grasslands, where spring warming and aerial precipitation contribute to an intense growing season. As temperatures warm and precipitation tapers back, grasses decrease productivity. They eventually die back as temperatures cool. The lower precipitation rates limit the amount of leaching of residual organic matter, and likely reduction in microbial degradation. Also, grasses have shallow root structures and do not create a deep and weathered soil profile. This increases the soil retention capacity for organic matter and slows turnover times by reducing its solubility. This could explain the lower average DOC concentration in discharge originating above St. Josephs, MO. Most importantly, the carbon retention in the soils together with lower NPP contribute older dissolved hydrophobic substances (lower ^{14}C) to upper watershed discharge.

^{13}C Measurements of DOC

The $\delta^{13}C$ value was analyzed on the same samples as the ^{14}C. The $\delta^{13}C$ value of bulk DOC changed approximately 2.5 per mil over the course of one year (Fig. 6). The lowest values were during the wintertime at near baseflow conditions, whereas high values were associated with warmer periods and higher flow. Note that the $\delta^{13}C$ of the DOC somewhat parallels the annual temperature cycle in the Missouri River, where lower temperatures correlate with more negative values (Fig. 7). The $\delta^{13}C$ values of the DOC do not correlate with ^{14}C or the hydrophobic content of the DOC, suggesting that the ^{13}C is controlled by a process somewhat de-coupled from that controlling the ^{14}C. The

$\delta^{13}C$ of the fulvic acid did not vary significantly among the samples measured. This suggests that the hydrophobic fraction likely originating from plant litter or soils in different parts of the watershed, has a constant source and does not originate from plant sources representing both C3 and C4 metabolic pathways. The $\delta^{13}C$ of the humic acid (typically 10% of hydrophobic fraction) is much higher and also shows little variation among the samples measured. These humic acid values are similar to high $\delta^{13}C$ values measured in decomposed forest soil organic matter (Nadelhoffer and Fry, 1988). The $\delta^{13}C$ values and low concentrations of humic acids in the river water are consistent with their low solubility and their close association with soil organic matter (e.g. Stevenson, 1985).

The small $\delta^{13}C$ variation in the hydrophobic fraction of the DOC indicates that most of the seasonal variability of the measured $\delta^{13}C$ values is in the non- hydrophobic fraction, or the hydrophilic substances. This observation, and the close relation of the $\delta^{13}C$ variation to water temperature, suggest that the hydrophilic fraction comprises variable amounts of soluble organic matter originating from algae. This is not surprising given that the upper Missouri River is dominated by six large dams with a total storage capacity exceeding the annual discharge. Shallow water in each reservoir provides an obvious environment for promoting algae growth. To determine the amount of DOC originating from algal material, a mass balance equation is constructed to calculate the ratio of algal-derived DOC to total DOC. It follows that this ratio can be defined by

$$\frac{DOC_{alg}}{DOC_{tot}} = \frac{\dfrac{\delta^{13}C_{non\text{-}alg}}{DOC_{tot}} + \dfrac{DOC_{hyd}}{DOC_{tot}}\delta^{13}C_{hyd} - \delta^{13}C_{tot}}{\delta^{13}C_{alg} - \delta^{13}C_{non\text{-}alg}}$$

where subscripts *alg*, *non-alg*, *tot*, and *hyd* refer to, respectively, algal component of DOC, non-algal portion of hydrophilic DOC (e.g. low molecular weight acids), total DOC, and the hydrophobic substances of DOC. If we assume that the $\delta^{13}C_{alg}$ is –23 per mil (Thurman, 1985), and the $\delta^{13}C_{non\text{-}alg}$ is –28 per mil, then DOC_{alg}/DOC_{tot} ratio can be calculated. Results are plotted against the fraction of hydrophobic content in Figure 8. The highest algal DOC ratio is for a sample collected in late summer at near baseflow conditions. This sample was collected when upstream discharge comprised 88% of the flow ($X_{Her} = 0.12$), and at a time of the year when the runoff would be dominated by reservoir discharge. At baseflow in mid-winter, when algal production is anticipated to be lowest, the mass balance suggests algal DOC is nearly absent. The remaining samples represent late winter to early summer runoff. The linear inverse correlation in Figure 8 has a y-intercept of nearly 0.5, suggesting at that end-member, the water could have nearly half its DOC from algal origin and be absent of hydrophobic substances. This end-member may be realistic for shallow reservoir water (e.g. above thermocline) in the upper watershed during the summertime, since the Missouri River channel itself does not have the requisite surface area to supply this photosynthetic fixation capacity and also be free of hydrophobic substances.

