

**DISINFECTION BY-PRODUCT PRECURSORS AND FORMATION
POTENTIALS OF MISSOURI RESERVOIRS**

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Missouri-Columbia

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Of the Requirements for the Degree
Master of Science

by

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The undersigned, appointed by the dean of the Graduate School, have examined the thesis entitled

DISINFECTION BY-PRODUCT PRECURSORS AND FORMATION POTENTIALS
OF MISSOURI RESERVOIRS

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DISINFECTION BY-PRODUCT PRECURSORS AND FORMATION POTENTIALS OF MISSOURI RESERVOIRS

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ABSTRACT

Dissolved organic carbon (DOC) in surface water affects finished drinking water quality, in particular the formation of halogenated disinfection by-products (DBP). In Missouri, 62% of the public is served by 221 drinking water systems utilizing surface waters. Both the quality and quantity of DOC impacts DBP formation and it is known that allochthonous DOC is more reactive with halogens than autochthonous DOC. Our goal in this study was to determine the relative influence of allochthonous and autochthonous DOC on the DBP precursor pool. Samples were collected from 76 reservoirs spanning a 12 month period from January 2004 through December 2004 and regression models were developed for DBP surrogates. In a cross-system analysis of annual reservoir means, 77% of the variation in DOC [1.35 – 12.37 mg/L] was explained by hydraulic flushing rate. Total phosphorus [4.0 – 32.2 µg/L] and DOC accounted for 97% of the variation in chlorine demand [4.5 - 19.2 mg/L] while total phosphorus and hydraulic flushing rate

explained 88%. Additionally, time-series plots were compared to stream gauge data and UV₂₅₄ absorbance peaks coincided well with peaks in the hydrographs. Chlorophyll [0.6 – 195.2 µg/L] was weakly correlated with the DBP surrogates within and across seasons ($R^2 = 0.31 - 0.62$). These results indicate that watershed hydrology and allochthonous inputs controlled the DBP precursor pool in Missouri reservoirs in 2004 and that hydraulic flushing rate may have more predictive value modeling DBP formation than chlorophyll.

INTRODUCTION

Source water supply and quality are fast becoming limiting factors in urban expansion, population growth and human health in many parts of the world. In developing countries, access to clean, safe drinking water is often rare or non-existent while in much of the United States and other developed countries it is generally abundant. Chlorinating raw water for disinfection has been in practice for over 100 years due to its effectiveness, availability and low cost (Cox 1969). Use of chlorine and its compounds including chloramines and chlorine dioxide, however, is increasingly a concern due to the formation of halogenated disinfection by-products (DBP) in finished drinking water. Recent medical research has determined that many of these common disinfection by-products are potentially toxic and mutagenic (Singer 1999, CA DOH 2001).

Concern over the adverse health effects of halogenated compounds has prompted increasingly restrictive US Environmental Protection Agency (US EPA) regulations for four trihalomethane (THM-4) and five haloacetic acid (HAA-5) species. In an effort to comply with the new maximum contaminant levels (MCL) established by the US EPA, many changes in treatment plant processes have been implemented. In some cases, treatment changes are insufficient or cost prohibitive (CA DOH 2001) leading to increased interest in source water protection measures. Several studies have evaluated reservoirs for DBP formation potential or its surrogate measures to determine the contributing environmental factors and model DBP formation.

Dissolved organic carbon (DOC), the precursor to DBP, is present in all natural waters but the concentration and composition varies regionally and globally due to different source and transport mechanisms (Sachse et al. 2001, Xenopoulos et al. 2003). Reactivity of DOC with chlorine also varies and several studies have attempted to elucidate the origin of the more reactive carbon compounds, often with contradictory results. Many studies have demonstrated a strong link between algal productivity and DBP formation potential (Walker 1983, Hoehn et al. 1983, Wardlaw 1991) while other studies have found this relationship weak (Hoehn et al. 1980, Stepczuk 1998). It is known that biologically refractory humic and fulvic acid fractions of the carbon pool, generally of allochthonous origin, are the most reactive with chlorine (Rook 1977, Oliver and Lawrence 1979, Chang et al. 2000, Goslan et al. 2002). Reservoir hydrology, however, affects the relative amounts of allochthonous and autochthonous carbon in the system (Gergel et al. 1999, Cole et al. 2002).

Research Objectives

Missouri has approximately 2,700 public drinking water supply systems and of those, over 200 utilize surface waters. These surface waters, while constituting only 8% of the public systems, serve 62% of Missouri's population (MO-DNR personal communication). Most surface water contains higher levels of DOC than ground water (Wetzel 2001) and has the potential to produce DBP upon chlorination. The characteristics of the DOC, in addition to the concentration, influence the formation of DBP. Allochthonous and autochthonous inputs, however, vary both spatially and

temporally within and among reservoir systems and hence the composition and character of DOC also varies. The goal of this study was to determine the relative importance of allochthonous and autochthonous carbon inputs in the formation of DBP in Missouri reservoir waters in 2004. Globally, DOC predictors vary due to regional differences in landscape, hydrology and anthropogenic factors (Xenopoulos et al. 2003). These controlling factors differ in importance in different ecoregions resulting in regional DOC models that are not applicable on larger geographic scales (Xenopoulos et al 2003). Within Missouri, different physiographic regions (Figure 1, Jones and Knowlton 1993) contribute unique hydrological and geological influences over lake chemistry and biology (Jones 1977, Jones and Knowlton 1993). Land use and catchment hydrology are also known to influence reservoir water chemistry (Jones et al. 2004, del Giorgio and Peters 1994) and in particular, Midwestern agricultural soils contain a large pool of organic carbon (Royer and David 2005). Missouri has few natural lakes; nearly all water bodies are artificial impoundments having high watershed to reservoir volume ratios and hence high flushing rates. In 2004, Missouri experienced higher than normal precipitation rates for most of the spring and summer and for the year overall. This above normal precipitation followed nine years of below normal precipitation (USGS 2005). We suspected that the high flushing rates of Missouri reservoirs in 2004 would increase the proportion of allochthonous carbon DBP precursors. Our goal in this study was two-fold: to examine the temporal relationships between DBPFP, the carbon precursor pool and other environmental variables and to identify the proportional influence of allochthonous and autochthonous carbon sources in Missouri reservoirs.

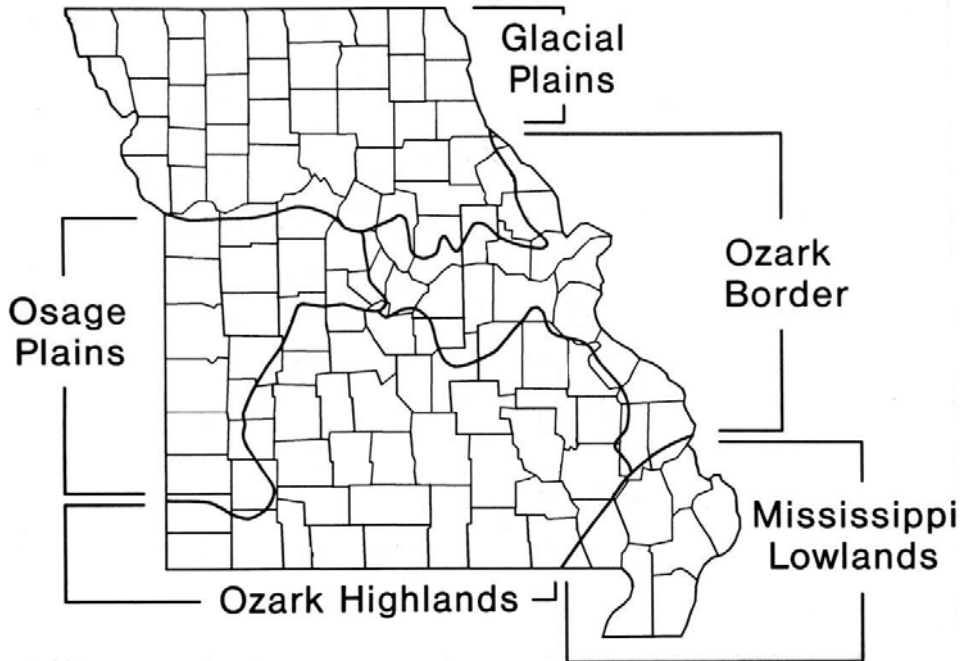


Figure 1. Physiographic map of Missouri.

LITERATURE REVIEW

Toxicology and Epidemiology

High doses of disinfection by-products (DBP) are carcinogenic, mutagenic and teratogenic (Singer 1999, CA DOH 2001). DBP are associated with colon, rectal and bladder cancer in humans (Singer 1999). Reproductive problems including miscarriage have also been implicated, although the American Water Works Association Research Foundation (2005) found no significant relationship between trihalogenated methane

(THM) levels in drinking water and rates of miscarriage. The nature of drinking water consumption is such that the presence of carcinogenic compounds may cause chronic, repetitive and/or potentially high dose exposure. The debate over the health effects of DBP has not been resolved, but the US EPA has responded by promulgating DBP regulations for THM, halogenated acetic acids (HAA) and other chlorination by-products (Teuschler et al. 2003). Currently, the maximum contaminant level (MCL) for the sum of four THM and five HAA species stands at 80 ppb and 60 ppb respectively (US EPA 1998), regulated under the Safe Drinking Water Act (SDWA). DBP regulations were first promulgated for systems serving greater than 10,000 people, but now apply to smaller public water supply systems as well.

Chemistry of DBP Formation

THM levels in raw water are typically low, usually less than 10 ppb (Arguello et al. 1979). Formation of THM occurs both during and after the disinfection process in the water treatment plant and subsequently in the distribution system. In water, chlorine gas rapidly converts to hypochlorous acid (HOCl) and the unprotonated hypochlorite ion (OCl⁻). The chlorine substitutes into the organic matrix forming organohalides (Johnson and Jensen 1986). The organic matrix is referred to as the DBP precursor pool. However, of this total carbon pool, dissolved organic carbon (DOC) is more reactive with chlorine than particulate organic carbon (POC) (Stepczuk et al. 1998a). The reactivity of dissolved organics is problematic for DBP control in drinking water treatment plants, as standard treatment processes are less effective in removing dissolved constituents. DOC more readily passes through the system and remains available for reaction with Cl₂.

Halogens react with organics to form a variety of compounds; chloroform being the dominant THM species (Hoehn et al. 1980, Johnson and Jensen 1986, Karimi and Singer 1991, Stepczuk et al. 1998a). Formation of other halogenated by-products is also of concern and the concentrations can be high, but usually 15-30% of the total organohalides (TOX) formed can be attributed to THM (Walker 1983, Palmstrom et al. 1988, Amy et al. 1990). Brominated species, although not as prevalent in surface water supplies, will inordinately contribute to THM levels due to their high molecular weight. Typically, brominated species are more common in coastal regions where intrusion of brine can occur or in regions with local geologic contributions of bromine (CA DOH 2001).

Distribution of THM precursors in a water body is measured as trihalomethane formation potential (THMFP). When all four THM species are summed together it is referred to as total trihalomethane formation potential (TTHMFP). Raw water samples are filtered, buffered, dosed with excess chlorine and then incubated for a period of time simulating the treatment system. At the end of the incubation period, a chlorine fixative is added and the sample is analyzed (APHA 1998). Surrogate measurements are often used in the water industry in place of time consuming and/or expensive analyses with a large degree of success (CA DOH 2001). Several surrogate measurements exist for THM formation potential including DOC, chlorophyll content, algal biomass, ultraviolet absorbance at 254 nm (UV_{254}) and chlorine demand.

Control of DBP Formation

DBP formation is typically reduced through alteration of the treatment process or the distribution system. The formation of THM is known to increase with increased chlorine dose, contact time, pH and temperature (Oliver and Shindler 1980), thus timing of chlorination, the pH of water during the treatment process and main flushing regimes in the distribution system all impact the THM levels of finished water (Oliver and Lawrence 1979). Chloramines and chlorine dioxide, alternatives to chlorine gas, have been shown to react more slowly or not at all with organic matter to form chlorinated by-products (Hoehn et al. 2003). More recently, source water management practices to reduce THM levels including precursor control, timing of intake, location of intake and reduction of nutrient loading have garnered attention.

Organic Matter

Natural organic matter (NOM) is widely accepted as the primary precursor of DBP compounds. NOM is also implicated in other water-related issues such as taste and odor, which are aesthetic problems rather than health issues (Smith et al. 2002). Typical DOC concentrations of natural waters range from less than 1 mg/l up to 60 mg/l, varying by ecoregion (Kalff 2002, Xenopoulos et al. 2003). Carbon concentration, however, does not dictate DBPFP. The reactivity of different organic fractions with chlorine is not equal. Humic and fulvic acids, hydrophobic fractions of NOM, are the dominant THM precursors (Rook 1977, Oliver and Lawrence 1979, Chang et al. 2000, Chang et al. 2001, Goslan et al. 2002), with humics yielding more THM than fulvic acids (Reckhow et al.