Summary and Conclusions

DOC can be linearized against the fractional amount of downstream discharge (derived from within the State of Missouri) and divided into two principle sources. This correlation relates directly to differences in land use and climate between the upstream and downstream portions of the river basin.

The ^{14}C abundance of DOC decreased with increasing hydrophobic substances, indicating that at various times DOC comprises older sources of carbon. These hydrophobic substances also preferentially forms tri-halomethanes during chlorination, relative to the remaining portion of DOC. The ^{14}C abundance of hydrophobic substances showed a strong inverse correlation to electrical conductivity. This relationship provided a basis to delineate the geographic source of the DOC.

The ^{13}C on DOC in the Missouri River distinguished carbon originating from algae photosynthesis versus that generated from land plant material. Their relative proportions correlated with season and water temperature.

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Figure Captions

Figure 1. The fraction of downstream discharge X in the lower Missouri River correlates linearly with the electrical conductivity (Fig. 1a) and monthly average DOC concentrations (Fig. 1b), indicating two principle sources of water quality parameters. Exceptions are baseflow (January only), where groundwater discharge may influence DOC concentration, and during El Nino when DOC was unusually low.

Figure 2. Monthly average DOC values are strongly correlated with monthly stage (and discharge) of the Missouri River at St. Louis, but daily values (not shown) have only a weak correlation..

Figure 3. The ^{14}C abundance in DOC and hydrophobic fractions of DOC show variation during the course of one year that did not correlate to discharge. The hydrophobic fractions are distinctly older than the bulk DOC.

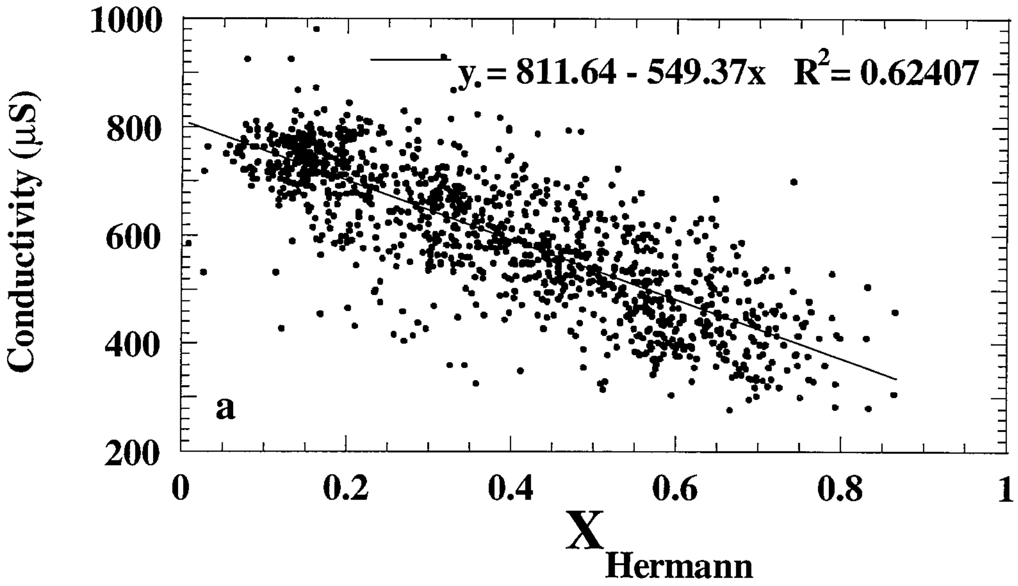
Figure 4. The ^{14}C abundance of bulk (total) DOC negatively correlated with the fractional amount of hydrophobic content, indicating the hydrophobics carry the older radiocarbon signature.