1990). This increased reactivity has been attributed to the high aromatic carbon content of humic substances (Singer 1999). Higher molecular weight compounds have also demonstrated increased reactivity with chlorine compared to lower molecular weight compounds (Oliver and Lawrence 1979, Hoehn et al. 1980, Amy et al. 1987). This molecular weight relationship, however, has been contested by Palmstrom et al. (1988) and Chang et al. (2001).

Dissolved organic carbon (DOC) has been used with some success as a surrogate estimator of the THM formation potential of raw waters. Upwards of 94% of THMFP has been attributed to dissolved constituents (Stepczuk 1998a). The impact of dissolved constituents on THM formation is further magnified by the relative inability of the traditional coagulation and sedimentation treatment processes to remove dissolved organics, leaving much of the dissolved carbon precursors available in the finished water to react with chlorine. In reservoirs, dissolved carbon is usually more abundant than the particulate form, usually comprising upwards of 80% of the total carbon load (Walker 1983, Sachse et al. 2001). The following equation describes the relationship between TOC and THMFP, as determined by Chapra et al. (1997), which indicates higher TOC loads have greater yield coefficients:

$$\text{THMFP} = 43.78 \text{ TOC}^{1.248} \quad (n = 133; R^2 = 0.94)$$

Data from eutrophic systems, however, do not always support the use of TOC or DOC as surrogate indicators of precursor concentration (Stepczuk et al. 1998a,b), suggesting that

this particular model may not be applicable in all systems. This relationship is affected by both precursor concentration and precursor reactivity.

Allochthonous and Autochthonous Precursors

The primary source of precursor molecules in a reservoir can be either allochthonous or autochthonous, depending on the system, season and year. The source of the DOC precursors has implications for its reactivity with chlorine. Allochthonous inputs tend to consist of humic substances and eroded organics from the watershed and are of greater importance in river systems (Pomes et al. 2000). Humic acids are a heterogenous mixture of biologically refractory but chemically very reactive macromolecules. These complex refractory molecules persist in aquatic systems, having low turn-over rates of months to years, but when encountered by a strong oxidant such as HOCl, react readily to form DBP (Ghabbour and Davies 2001). Autochthonous sources from internal primary productivity include algal biomass, extra-cellular products (ECP) and products of cell lysis. These autochthonous precursors generally play a greater role in reservoir (lentic) systems, especially in the lacustrine zone and in eutrophic systems. These autochthonous precursors are generally more labile in nature, are rapidly cycled through the microbial loop and generally constitute a small proportion of the total organic carbon pool (Norrman et al. 1995). In many studies of reservoir systems, trophic state dictated the relative importance of autochthonous carbon versus allochthonous carbon (Palmstrom et al. 1988, Karimi and Singer 1991, Canale et al. 1997, Stepczuk et al. 1998a,b) where higher levels of eutrophy exhibited more autochthonous influence.

Algal Contributions

Although humic and fulvic acids have been the focus of many THMFP studies, algae can potentially contribute equally to THMFP (Hoehn et al. 1980, Walker 1983, Scully et al. 1988, Wardlaw 1991). Algal biomass and ECP can be significant sources of DBP precursors, contributing during the growth phase as well as during decomposition. Links between algal productivity and THMFP have been shown in several major studies (Hoehn et al. 1980, Oliver and Shindler 1980, Walker 1983, Palmstrom et al. 1988, Scully et al. 1988, Karimi and Singer 1991, Martin et al. 1993). However, the relationship between chlorophyll, a proxy for algal productivity, and THMFP is not always consistent (Hoehn et al. 1980, 1983 and Stepczuk 1998). Algal growth rate, growth phase, rate of photosynthesis and species composition also impact ECP and have been shown to influence the generation of THM precursors (Hoehn et al. 1980). During summer months, the contribution of algal-derived precursors is thought to be more significant due to algal blooms (Scully et al. 1988). Algal growth is controlled by P and light (Kalff 2002, Xenopoulos et al. 2002, Xenopoulos and Frost 2003), which makes nutrients and light potentially important secondary variables in DBP formation from labile organic carbon. In addition to TOX formation, algal productivity can compromise the quality of finished water through the formation of blue-green algal toxins and a variety of taste and odor related compounds such as 2-methyl isoborneol (MIB) and geosmin (Smith et al. 2002).

Graham et al. (1998) evaluated the significance of algal biomass versus algal derived precursors in THMFP in stock laboratory cultures of two common algal species. The relative formation potential of cells versus ECP varied between species. A comparison of

species-specific and growth phase biomass contributions to THM yields was compiled by Wardlaw (1991), exemplifying the wide range of formation potentials observed in laboratory cultures. In general, THM formation increased with increasing biomass and ECP.

Hoehn et al. (1980) also investigated the role of algae in THM precursor formation and found high concentrations of precursors associated with algal blooms, but correlations between THM precursors and chlorophyll-a were not found in subsequent studies of the same lake (Hoehn 1983). A consistent relationship between algal population densities and THMFP was not established by Hoehn, nor was chlorophyll-a concentration a good predictive tool in Cannonsville Lake (Stepczuk et al. 1998a). Instead, these studies imply that dissolved precursors, not particulate algal biomass, may be the most important source of precursors resulting from primary productivity. Nguyen et al. 2005 found in a study of three algal species that both biomass and ECP formed DBP, with highest yields in the late exponential growth phase. All three species produced nearly equivalent amounts of DOC, however, diatoms produced more than 20 times as much chlorophyll-a than blue-green algae. This has implications in systems that experience algal species shifts. In effect, chlorophyll concentration itself is not a reliable indicator of ECP or reactive carbon levels (Canale et al. 1997).

Surrogate Measures

Surrogate measures are often used in place of difficult or costly analyses in the drinking water industry. DOC is generally the most useful measure in the prediction of DBP

formation including THM. DOC is the precursor of disinfection by-products and as a result, correlates well with THMFP (Kitis et al. 2001, Nguyen et al. 2002). Reactivity of organic carbon compounds with chlorine varies, however, and the relationship between DOC and THMFP is not perfect (Amy et al. 1990, Chapra et al. 1997, Kitis et al. 2001). Another DBP surrogate, UV_{254} , is a general measure of the aromatic and conjugated nature of the organic carbon and loosely translates to a measure of its reactivity with chlorine. A third surrogate, chlorine demand, is a measure of the amount of chlorine lost when reacted with raw water over time. Presumably, the difference between the amount of free chlorine added and the amount of residual chlorine equates to DBP formation (Gang et al. 2002). This measure is also an imperfect surrogate due to the formation of other chlorinated compounds such as ferric chloride (APHA 1998).

UV_{254}

Ultraviolet absorbance at 254 nm (UV_{254}) has been evaluated as an indicator of TOC reactivity and thus THMFP. Aromatic and conjugated double bonds absorb light in this region, imparting color to lake water, and these unsaturated bonding sites are highly reactive with chlorine (Edzwald et al. 1985, Singer 1999). High water color is also associated with compounds of allochthonous origin such as the refractory humic acids (Rasmussen et al 1989). Drinking water treatment systems that use ozonation experience a reduced correlation between UV absorbance and TOC, because the ozonation process will cleave apart the macromolecules and lower the UV_{254} absorbance without reducing the TOC load (Amy et al. 1992, Chiang et al. 2002). Positive interference by nitrate, which absorbs in the same region, has been noted in several studies (Nguyen et al 2005).

Chlorine Demand

Long period (7 day) and short period (2 hour) chlorine demand are highly correlated with TOC and THMFP (Edzwald et al. 1985). Complex molecular structure of DOC, in particular conjugated bonds and aromatic moieties, have a stronger relationship with chlorine demand than with THMFP (Reckhow et al. 1990).

Nutrient Loading and Trophic State

Nutrient enrichment contributes directly to several common drinking water quality problems including organohalide formation (Walker 1983). Algal productivity and ECP generation are modulated by nutrient loading. Nutrient concentration is determined by allochthonous inputs and internal loading, especially in stratified, eutrophic reservoirs where oxygen levels and iron chemistry play a major role in phosphorous availability. Eutrophic lakes, with high nutrient and chlorophyll levels, are particularly prone to high THMFP and other water quality problems. A strong correlation between phosphorous load and THM formation in lakes and reservoirs exists (Walker 1983). This association may be the direct result of stimulated algal growth, but a causal link is uncertain because the increased P load occurs with a concomitant increase in TOC load from the watershed.

Oligotrophic lakes rarely experience the same problems with THMFP as eutrophic lakes (Cooke and Kennedy 2001). Canale et al. (1997) modeled THMFP as a function of watershed TP and TOC loading in an oligotrophic lake. They determined that the

THMFP was due to external TOC loading and that the oligotrophic lake was more sensitive to changes in TOC loading than to TP changes. On the other hand, their model predicts that an increase in TP loading with a decrease in TOC loading would result in more significant algal related THMFP in reservoir systems.

Temporal and Spatial Variation

Seasonal trends in THMFP have been demonstrated in several studies (Hoehn et al. 1980, 1983, Edzwald et al. 1985, Palmstrom et al. 1988, Canale et al. 1997). In general, THMFP begins increasing in the epilimnion in spring, rising through summer and reaching a maximum in late summer or fall followed by a decline (Graham et al. 1998, Stepczuk et al. 1998a,c). This trend reflects the increase in autochthonous productivity due to algal blooms in late summer to fall (Royer and David 2005). Peaks in THMFP during periods of low productivity correlate with storm events, demonstrating the importance of allochthonous inputs year-round (Palmstrom et al. 1988). Trophic state variation within a given reservoir also determines spatial variation in THMFP, with the more eutrophic riverine zones exhibiting higher levels than the lacustrine zones (Stepczuk et al. 1998a).

Hydraulic Flushing Rate

The influence of hydraulic flushing rate (HFR) on autochthonous productivity is debated. Longer reservoir residence times potentially increase THMFP through several routes. According to Walker (1983), lower HFR allows for more decay and decay products to accumulate from bacterial activity. Decreased HFR also allows for increased algal growth

and algal ECP accumulation as well as the concentration of external nutrient and carbon inputs from the watershed before getting 'flushed' out of the system. In general, Walker (1983) indicated that lower HFR may increase autochthonous productivity from the breakdown of refractory allochthonous inputs into more labile carbon compounds, stimulate the trophic state of a reservoir and result in higher DBPFP.

Contrary to Walker (1983), several studies show that increased HFR can increase DBPFP by increasing the reactive, refractory allochthonous carbon as well as the autochthonous carbon. A concomitant influx of nutrients from the watershed can stimulate algal productivity and subsequently autochthonous carbon. Del Giorgio and Peters (1994) and Pace and Cole (2002) found that shallow lakes with higher HFR also had higher concentrations of chlorophyll and DOC.

MATERIALS AND METHODS

Field Collection and Storage of Samples

Samples for this study were combined from two different sampling efforts. Samples for the first data set were collected weekly in 2004 from 15 reservoirs in northern Missouri (Figure 2) between 12 January 2004 and 14 December 2004 for a total of 49 samples. This data set is referred to as “the northern Missouri reservoirs.” An additional 61 reservoirs located throughout Missouri (Figure 3) were sampled during summer 2004 on four occasions, (approximately once every 3 weeks from mid-May to mid-August). This data set is referred to as “the statewide reservoirs.” Additionally, data collected between May and August from all 76 reservoirs were combined into a summer 2004 data set, referred to as “the combined summer data.”

All water samples were collected from the surface at a site near the dam. Samples for DBP analyses were collected in 500 ml glass amber bottles with TFE-lined screw caps and kept on ice until reaching the laboratory. Samples were refrigerated in the dark and filtered within 24 hours of collection using washed 0.45 μm membrane filters. All DBP and DBP-surrogate analyses were performed on aliquots of these filtrates.

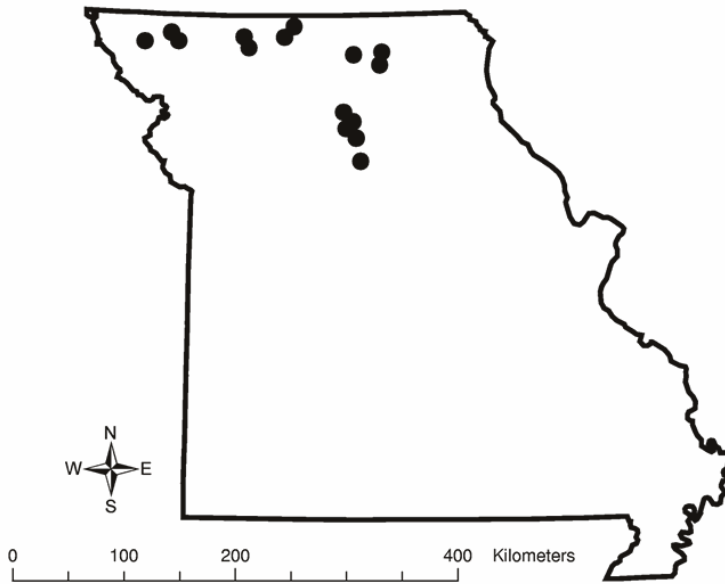


Figure 2. Location of the 15 northern Missouri reservoirs sampled weekly during 2004.