Figure 5ab. The ^{14}C abundance of the fulvic acid fraction of DOC is highly correlated with the conductivity of Missouri River water, and also correlates well with the fraction of downstream discharge.

Figure 6. The $\delta^{13}C$ value of bulk DOC varies over 2 per mil during the course of one year, consistent with, but of lower variability than particulate organic carbon observed by previous workers (Bird et al., 1998 and Barth et al., 1998). The hydrophobic fractions show little $\delta^{13}C$ variation, suggesting that the bulk $\delta^{13}C$ variation is not linked to vegetation type, but rather algal production.

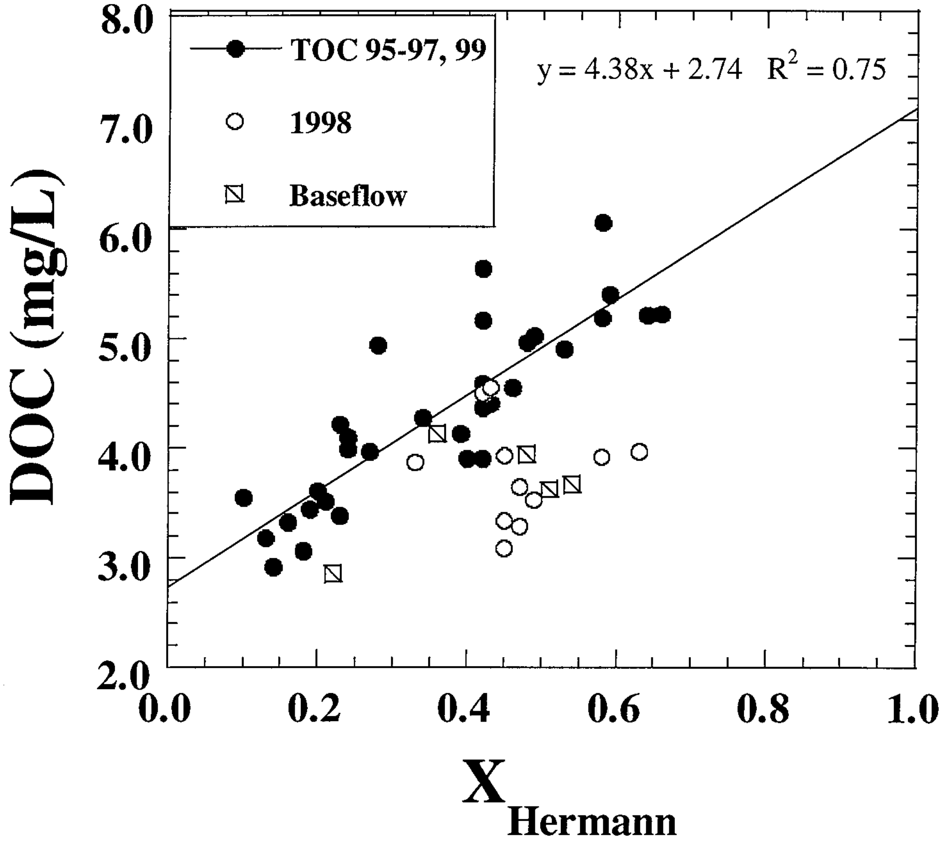
Figure 7. The $\delta^{13}C$ of bulk DOC in the Missouri River varies closely with water temperature, suggesting a relationship with algal sources of DOC.