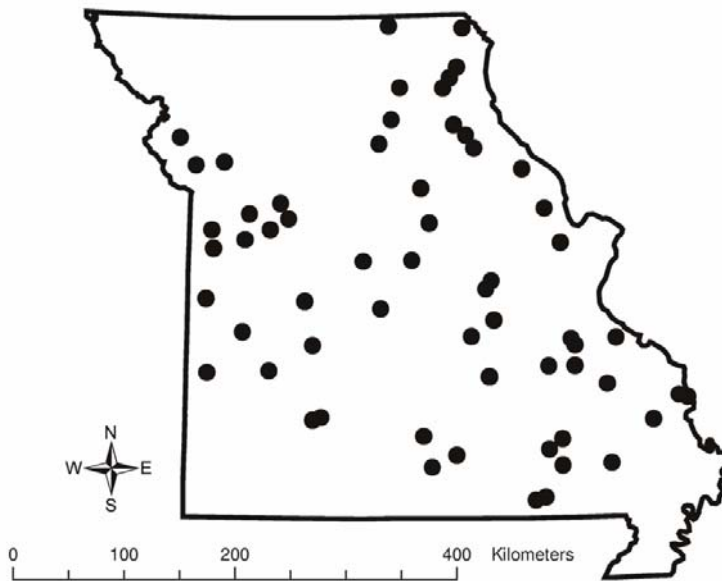


Figure 3. Location of the 61 statewide Missouri reservoirs sampled during summer 2004.

Dissolved Organic Carbon

Dissolved organic carbon (DOC) analysis was performed using a wet oxidation – persulfate method on a Tekmar-Dohrmann Phoenix 8000 TOC Analyzer with nitrogen as the carrier gas and a flow rate of ~200 ml/minute. Raw water samples were filtered through washed 0.45 µm pore-diameter membrane filters to remove particulates prior to analysis. Filtrates were then decanted into 40-ml glass vials, immediately acidified with concentrated reagent grade phosphoric acid to pH < 2 and stored refrigerated in the dark for a maximum of 28 days (typically 14 days) prior to analysis. Filtration and acidification were completed within 48 hours of collection. Samples were analyzed using potassium persulfate ($S_2O_8^{2-}$) in the presence of UV light, with the resulting CO_2 sparged and measured directly by a nondispersive infrared (NDIR) detector. The linearized NDIR signal was then converted to a DOC equivalent result based on a calibration curve. Samples were analyzed in triplicate. Standards ranging from 0.0 to 16 mg/L were prepared with reagent deionized, ultra-filtered (DIUF) water. Calibration standards, field blanks, filter blanks, system blanks, reagent blanks, check solutions and field duplicates were analyzed with each batch of samples for quality control purposes.

UV₂₅₄

UV₂₅₄ is a measure of the unsaturated organic bonds in a sample, indicating the potential for chlorine reaction sites (Kitis et al. 2001). It is often used to measure color, a secondary (aesthetic) regulated variable under the Safe Drinking Water Act. Common

interferences with UV₂₅₄ include ionic iron, nitrates, nitrites and bromide. UV₂₅₄ samples were filtered through washed 0.45 µm membrane filters and were not acidified. Samples were stored refrigerated in the dark and analyzed within 48 hours of collection. Two readings from each sample were made at 254 nm on a Spectrogenesys spectrophotometer using a 1-cm quartz cell. The instrument was zeroed using DI water (APHA 1998). UV₂₅₄ absorbance in this study was reported as absorbance per centimeter multiplied by 1000.

Specific Ultra-Violet Absorbance (SUVA)

SUVA represents the normalized aromaticity per mg of DOC of a water sample. SUVA was calculated by dividing the UV absorbance by the DOC content and multiplying by 1000. It is reported as L/mg-m. Both the DOC and UV analyses were performed on a split sample from the same location, from the same time and the same filtrate. SUVA was calculated as follows (APHA 1998):

$$\text{SUVA (L/mg-m)} = \text{UVA (cm)} / \text{DOC (mg/L)} * 1000$$

Where:

UVA = the measured UV absorbance of the sample (cm⁻¹)

DOC = dissolved organic carbon concentration of the sample (mg/L)

7- Day Chlorine (Oxidant) Demand

As detailed in Standard Methods (APHA 1998), THMFP can be evaluated as reactivity-based potential or dose based potential. Reactivity based analyses provide more

consistent results while dose based analyses generally result in widely variable THM formation. THMFP is useful for the evaluation of a treatment system or for the prediction of THM levels from particular source waters. In this study, THMFP was measured to estimate the amount and reactivity of THM precursors in the source water. Obtaining meaningful results from THMFP tests requires that certain variables be controlled including temperature, pH, contact time and chlorine residual, all known to increase THMFP as they increase. Total trihalomethane, TTHM, is the sum of the four regulated THM species: chloroform, bromoform, dibromochloroform and bromodichloroform. THMFP is the difference between the final and initial THM concentrations. The initial concentrations of THM in raw water are close to zero and considered negligible, and THMFP is equated to the final THM concentration of the sample (APHA 1998).

Standard Reaction Conditions: A predetermined chlorine dose providing a free chlorine residual of 1.0 mg/L +/- 0.4 mg/L at the end of a 7-d reaction (incubation) period is added to the sample. The incubation pH is controlled at 8.0 +/- 0.2 with phosphate buffer, temperature controlled at 20 °C and light exposure was limited by using amber glass bottles stored in a Styrofoam cooler. All bottles had Teflon-lined septa caps and care was used to eliminate all head space at the start of the incubation (APHA 1998).

Colorimetric TTHMFP Method

A non-EPA compliance DBP screening method was adapted and used instead of standard GC/MS methods due to time and cost restrictions. This method is currently not

acceptable for THM reporting in compliance with the EPA's DBP rule. The patented Hach THMPlus wet-chemistry, colorimetric method, analogous to the Fujiwara method, was modified for use in the laboratory. This method provides results of total trihalomethane-4 (chloroform, bromoform, dichlorobromomethane and dibromochloromethane) instead of results for individual species of THM. The method uses four reagents and a five minute digestion in boiling water. A linear response ranges from 0-200 µg/L and it has a detection limit of ~ 6 µg/L. Following the 7-day chlorination, samples were neutralized with sodium thiosulfate and decanted into 40 ml glass vials with Teflon-lined septa, ensuring no head space. Samples were then refrigerated at 4°C, in the dark, for no more than 14 days until analysis. For analysis, samples were equilibrated to room temperature and triplicate 10 ml samples were pipetted from the 40 ml vials into 15 ml test tubes. Three drops of a strong base (65% w/v reagent grade KOH) was repipetted and the samples capped and gently swirled. Three ml of the second reagent, N, N-diethylnicotinamide (CAS #5-92-67), at room temperature, was added with a repipet and the sample thoroughly mixed. THM in the sample react with N, N-diethylnicotinamide in the presence of the strong base and heat (immersion in boiling water for 5 minutes), forming an intermediate dialdehyde: 5-hydroxy-2-(n,n-diethylcarboxamide)-2,4-pentadienal. After digestion, samples were placed in a cold water bath and acidified with 1 mL of a strong acid (65% H₃PO₄ w/w and 15% H₂SO₄ w/w) to a pH of 2.5. Samples were cooled for 3 minutes in a cold water bath. In the final step, 0.44 g (+/- 0.04 g) of the color-developing reagent, 7-naphthalamine-1,3-disulfonic acid (G-amino acid), was added, which reacted with the aldehyde to form a reddish-yellow Schiff base. Color was developed for 15 minutes and the absorbance was read at

515 nm in a 5 cm quartz cell on a Spectrogenesys II spectrophotometer. A stock standard was prepared in reagent grade methanol and calibration standards in DIUF water, injected using a microsyringe placed well below the sample surface to minimize volatilization. All standards were prepared at the time of analysis and used immediately; standards were not prepared in advance. Sources of error include volatilization losses from the dilution process and positive interference from additional chlorinated compounds.

Environmental Variables

Numerous environmental variables were evaluated in addition to the DBP analyses (Table 1). Total phosphorus, total nitrogen and chlorophyll were determined by standard methods (Knowlton and Jones 1995). Suspended solids (total, volatile and non-volatile) were determined as detailed by Jones and Knowlton (2005). All other laboratory analyses used to generate data for model development also followed standard methods.

Dissolved Organic Carbon	Volatile Suspended Solids	Total Chlorophyll
Total Phosphorus	Non-Volatile Suspended Solids	Chlorophyll-a
Dissolved Phosphorus	Turbidity	Chlorophyll Fractions
Total Nitrogen	Filtrate Turbidity	Pheophytin
Dissolved Nitrogen	Secchi Depth	Dissolved Oxygen
Ammonia	Conductivity	Silica
Nitrate	440 nm Absorbance	pH
Soluble Reactive Phosphorus	Chlorine Demand	Hydraulic Flushing Rate
Various Nutrient Ratios	254 nm Absorbance	Reservoir Morphology
Total Suspended Solids	Colorimetric TTHMFP	Watershed Land-Use

Table 1. Environmental variables evaluated in model building.

Data Aggregation & Statistical Analyses

All samples used in this 2004 study were collected from 76 Missouri reservoirs. Data from 15 northern Missouri reservoirs were analyzed separately using un-aggregated weekly data (n = 49 for each reservoir) and un-aggregated data separated into seasons: winter (December – February), spring (March – May), summer (June – August) and fall (September – November). These data were also aggregated into arithmetic seasonal means (n = 4 for each reservoir) and arithmetic annual lake means (n = 1 for each reservoir), for comparison per Jones et al. (1998). The statewide data from the additional 61 reservoirs across the state of Missouri (n = 4 for each reservoir) were analyzed as a separate data set and also combined with summer data from the 15 northern reservoirs.

This combined data set was analyzed as un-aggregated data and as arithmetic summer means ($n = 1$ for each of the 76 reservoirs).

Data transformations were performed when appropriate including logarithmic and square-root transformations. All phosphorus, nitrogen, chlorophyll and chlorine demand data were log-transformed. Hydraulic flushing rate and UV_{254} data were square-root transformed. Hydraulic flushing rate for each reservoir was estimated using rainfall data from Missouri Agricultural Weather Stations, watershed area and reservoir volume as follows:

$$\text{HFR} = \text{rainfall (ft)} * \text{watershed area (Ac)} / \text{Volume (Ac-ft)}$$

When generating box-plots to illustrate temporal trends in the data, results were normalized as follows:

$$(X - N) / (SD)$$

Where:

X = raw data

N = arithmetic mean

SD = standard deviation

Linear regression models were developed for each data set using the list of potential explanatory variables found in Table 1. Ordinary least squares regression analysis was performed using SAS software and all parameters in the final models were significant at

$p < 0.05$ or better. The un-aggregated data (collected weekly) were not corrected for temporal autocorrelation. In order to balance the complexity of the models with goodness-of-fit, model selection was based upon the Akaike Information Criterion (AIC), Schwarz's Bayesian Information Criterion (BIC), Mallows C(p) and Adjusted R-Square SAS output. These statistical model-fit measures account for goodness-of-fit inflation which results when using multiple parameters; they balance fit with complexity, avoiding the problems of over-fitted models by penalizing models with more parameters. A maximum of three explanatory variables was allowed in any given model due to the limited sample size for many of the models, in particular models using annual means from the 15 northern Missouri reservoirs ($n = 15$).

Box-plots (Figures 7, 8, 9, 15, 16, 17, 18, 19, 20 and 21) were generated using normalized data (see earlier explanation of the data normalization process used in this study) where the horizontal bars indicate the median, 25th and 75th percentiles. The circles and stars represent outliers not included in the above calculations.

RESULTS

DBP Surrogate Measurements

Four DBP surrogate measurements (DOC, colorimetric TTHMFP, chlorine demand and UV₂₅₄) commonly used in the drinking water industry as proxies of DBP formation potential were included in this study. Detailed methods for each surrogate analysis can be found in the Methods and Materials section.. Validation of the adapted colorimetric TTHM results was performed on a set of 15 split samples using the EPA approved compliance GC/ECD Method 502, a liquid/liquid extraction with methyl tertiary-butyl ether (MTBE). The validation analysis was performed at the EPA-certified St. Louis Water Division Chain of Rocks Laboratory. The four THM species were individually analyzed then combined for a total THM-4 result. Sodium sulfite was used to neutralize the residual chlorine at the end of the incubation instead of sodium thiosulfate. All samples were carefully diluted prior to analysis using DIUF water. On average, the colorimetric TTHM results were 10.7% higher than the results obtained from the EPA approved method (Figure 4). This difference was expected due to known positive interferences from other chlorinated compounds in the adapted colorimetric method. The colorimetric method produced results ranging between 154 µg/L and 526 µg/L while the GC/MS method produced results ranging from 124 µg/L to 453 µg/L. The relationship between the colorimetric method and the GC/MS method had an R² value of 0.94 with the following regression equation:

$$[\text{Colorimetric TTHM}] (\mu\text{g/L}) = 1.17 [\text{THM-4}] (\mu\text{g/L}) - 15.4$$

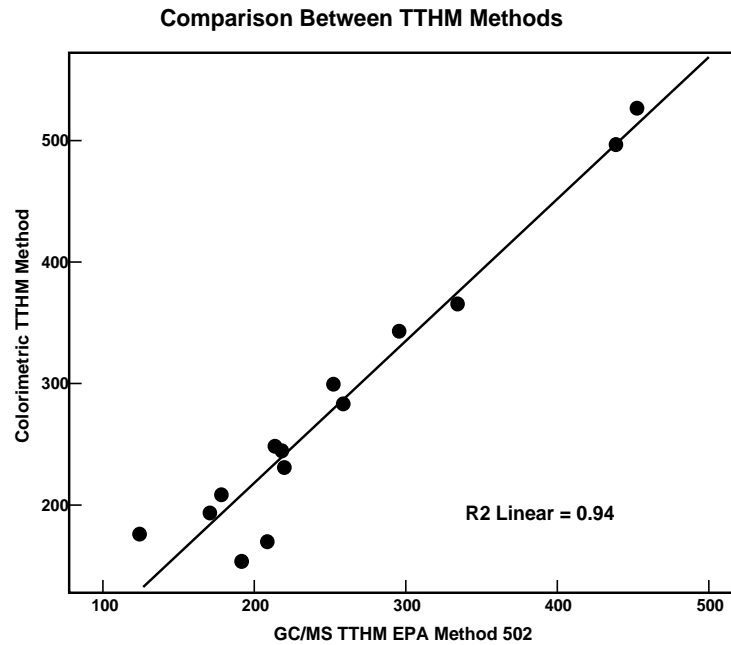


Figure 4. Comparison between EPA approved GC/MS method and adapted colorimetric method.

To confirm the efficacy of the remaining surrogates, they were compared in a cross-system analysis using data collected weekly from 15 northern Missouri reservoirs. Comparisons were made using un-aggregated weekly data, seasonal means and annual means from each reservoir (Table 2). Seasonal means were calculated as the arithmetic mean of all samples collected during the given season at a particular reservoir. Seasons were defined as follows: Winter (December – February), Spring (March – May), Summer (June – August) and Fall (September – November). Annual lake means were calculated as arithmetic means of the four seasonal means for each reservoir. Using un-aggregated data, square root-transformed UV_{254} had the best relationship to TTHMFP ($R^2 = 0.88$)

followed by DOC ($R^2 = 0.76$) and log-transformed chlorine demand ($R^2 = 0.67$, Table 2). Using seasonal means, the other three surrogate measures were strong predictors of TTHMFP for summer and fall ($R^2 = 0.73 - 0.90$). DOC accounted for 96% of the variation in chlorine demand in the summer but only 79% and 80% in the spring and fall, respectively. UV_{254} also had the strongest relationships with both chlorine demand and DOC in the summer ($R^2 = 0.93$ and 0.90 , Table 2). Using annual means, the other three surrogates had a strong relationship with TTHMFP ($R^2 = 0.82 - 0.85$). Chlorine demand also demonstrated strong relationships with both DOC and UV_{254} ($R^2 = 0.95$ and 0.93 respectively, Table 2). Overall, these measurements demonstrated increased correlation coefficients and reduced variability with increased level of aggregation as in Jones et al. (1998). As expected, the surrogate measurements were strong predictors of DBP formation potential.

Coefficients of Determination for DBP Surrogate Relationships

Variables	Weekly Data	Winter Means	Spring Means	Summer Means	Fall Means	Annual Means
TTHMFP / UV ₂₅₄	0.89 (n = 377)	No Data	No Data	0.90 (n = 15)	0.88 (n = 15)	0.85 (n = 15)
TTHMFP / DOC	0.76 (n = 377)	No Data	No Data	0.86 (n = 15)	0.73 (n = 15)	0.82 (n = 15)
TTHMFP / CD	0.67 (n = 377)	No Data	No Data	0.84 (n = 15)	0.90 (n = 15)	0.84 (n = 15)
CD / DOC	0.67 (n = 633)	No Data	0.79 (n = 15)	0.96 (n = 15)	0.80 (n = 15)	0.95 (n = 15)
CD / UV ₂₅₄	0.64 (n = 633)	No Data	0.82 (n = 15)	0.93 (n = 15)	0.86 (n = 15)	0.93 (n = 15)
UV ₂₅₄ / DOC	0.74 (n = 963)	0.71 (n = 15)	0.75 (n = 15)	0.90 (n = 15)	0.78 (n = 15)	0.84 (n = 15)

Table 2. Coefficients of determination for total trihalomethane formation potential in $\mu\text{g/L}$ (TTHMFP), square root transformed UV absorbance at 254 nm/cm*1000 (UV₂₅₄), log transformed chlorine demand in mg/L (CD) and dissolved organic carbon in mg/L (DOC) for 15 northern Missouri reservoirs in 2004.

Overall Trends

TTHM Formation Potential

Seven-day TTHMFP, measured weekly from July through October, 2004 on 15 northern Missouri reservoirs (n = 255), ranged from 149 $\mu\text{g/L}$ in mid-July in Brookfield Reservoir to 685 $\mu\text{g/L}$ in July in Harrison County Reservoir. The median value was 270 $\mu\text{g/L}$ (Table 3). Several reservoirs showed a precipitous decline in TTHMFP in fall following a mid to late summer peak as seen in Harrison County Reservoir (Figure 5) while other reservoirs such as Lake Marie exhibited the opposite trend, increasing from late summer through fall (Figure 6). This variability among reservoirs masked individual temporal trends in cross-system analysis of TTHMFP. Box plots of normalized TTHMFP data for the 15 northern Missouri reservoirs exhibited only a slight increase in August and a small dip in late October following overturn (Figure 7). Seven-day TTHMFP was also measured twice on each of the 61 statewide reservoirs between July and August, 2004 (n = 377) resulting in a TTHMFP range for the summer of 2004 from 95 $\mu\text{g/l}$ in Clearwater Reservoir in late July to 685 $\mu\text{g/l}$ in Harrison County Reservoir in mid-July. The median value was 238 $\mu\text{g/L}$ (Table 4).

Minimum, Maximum and Median Values for 15 MO Reservoirs Sampled Weekly in 2004

Variable	Min	Date	Reservoir	Max	Date	Reservoir	Median	n	Period
TTHMFP	149	July 19	Brookfield	685	July 12	Harrison	270	255	July – Oct.
CD	4.8	May 24	Nehai	19.2	Aug. 31	Harrison	8.4	390	May – Oct.
UV ₂₅₄	37	Feb. 23	Nodaway	392	June 22	Harrison	120	719	Jan. – Dec.
DOC	2.68	Feb. 23	Nodaway	12.37	Aug. 24	Harrison	5.65	734	Jan. – Dec.
TP	4.5	Nov. 23	Nehai	251.8	Aug. 10	Sterling	32.9	734	Jan. – Dec.
TN	0.21	Oct. 19	Nehai	2.21	July 19	Sterling	0.84	734	Jan. – Dec.
Chl	0.60	Apr. 12	Nehai	195.2	June 21	Sterling	12.0	734	Jan. - Dec.

Table 3. Minimum, maximum and median values for total trihalomethane formation potential (TTHMFP $\mu\text{g/L}$), 7-day chlorine demand (CD mg/L), UV absorbance at 254 $\text{nm/cm} \times 1000$ (UV₂₅₄), dissolved organic carbon (DOC mg/L), total phosphorus (TP $\mu\text{g/L}$), total nitrogen (TN mg/L) and total chlorophyll (Chl $\mu\text{g/L}$) for 15 northern Missouri reservoirs sampled weekly in 2004.

Minimum, Maximum and Median Values for all 76 MO Reservoirs Sampled in 2004

Variable	Min	Date	Reservoir	Max	Date	Reservoir	Median	n	Period
TTHMFP	95	July 27	Clearwater	685	July 12	Harrison	238	377	July – Oct.
CD	4.5	June 22	McDaniel	19.2	Aug. 31	Harrison	8.1	633	May – Oct.
UV ₂₅₄	18	July 6	Nodaway	526	June 2	Manito	122	963	Jan. – Dec.
DOC	1.35	May 17	Noblet	12.37	Aug. 24	Harrison	5.85	978	Jan. – Dec.
TP	4	June 9	Capri	251.8	Aug. 10	Sterling	32.2	978	Jan. – Dec.
TN	0.1	June 7	Noblet	2.21	July 19	Sterling	0.79	978	Jan. – Dec.
Chl	0.6	Apr. 12	Nehai	195.2	June 21	Sterling	12.6	978	Jan. – Dec.

Table 4. Minimum, maximum and median values for total trihalomethane formation potential (TTHMFP $\mu\text{g/L}$), 7-day chlorine demand (CD mg/L), UV absorbance at 254 nm/cm*1000 (UV₂₅₄), dissolved organic carbon (DOC mg/L), total phosphorus (TP $\mu\text{g/L}$), total nitrogen (TN mg/L) and total chlorophyll (Chl $\mu\text{g/L}$) for all 76 Missouri reservoirs sampled in 2004.

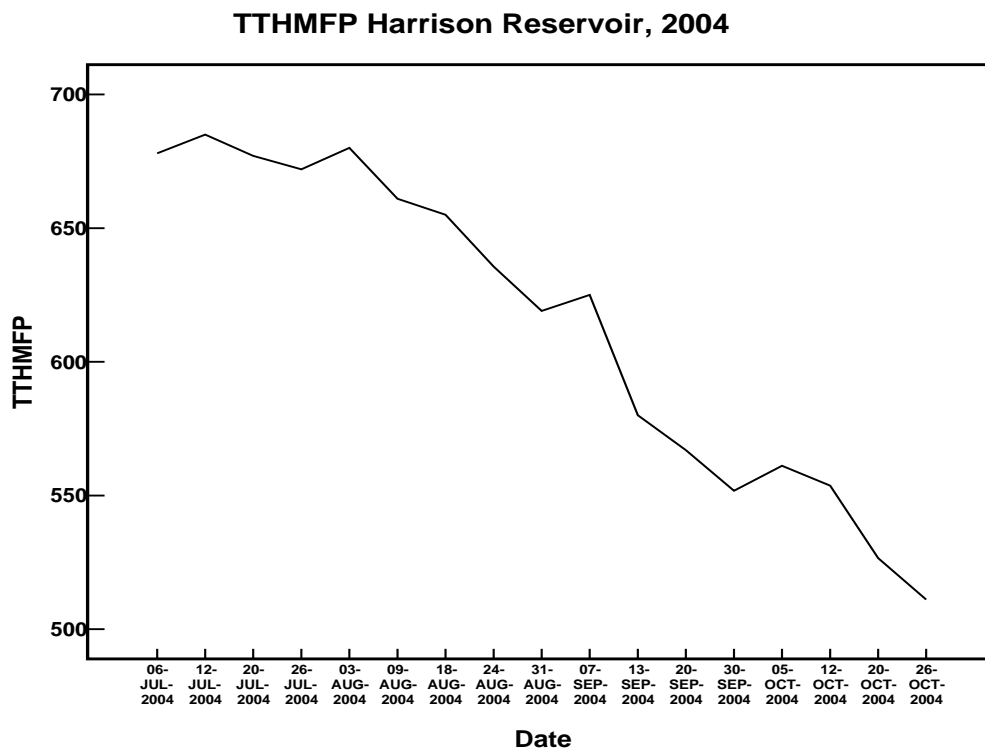


Figure 5. Total Trihalomethane Formation Potential (THMFP) in µg/L in Harrison County Reservoir, 2004. Note steady decline in formation potential from late summer through fall.