Figure 8. Algal DOC was calculated by mass balance using the DOC concentrations, hydrophobic contentm, and the $\delta^{13}C$ values. The highest and lowest algal content correlate to summer baseflow and winter baseflow, respectively.



y = 811.64 - 549.37x R^2= 0.62407
Conductivity (μS)
1000
800
600
400
200
0
0.2
0.4
0.6
0.8
1
a
X Hermann

Figure 1a



8.0
7.0
6.0
5.0
4.0
3.0
2.0
DOC (mg/L)
TOC 95-97, 99
1998
Baseflow
y = 4.38x + 2.74 R^2 = 0.75
0.0
0.2
0.4
0.6
0.8
1.0
$X_{Hermann}$

Figure 1b

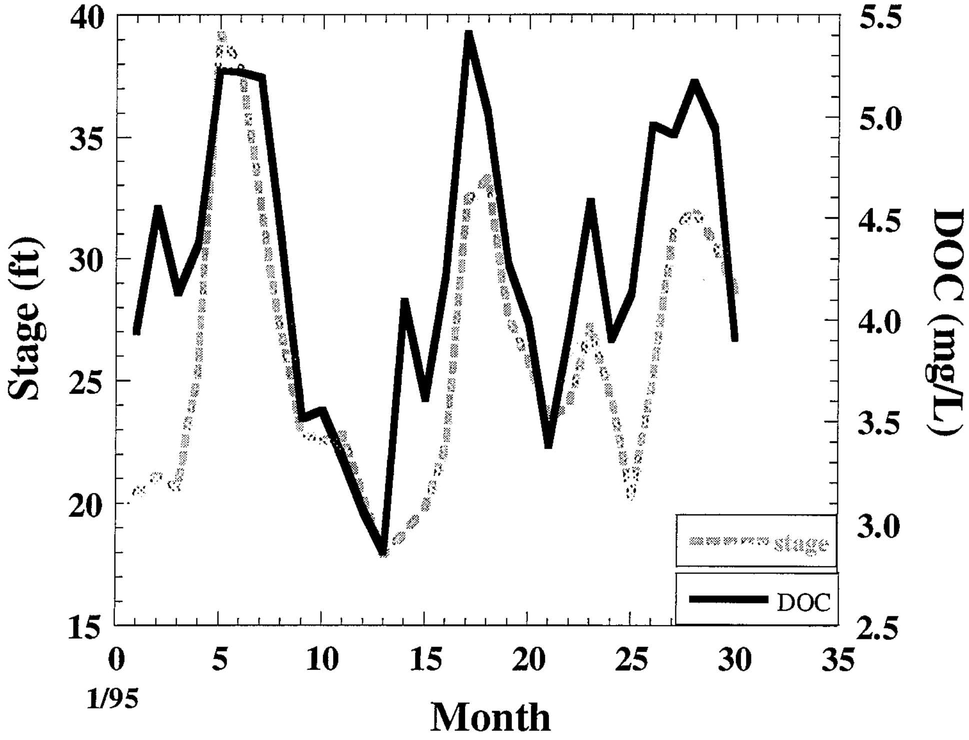

Stage (ft)
DOC (mg/L)
Month
1/95
0
5
10
15
20
25
30
35
40
2.5
3.0
3.5
4.0
4.5
5.0
5.5
stage
DOC

Figure 2

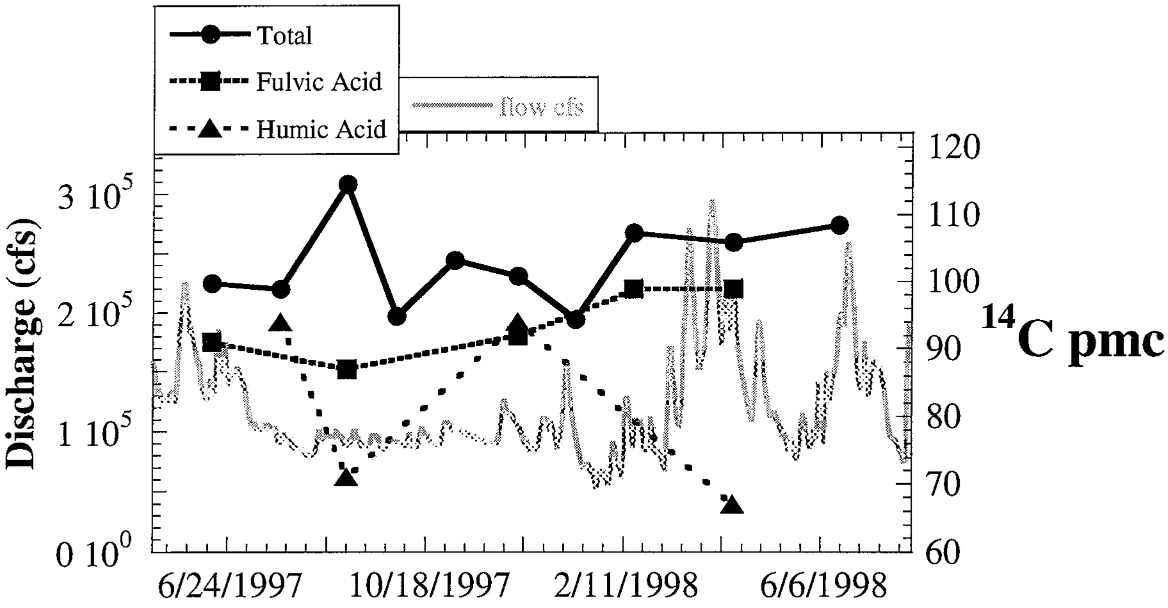

Total
Fulvic Acid
Humic Acid
flow cfs
Discharge (cfs)
3 10^5
2 10^5
1 10^5
0 10^0
120
110
100
90