TTHMFP Lake Marie 2004

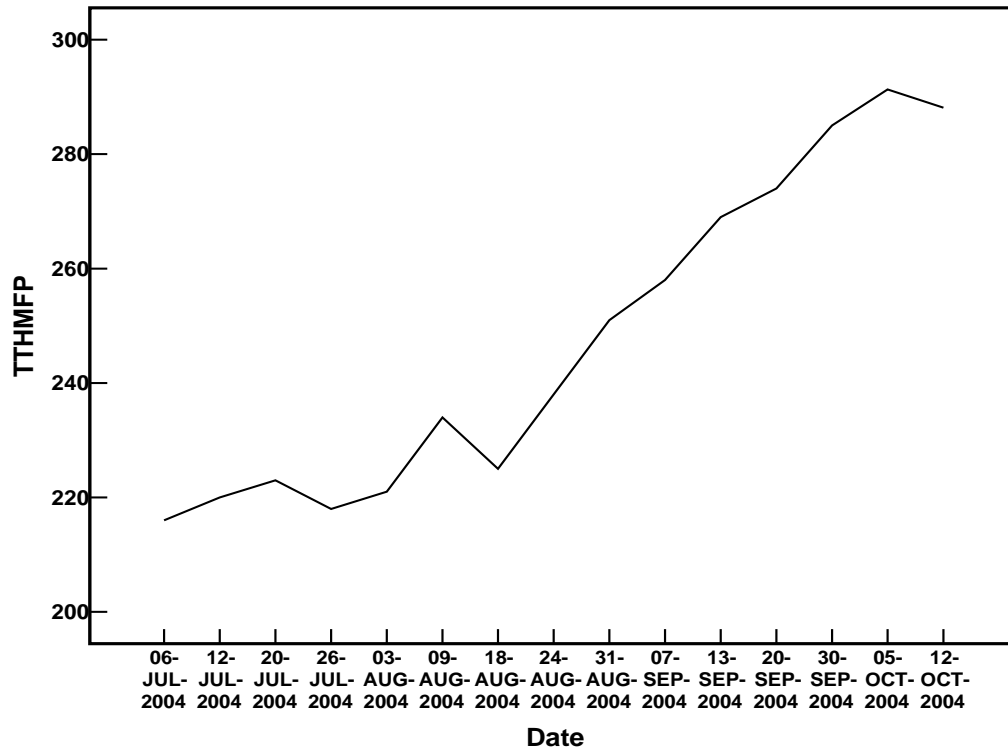


Figure 6. Total Trihalomethane Formation Potential (THMFP) in µg/L in Lake Marie, 2004. Note steady increase in formation potential from late summer through fall

TTHMFP Box Plots for 15 Northern Missouri Reservoirs, 2004

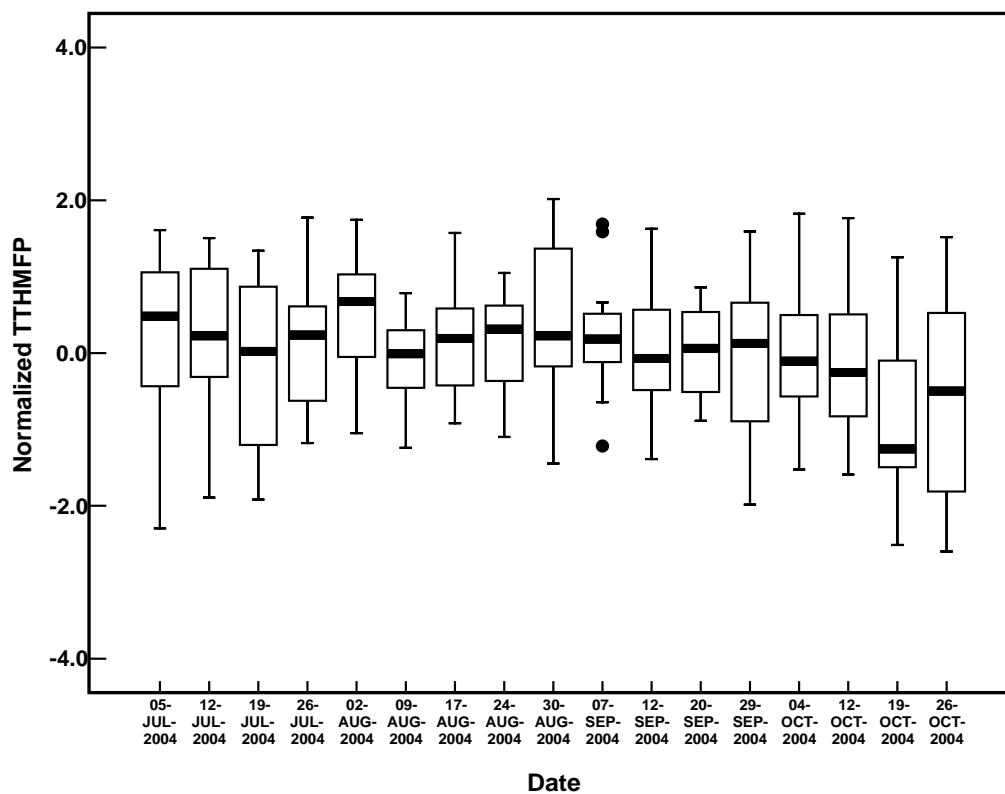


Figure 7. Box plots of normalized Total Trihalomethane Formation Potential (TTHMFP) for 15 northern Missouri reservoirs. Note small peaks in early July and again in early August and small dip in mid-October.

7-Day Chlorine Demand

Chlorine demand was chosen as a proxy to model DBP formation potential in the reservoirs and was measured weekly from May through October, 2004 in 15 northern Missouri reservoirs and during summer (4 times each) in 61 statewide reservoirs.

Chlorine demand data were not collected during winter. In the northern Missouri data set, a dramatic summer peak followed by a decline in fall was seen in chlorine demand data

(Figure 8). This summer peak may be the combined effect of both increased algal productivity and the summer precipitation events (see Figures 11-14) that delivered allochthonous organic carbon to the reservoirs. Chlorine demand can also be attributed to reaction with inorganic compounds such as iron, which may have also been introduced to the system at that time, or to the formation of chlorinated compounds other than the THM species in question. In this data set, chlorine demand ranged from a minimum of 4.8 mg/L in late May in Nehai Tonkyea Reservoir to 19.2 mg/L in late August in Harrison County Reservoir (n = 390). The median value was 8.4 mg/L (Table 3). In the combined summer study, chlorine demand ranged from 4.6 mg/L in late June in McDaniel Reservoir to 19.2 mg/L in late August in Harrison County Reservoir (n = 633). The median value was 8.1 mg/L (Table 4).

Chlorine Demand Box Plots for 15 Northern Missouri Reservoirs, 2004

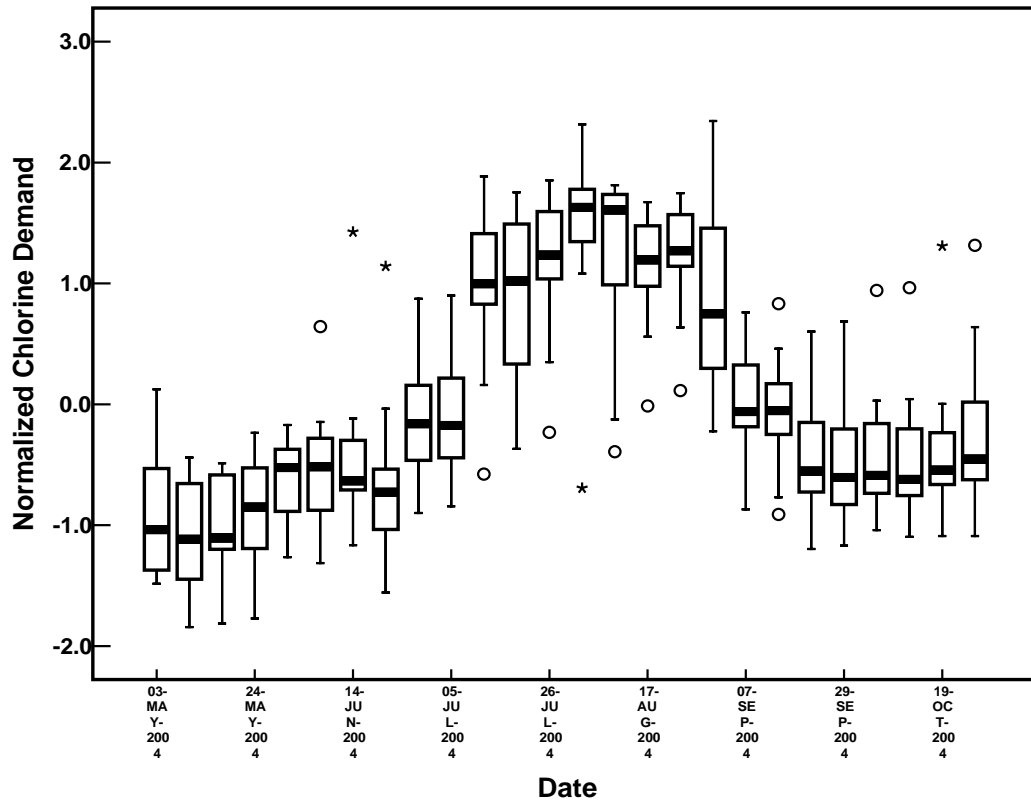


Figure 8. Normalized chlorine demand box-plots for weekly data from 15 northern Missouri reservoirs in 2004. Note dramatic increase in mid to late summer followed by a sharp decline in fall.

UV₂₅₄

UV₂₅₄, also a proxy for DBP formation potential, was measured on all samples collected in 2004. Data collected weekly between January and December for the 15 northern Missouri reservoirs showed a primary peak in early June as well as secondary peaks in late summer, early fall and again in early spring (Figure 9). Values ranged from 37 in late

February in Nodaway Reservoir to 392 in late June in Harrison County Reservoir (n = 719). The median value was 120 (Table 3). Most reservoirs peaked in early summer and declined as seen in Harrison County Reservoir (Figure 10). In the combined summer study, UV₂₅₄ ranged from a minimum of 18 in early July in Nodaway Reservoir to 526 in early June in Manito Reservoir (n = 963). The median value was 122 (Table 4).

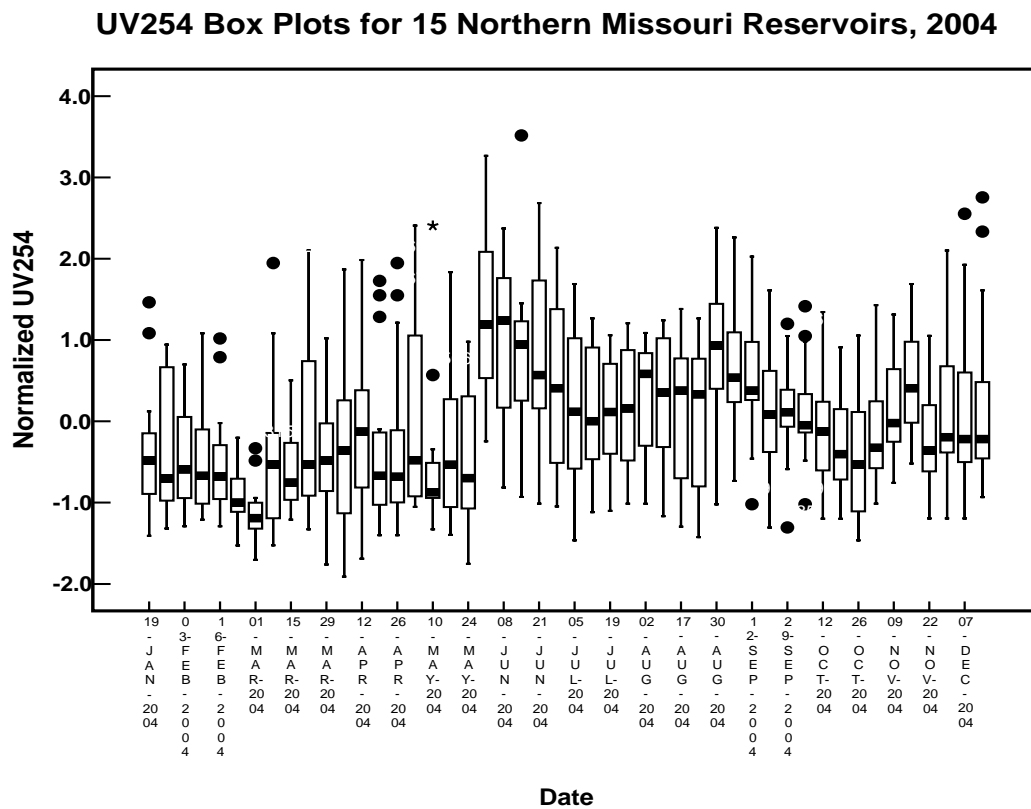


Figure 9. Normalized UV₂₅₄ [absorption at 254 nm/cm*1000] box-plots for weekly data from 15 northern Missouri reservoirs sampled weekly in 2004.

UV254 Absorbance Harrison County Reservoir 2004

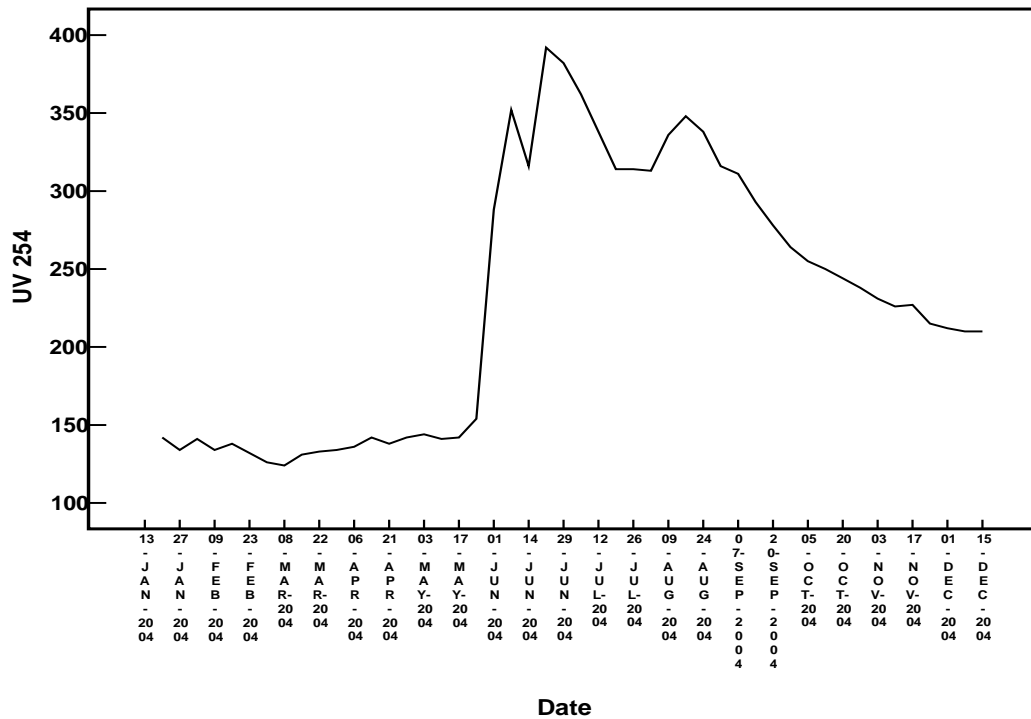


Figure 10. Weekly UV₂₅₄ [absorbance at 254 nm/cm*1000] for Harrison County Reservoir, 2004.

Stream discharge data was also visually compared to UV₂₅₄ using USGS real-time gauge data (USGS 2006). Fluctuations in UV₂₅₄ absorbance (Figures 11-14) coincided well with stream discharge data, in particular the dramatic early summer peak. Discharge data for Missouri generally reflects precipitation patterns for unregulated streams (USGS 2005) and may more accurately represent runoff and hence HFR than precipitation data (Kalff 2002). Stream gauge data, however, was limited and HFR was estimated using precipitation data for the models developed in this study.

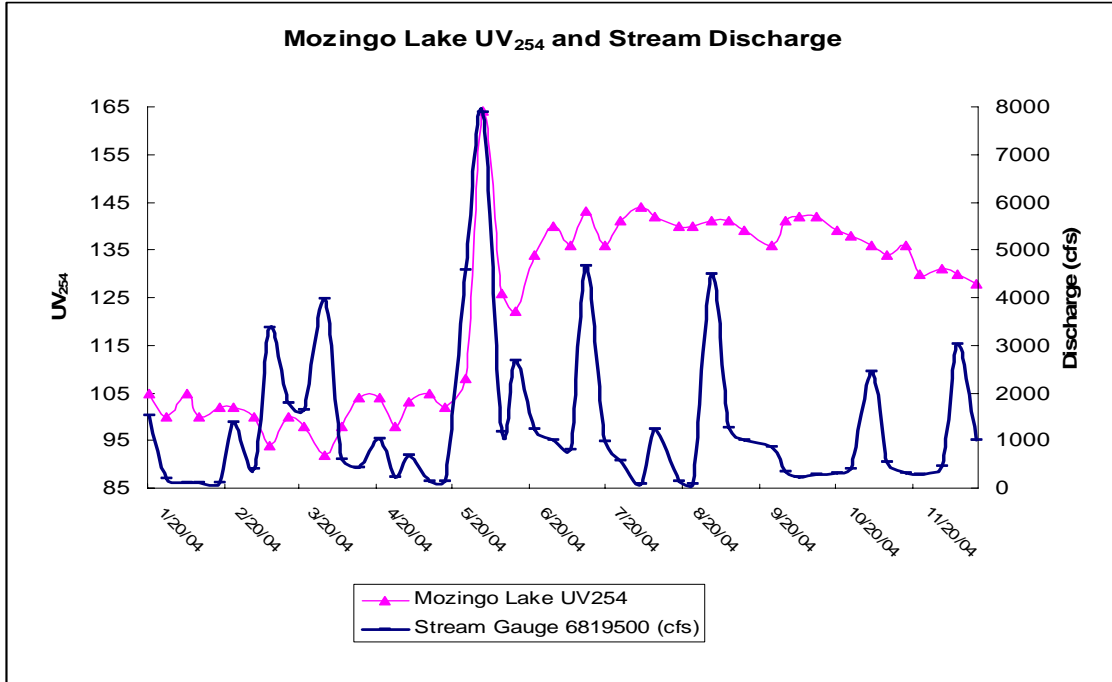


Figure 11. Mozingo Lake UV₂₅₄ [absorbance at 254 nm/cm*1000], and local stream discharge data.

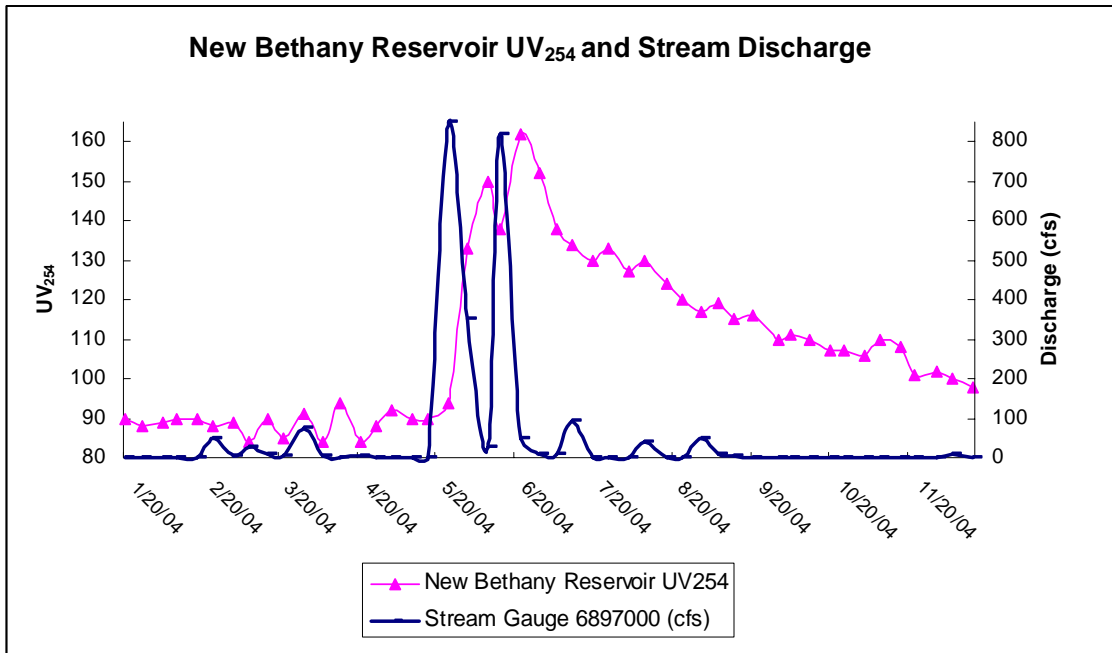


Figure 12. Bethany Reservoir UV₂₅₄ [absorbance at 254 nm/cm*1000] and local stream discharge data.

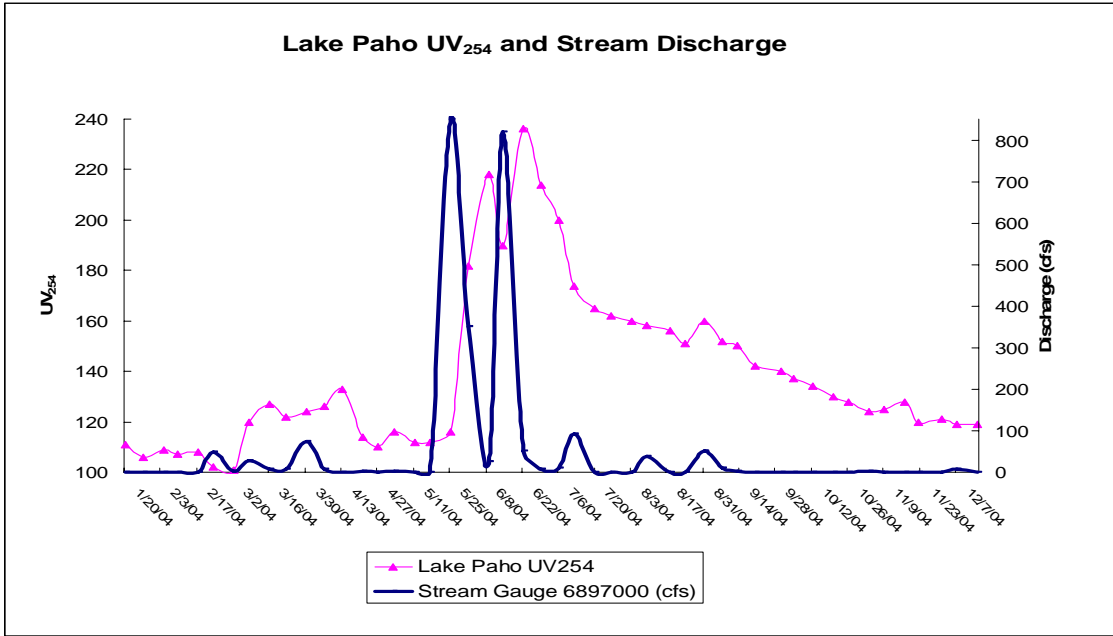


Figure 13. Lake Paho UV₂₅₄ [absorbance at 254 nm/cm*1000] and local stream discharge data.

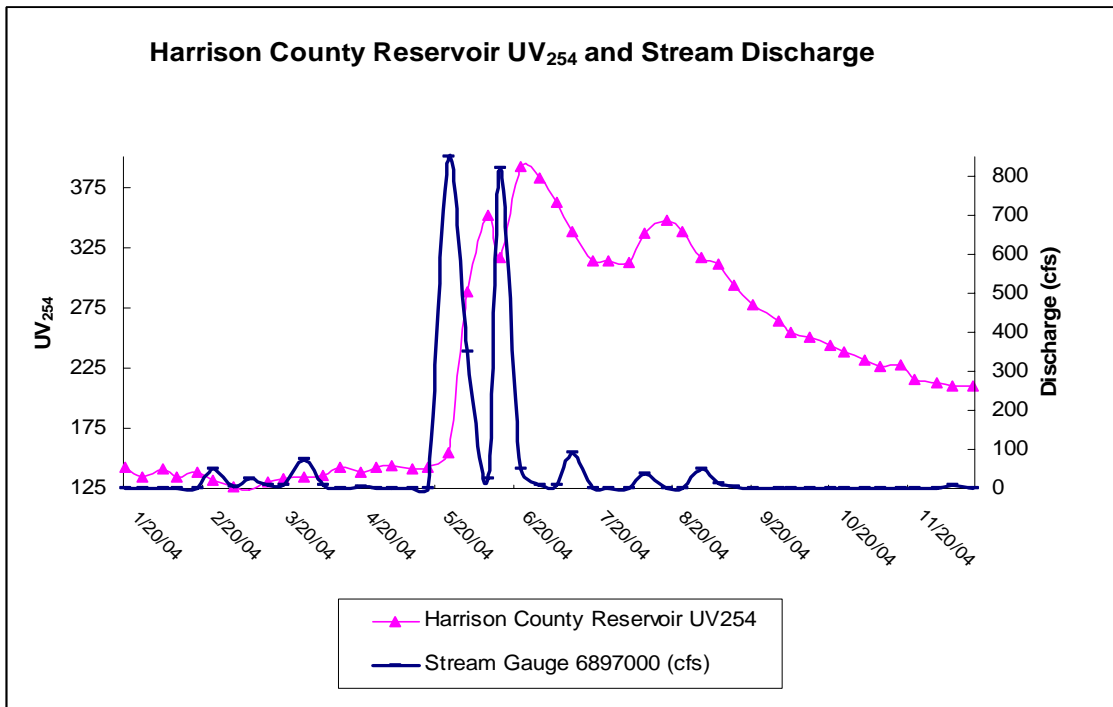


Figure 14. Harrison Reservoir UV₂₅₄ [absorbance at 254 nm/cm*1000] and local stream discharge data.