80
70
60
14C pmc
6/24/1997
10/18/1997
2/11/1998
6/6/1998

Figure 3

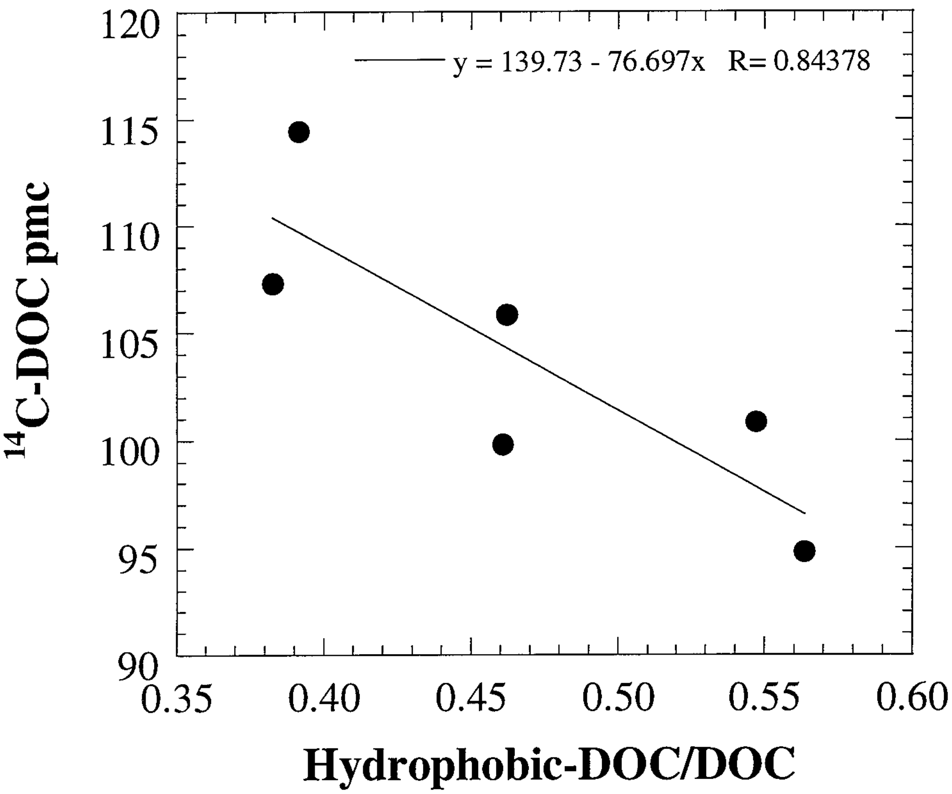
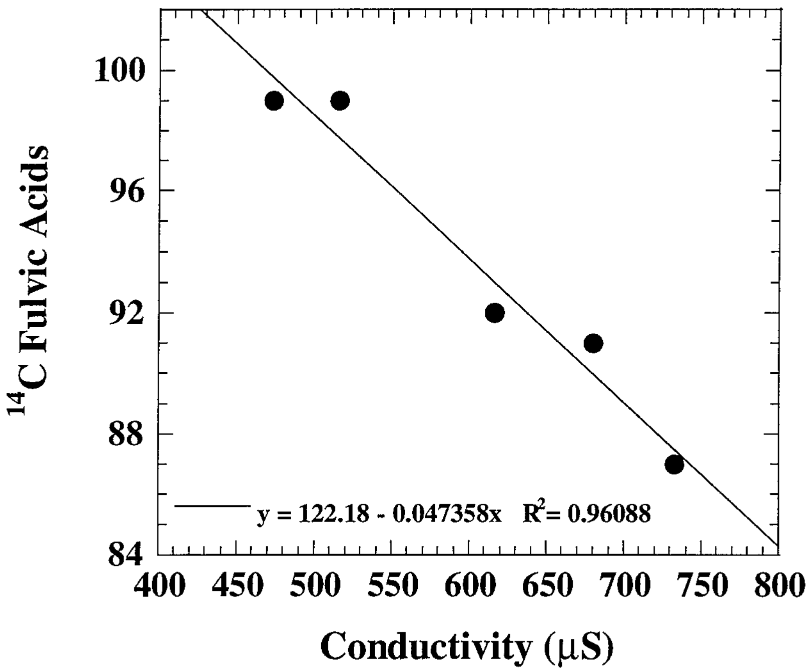