DOC

Dissolved organic carbon was measured on all samples collected in 2004. Similar to chlorine demand, DOC exhibited an increase through the summer followed by a gradual decline in fall among the 15 northern Missouri reservoirs sampled weekly in 2004 (Figure 15). DOC values were more variable during winter and early spring than summer and fall and ranged from 2.68 mg/L in Nodaway Reservoir in late February to 12.37 mg/L in late August in Harrison County Reservoir (n = 734). The median value was 5.65 mg/L (Table 3). In the combined summer data set, DOC ranged from 1.35 mg/L in mid-May in Noblet Reservoir to 12.37 mg/L in late August in Harrison County Reservoir (n = 978). The median value was 5.85 mg/L (Table 4).

DOC Box Plots for 15 Northern Missouri Reservoirs, 2004

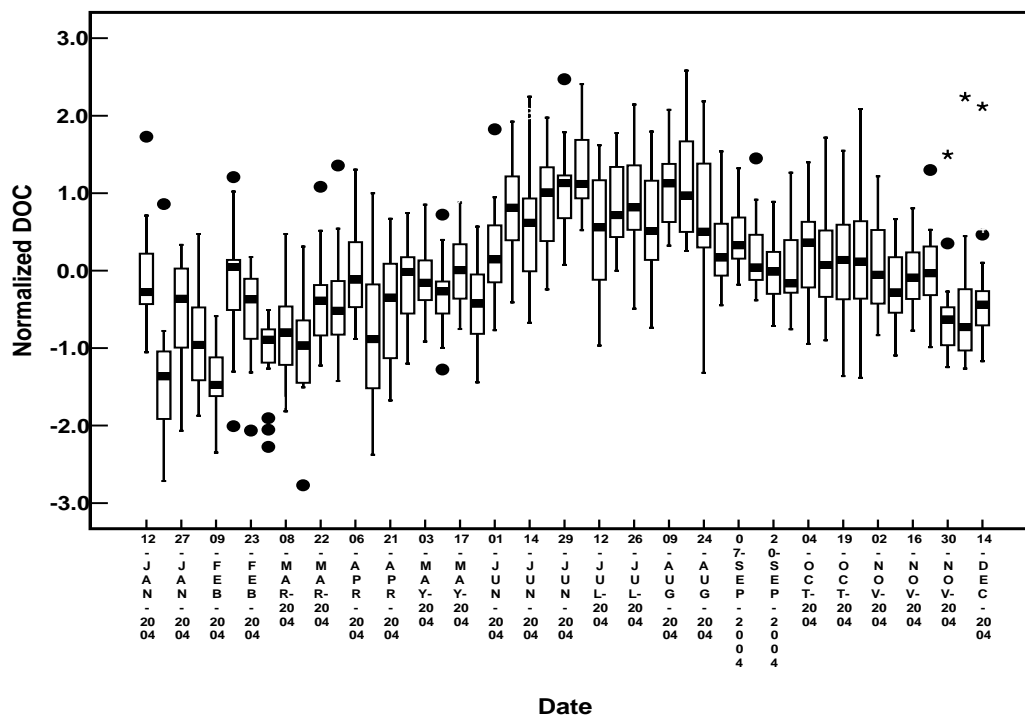


Figure 15. Normalized dissolved organic carbon (DOC) box plots for data collected weekly from 15 northern Missouri reservoirs in 2004. Four outliers were removed from the graph for clarity.

Models Based on Un-aggregated Data

Models for TTHMFP, chlorine demand, UV₂₅₄ and DOC were developed using un-aggregated weekly data from the 15 northern Missouri reservoirs (Table 5) without correcting for temporal autocorrelation. For each response variable, models were developed to elucidate contributing environmental factors in DBP formation potential.

Models for 15 N-MO Reservoirs: Un-aggregated Data	R²	n	Sampling Period
TTHMFP = 67.77 [DOC] – 156.0	0.76	255	July - October
log CD = 0.49 + 0.05 [DOC] + 0.071 log [TP]	0.68	390	May - October
sqrt UV ₂₅₄ = 0.94 [DOC] + 3.658 log [TP] - 0.01	0.82	719	January - December
DOC = 3.33 + 2.14 log [TP] + 2.97 log [TN] + 1.09 sqrt HFR	0.62	735	January - December

Table 5. Models developed using un-aggregated weekly data collected from 15 northern Missouri reservoirs in 2004. TTHMFP = Total Trihalomethane Formation Potential (µg/L). CD = 7-day Chlorine Demand (mg/L). UV₂₅₄ = Ultraviolet Absorbance at 254 nm/cm*1000, 1 cm cell. HFR = Hydraulic Flushing Rate = Rainfall (ft) * Watershed Area (ac) / Volume (ac-ft). DOC = Dissolved Organic Carbon (mg/L). TP = Total Phosphorus (µg/L). TN = Total Nitrogen (mg/L).

As expected, DOC accounted for a large proportion of the variability in TTHMFP (R² = 0.76). Sixty-eight percent of the variation in chlorine demand was explained by a combination of DOC and TP while 82% of the variation in UV₂₅₄ absorbance was accounted for by DOC and TP. Overall, 62% of the variation in DOC was explained by the nutrients TP and TN in conjunction with hydraulic flushing rate (HFR). Chlorophyll was evaluated but did not enter any of these DBP models as an explanatory variable. Flushing rate coupled with nutrient data gave a better estimate of DBP formation potential in these Missouri reservoirs than chlorophyll content which indicates that

allochthonous inputs may have played a more important role in DBP formation than autochthonous inputs in 2004.

Seasonal Trends

Winter (December - February)

TTHMFP and chlorine demand data were not collected during winter. Winter models were developed for UV_{254} ($n = 126$) and DOC ($n = 141$) using weekly data from 15 northern Missouri reservoirs. During winter, UV_{254} ranged from 37 to 380 and DOC ranged from 2.68 mg/L to 9.31 mg/L (Table 6). Using un-aggregated winter data, 74% of the cross-system variation in UV_{254} was explained by TP while 81% of the variation was explained by TP and DOC together (Table 7). Seventy-four percent of the variability in DOC ($R^2 = 0.74$) was accounted for by the nutrients TN and TP. Using lake means ($n = 15$), 90% of the variation in UV_{254} was explained by TP while DOC explained 71% of the variation in UV_{254} . DOC was best modeled using TN and hydraulic flushing rate ($R^2 = 0.84$) (Table 8). Chlorophyll did not enter as an explanatory variable in any model.

Minimum, Maximum and Median Winter Values for 15 N-MO Reservoirs

Variable	Min.	Date	Reservoir	Max.	Date	Reservoir	Median	n
UV ₂₅₄	37	Feb. 23	Nodaway	380	Dec. 14	Marceline-1	108	126
DOC	2.68	Feb. 23	Nodaway	9.31	Jan. 12	Marceline-1	5.82	141
TN	0.23	Dec. 8	Nehai	2.00	Feb. 10	Sterling	0.86	141
TP	8.1	Feb. 24	Nehai	142.0	Jan. 12	Marceline-1	28.1	141
Chl	0.9	Dec. 8	Nehai	55.1	Jan. 28	Marceline-1	9.6	141

Table 6. Maximum, minimum and median winter values for the 15 northern Missouri in 2004. UV₂₅₄ = Ultraviolet Absorbance at 254 nm/cm*1000. DOC = Dissolved Organic Carbon (mg/L). TN = Total Nitrogen (mg/L). TP = Total Phosphorus (µg/L). Chl = Total Chlorophyll (µg/L).

Winter Models for 15 N-MO Reservoirs: Un-aggregated Data	R ²	n
$\text{sqrtUV}_{254} = 7.76 \log [\text{TP}] - 0.23$	0.74	126
$\text{sqrtUV}_{254} = 5.56 \log[\text{TP}] + 0.68 [\text{DOC}] - 1.14$	0.81	126
$\text{DOC} = 4.80 + 4.11 \log[\text{TN}] + 1.11 \log[\text{TP}]$	0.60	137

Table 7. Models developed using un-aggregated weekly data collected from 15 northern Missouri reservoirs in 2004. UV₂₅₄ = Ultraviolet Absorbance at 254 nm/cm*1000. HFR = Hydraulic Flushing Rate = Rainfall (ft) * Watershed Area (ac) / Volume (ac-ft). TP = Total Phosphorus (µg/L). TN = Total Nitrogen (mg/L). DOC = Dissolved Organic Carbon (mg/L).

Winter Models for 15 N-MO Reservoirs: Lake Means	R ²	n
$\text{sqrt UV}_{254} = 1.20 + 1.66 [\text{DOC}]$	0.71	15
$\text{sqrt UV}_{254} = 8.736 \log [\text{TP}] - 1.68$	0.90	15
$\text{DOC} = 4.97 + 3.39 \log[\text{TN}] + 3.58 \text{sqrtHFR}$	0.84	15

Table 8. Models developed using arithmetic means of winter data collected from 15 northern Missouri reservoirs in 2004. UV₂₅₄ = Ultraviolet Absorbance at 254 nm/cm*1000. HFR = Hydraulic Flushing Rate = Rainfall (ft) * Watershed Area (ac) / Volume (ac-ft). TP = Total Phosphorus (µg/L). TN = Total Nitrogen (mg/L). DOC = Dissolved Organic Carbon (mg/L).

Spring (March - May)

Spring DBP data included chlorine demand, UV_{254} and DOC collected weekly from 15 northern Missouri reservoirs. TTHMFP data was not collected during spring. Chlorine demand ranged from 4.8 mg/L to 10.4 mg/L, UV_{254} absorbance ranged from 56 to 332 and DOC ranged from 3.65 mg/L up to 9.50 mg/L (Table 9). Marceline-1 Reservoir was the location with maximum values for all three variables. Modeling un-aggregated weekly data, 77% of the cross-system variation in chlorine demand was explained by DOC and TP. Alternatively, 66% of the variation was explained by TP and hydraulic flushing rate. UV_{254} absorbance was best described using DOC and TP ($R^2 = 0.75$) or by hydraulic flushing rate and TP ($R^2 = 0.57$). DOC was modeled using TP and TN in conjunction with hydraulic flushing rate ($R^2 = 0.55$, Table 10). Lake means exhibited similar relationships (Table 11). TP explained 82% of the variation in chlorine demand while DOC and TP together explained 92%. UV_{254} was modeled with DOC ($R^2 = 0.75$) or TP ($R^2 = 0.66$). DOC was best modeled using TN and flushing rate ($R^2 = 0.78$). Chlorophyll did not enter as an explanatory variable in any model.

Minimum, Maximum and Median Spring Values for 15 N-MO Reservoirs

Variable	Min.	Date	Reservoir	Max.	Date	Reservoir	Median	n
CD	4.8	May 24	Nehai	10.4	May 24	Marceline-1	6.9	60
UV ₂₅₄	56	Apr. 7	Nehai	332	Apr. 12	Marceline-1	108	195
DOC	3.65	Mar. 1	Nehai	9.50	May 18	Marceline-1	5.81	195
TN	0.23	Apr. 26	Nehai	1.70	Mar. 9	Sterling	0.84	195
TP	6.9	Apr. 22	Nehai	120.8	Mar. 9	Marceline-1	31.1	195
Chl	0.6	Apr. 26	Nehai	100.5	Mar. 15	Marceline-1	9.5	195

Table 9. Maximum, minimum and median spring values for 15 northern Missouri reservoirs in 2004. CD = Chlorine Demand (mg/L). UV₂₅₄ = Ultraviolet Absorbance at 254 nm/cm*1000. DOC = Dissolved Organic Carbon (mg/L). TN = Total Nitrogen (mg/L). TP = Total Phosphorus (µg/L). Chl = Total Chlorophyll (µg/L).