y = 139.73 - 76.697x R= 0.84378
120
115
110
105
100
95
90
0.35
0.40
0.45
0.50
0.55
0.60
^{14}C-DOC pmc
Hydrophobic-DOC/DOC

Figure 4



^{14}C Fulvic Acids
100
96
92
88
84
400
450
500
550
600
650
700
750
800
Conductivity (μS)
y = 122.18 - 0.047358x R^2= 0.96088

Figure 5a

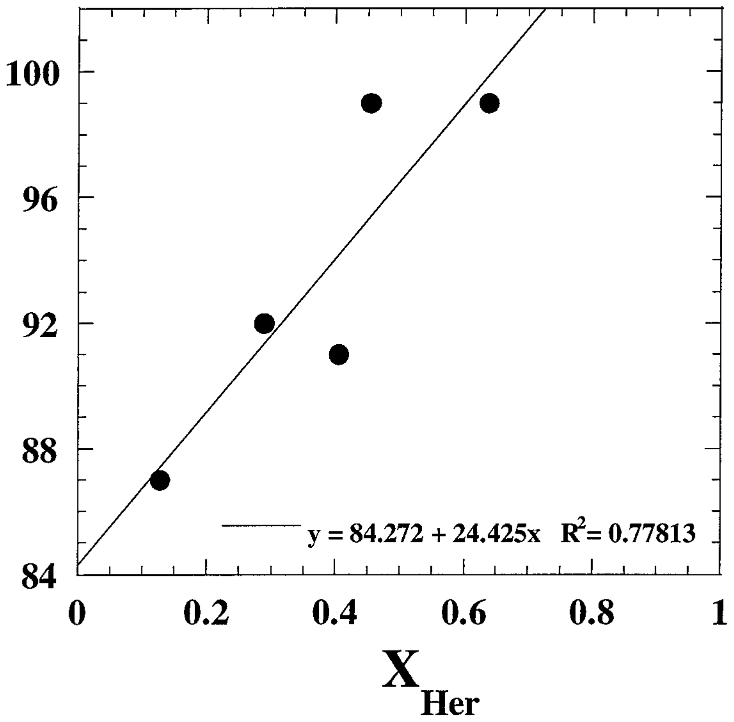
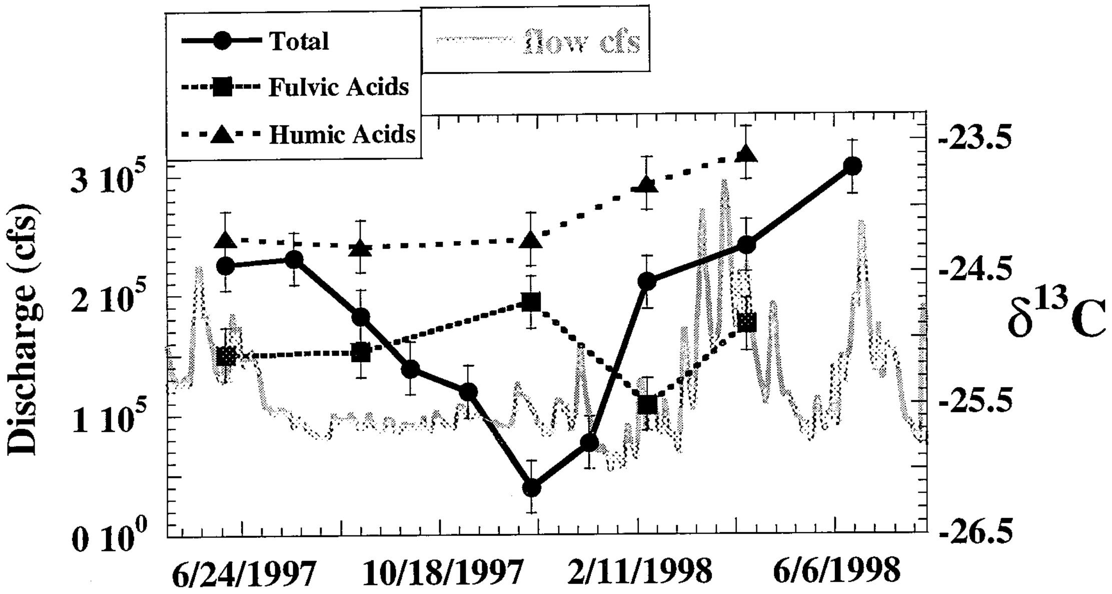
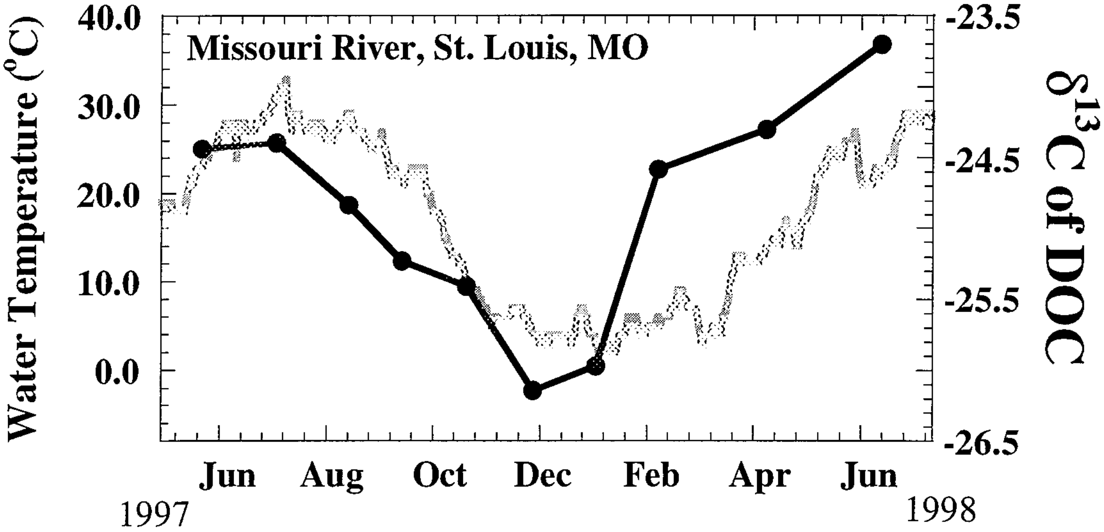


Figure 5b



Total
Fulvic Acids
Humic Acids
flow cfs
Discharge (cfs)
3 10^5
2 10^5
1 10^5
0 10^0
-23.5
-24.5
-25.5
-26.5
δ13C
6/24/1997
10/18/1997
2/11/1998
6/6/1998

Figure 6



Missouri River, St. Louis, MO
Water Temperature (°C)
40.0
30.0
20.0
10.0
0.0
δ13C of DOC
-23.5
-24.5
-25.5
-26.5
Jun
Aug
Oct
Dec
Feb
Apr
Jun
1997
1998

Figure 7

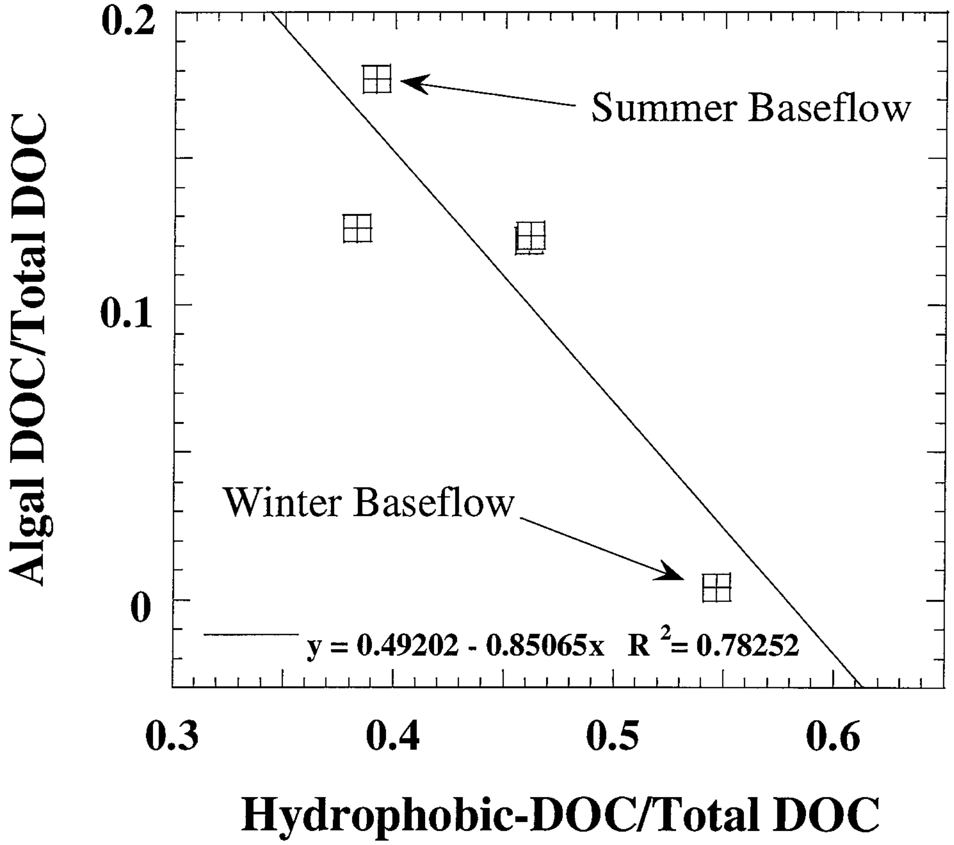

0.2
0.1
0
0.3
0.4
0.5
0.6
Algal DOC/Total DOC
Hydrophobic-DOC/Total DOC
Summer Baseflow
Winter Baseflow
y = 0.49202 - 0.85065x R ²= 0.78252

Figure 8

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