Spring Models for 15 N-MO Reservoirs: Un-aggregated Data	R ²	n
$\log CD = 0.34 + 0.04 [DOC] + 0.168 \log [TP]$	0.77	60
$\log CD = 0.35 + 0.319 \log [TP] + 0.09 \text{ sqrt HFR}$	0.66	60
$\text{sqrt UV}_{254} = 1.36 + 6.266 \log [TP] + 1.21 \text{ sqrt HFR}$	0.57	195
$\text{sqrt UV}_{254} = 0.31 + 1.01 [DOC] + 3.214 \log [TP]$	0.75	195
$DOC = 3.85 + 1.470 \log [TP] + 2.57 \log [TN] + 1.71 \text{ sqrt HFR}$	0.55	195

Table 10. Models developed using un-aggregated spring data collected from 15 northern Missouri reservoirs in 2004. CD = Chlorine Demand (mg/L). UV₂₅₄ = Ultraviolet Absorbance at 254 nm/cm*1000. HFR = Hydraulic Flushing Rate = Rainfall (ft) * Watershed Area (ac) / Volume (ac-ft). TP = Total Phosphorus (µg/L). TN = Total Nitrogen (mg/L). DOC = Dissolved Organic Carbon (mg/L).

Spring Models for 15 N-MO Reservoirs: Lake Means	R ²	n
$\log \text{CD} = 0.35 + 0.325 \log [\text{TP}]$	0.82	15
$\log \text{CD} = 0.32 + 0.04 [\text{DOC}] + 0.196 \log [\text{TP}]$	0.92	15
$\text{sqrt UV}_{254} = 1.43 + 1.57 [\text{DOC}]$	0.75	15
$\text{sqrt UV}_{254} = 0.46 + 7.067 \log [\text{TP}]$	0.66	15
$\text{DOC} = 4.71 + 2.98 \log [\text{TN}] + 1.77 \text{sqrt HFR}$	0.78	15

Table 11. Models developed using arithmetic means of aggregated spring data collected from 15 northern Missouri reservoirs in 2004. CD = Chlorine Demand (mg/L). UV_{254} = Ultraviolet Absorbance at 254 nm/cm*1000. HFR = Hydraulic Flushing Rate = Rainfall (ft) * Watershed Area (ac) / Volume (ac-ft). TP = Total Phosphorus ($\mu\text{g/L}$). TN = Total Nitrogen (mg/L). DOC = Dissolved Organic Carbon (mg/L).

Summer

Summer models were developed for TTHMFP, CD, UV_{254} and DOC using both the 15 northern Missouri reservoirs data set (June – August) and the combined summer data set of all 76 Missouri reservoirs (mid-May thru mid-August). In the 15 northern Missouri reservoirs, TTHMFP ranged from a minimum of 149 $\mu\text{g/L}$ in Brookfield Reservoir to a maximum of 685 $\mu\text{g/L}$ in Harrison County Reservoir. Chlorine Demand ranged from 4.9 mg/L in Nehai Tonkyea Reservoir to 19.2 mg/L, also in Harrison County Reservoir. UV_{254} ranged from 58 to 392 while DOC ranged from 2.68 mg/L to 9.31 mg/L (Table 12). Using un-aggregated summer data from the 15 northern reservoirs, 79% of the cross-system variation in TTHMFP was explained by DOC. DOC also explained 65% of the variation in chlorine demand in the same data set. UV_{254} absorbance was best modeled using DOC and TP ($R^2 = 0.65$) and DOC was best modeled with the nutrients TN and TP ($R^2 = 0.66$) (Table 13).

Aggregated summer lake means followed the same trends and exhibited even stronger relationships than un-aggregated data (Table 14). Eighty-six percent of the variation in TTHMFP was accounted for by DOC while 72% of the variation was explained by flushing rate. DOC and UV₂₅₄ explained 96% and 90% of the variation in chlorine demand respectively. Flushing rate explained 83% of the variation in DOC alone. Chlorophyll did not enter as an explanatory variable in these models. This finding suggests that allochthonous carbon inputs were influential in DBP formation potential in Missouri reservoirs in 2004.

Minimum, Maximum and Median Summer Values for 15 N-MO Reservoirs

Variable	Min.	Date	Reservoir	Max.	Date	Reservoir	Median	n
TTHMFP	149	July 19	Brookfield	685	July 12	Harrison	264	135
CD	4.9	June 2	Nehai	19.2	August 31	Harrison	9.1	210
UV ₂₅₄	58	Aug. 17	Nehai	392	June 22	Harrison	136	210
DOC	4.08	July 13	Nehai	12.37	August 24	Harrison	6.62	210
TN	0.26	Aug. 2	Nehai	2.21	July 19	Sterling	0.81	210
TP	7.6	July 27	Nehai	251.8	Aug. 10	Sterling	37.0	210
Chl	1.3	Aug. 10	Nehai	195.2	June 21	Sterling	14.5	210

Table 12. Maximum, minimum and median summer values for 15 northern Missouri reservoirs in 2004. TTHMFP = Total Trihalomethane Formation Potential (µg/L). CD = Chlorine Demand (mg/L). UV₂₅₄ = Ultraviolet Absorbance at 254 nm/cm*1000. DOC = Dissolved Organic Carbon (mg/L). TN = Total Nitrogen (mg/L). TP = Total Phosphorus (µg/L). Chl = Total Chlorophyll (µg/L).

Summer Models for 15 N-MO Reservoirs: Un-aggregated Data	R²	n
$TTHMFP = 68.49 [DOC] - 173.4$	0.79	129
$\log CD = 0.59 + 0.05 [DOC]$	0.65	210
$\text{sqrt } UV_{254} = 0.69 + 1.02 [DOC] + 2.822 \log [TP]$	0.65	210
$DOC = 2.86 + 2.885 \log[TP] + 2.93 \log[TN]$	0.66	188

Table 13. Models developed using un-aggregated summer data collected from 15 northern Missouri reservoirs in 2004. TTHMFP = Total Trihalomethane Formation Potential ($\mu\text{g/L}$). CD = Chlorine Demand (mg/L). UV_{254} = Ultraviolet Absorbance at 254 nm/cm*1000. HFR = Hydraulic Flushing Rate = Rainfall (ft) * Watershed Area (ac) / Volume (ac-ft). TP = Total Phosphorus ($\mu\text{g/L}$). TN = Total Nitrogen (mg/L). DOC = Dissolved Organic Carbon (mg/L).

Summer Models for 15 N-MO Reservoirs: Lake Means	R²	n
$TTHMFP = 76.30 [DOC] - 221.6$	0.86	15
$TTHMFP = 18.5 + 252.6 \text{sqrt } HFR$	0.72	15
$\log CD = 0.58 + 0.06 [DOC]$	0.96	15
$\log CD = 0.51 + 0.296 \log[TP]$	0.82	15
$\text{sqrt } UV_{254} = 1.67 + 1.52 [DOC]$	0.90	15
$DOC = 3.2 + 3.29 \text{sqrt } HFR$	0.83	15

Table 14. Models developed using arithmetic means of aggregated summer data collected from 15 northern Missouri reservoirs in 2004. TTHMFP = Total Trihalomethane Formation Potential ($\mu\text{g/L}$). CD = Chlorine Demand (mg/L). UV_{254} = Ultraviolet Absorbance at 254 nm/cm*1000. HFR = Hydraulic Flushing Rate = Rainfall (ft) * Watershed Area (ac) / Volume (ac-ft). TP = Total Phosphorus ($\mu\text{g/L}$). TN = Total Nitrogen (mg/L). DOC = Dissolved Organic Carbon (mg/L).

Summer: Combined Data Set

Maximum, minimum and median values from the combined summer data set are listed in Table 15. Models were developed using summer means from all 76 reservoirs (Table 16). Seventy-eight percent of the variation in TTHMFP was explained by DOC and flushing

rate. Both chlorine demand and UV_{254} were best modeled using DOC and TP ($R^2 = 0.85$ and 0.72 respectively). However, in this cross system analysis, DOC lacked strong explanatory variables and was best modeled using TN alone ($R^2 = 0.56$).

Minimum, Maximum and Median Summer Values for 76 Missouri Reservoirs

Variable	Min.	Date	Reservoir	Max.	Date	Reservoir	Median	n
TTHMFP	95	July 27	Clearwater	685	July 12	Harrison	221	212
CD	4.6	June 22	McDaniel	16.6	August 9	Harrison	7.9	438
UV_{254}	18	July 6	Clearwater	526	June 2	Manito	128	439
DOC	1.35	May 17	Noblet	11.32	Aug. 9	Harrison	5.69	439
TN	0.10	June 7	Noblet	2.21	July 19	Sterling	0.68	439
TP	4.0	June 9	Capri	251.8	Aug. 10	Sterling	32.1	439
Chl	0.9	May 17	Noblet	195.2	June 21	Sterling	13.9	439

Table 15. Maximum, minimum and median summer values for all 76 Missouri reservoirs in summer (mid-May thru mid-August), 2004. TTHMFP = Total Trihalomethane Formation Potential ($\mu\text{g/L}$). CD = Chlorine Demand (mg/L). UV_{254} = Ultraviolet Absorbance at 254 nm/cm*1000. DOC = Dissolved Organic Carbon (mg/L). TN = Total Nitrogen (mg/L). TP = Total Phosphorus ($\mu\text{g/L}$). Chl = Total Chlorophyll ($\mu\text{g/L}$).

Summer Models for 76 MO Reservoirs: Lake Means	R^2	n
$TTHMFP = 50.5 [\text{DOC}] + 21.1 \text{ sqrt HFR} - 78.7$	0.78	76
$\log \text{CD} = 0.57 + 0.04 [\text{DOC}] + 0.09 \log [\text{TP}]$	0.85	76
$\text{sqrt } UV_{254} = 1.41 + 0.98 [\text{DOC}] + 2.91 \log [\text{TP}]$	0.72	76
$\text{DOC} = 6.72 + 5.22 \log [\text{TN}]$	0.56	76

Table 16. Models developed using arithmetic means of summer data collected from 76 Missouri reservoirs in summer (mid-may thru mid-August), 2004. TTHMFP = Total Trihalomethane Formation Potential ($\mu\text{g/L}$). CD = Chlorine Demand (mg/L). UV_{254} = Ultraviolet Absorbance at 254 nm/cm*1000. HFR = Hydraulic Flushing Rate = Rainfall (ft) * Watershed Area (ac) / Volume (ac-ft). TP = Total Phosphorus ($\mu\text{g/L}$). TN = Total Nitrogen (mg/L). DOC = Dissolved Organic Carbon (mg/L).

Data from 61 statewide reservoirs, each sampled on four occasions during summer 2004, were analyzed separately. Box plots of normalized data were generated to identify temporal trends in the data. Reservoirs were sampled every three weeks between mid-May and mid-August (four collection periods). Overall, TP and TN declined from collection 1 to collection 3 and increased on collection 4 (Figures 16 & 17). The increase in nutrients seen in late summer (collection 4) corresponds to a similar increase in total chlorophyll (Figure 18).

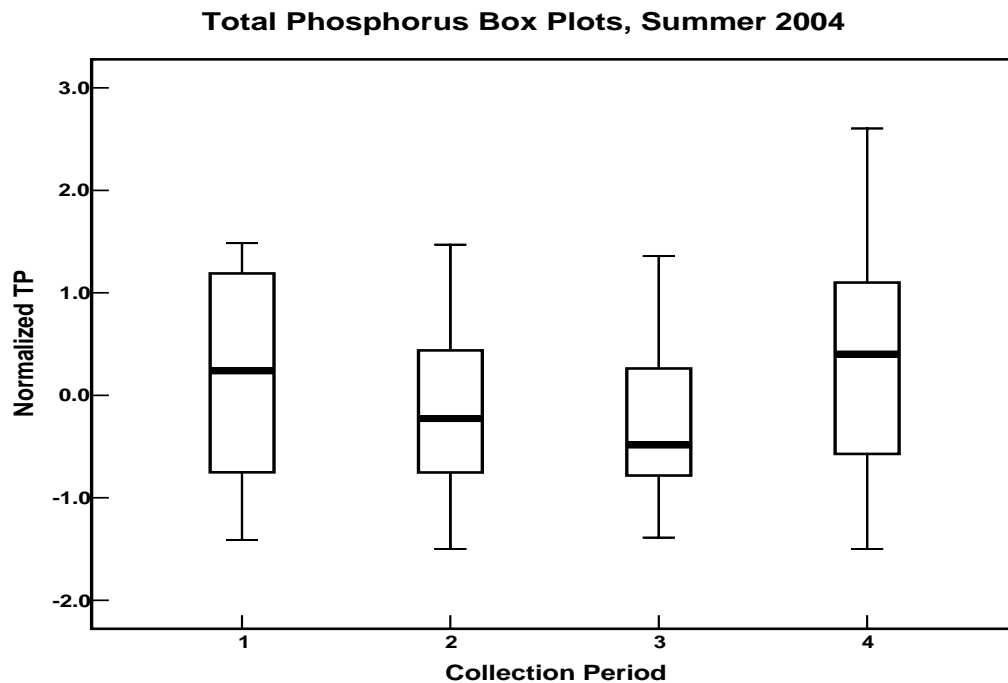


Figure 16. Normalized Total Phosphorus Box Plots for 61 Statewide Missouri Reservoirs, Summer 2004

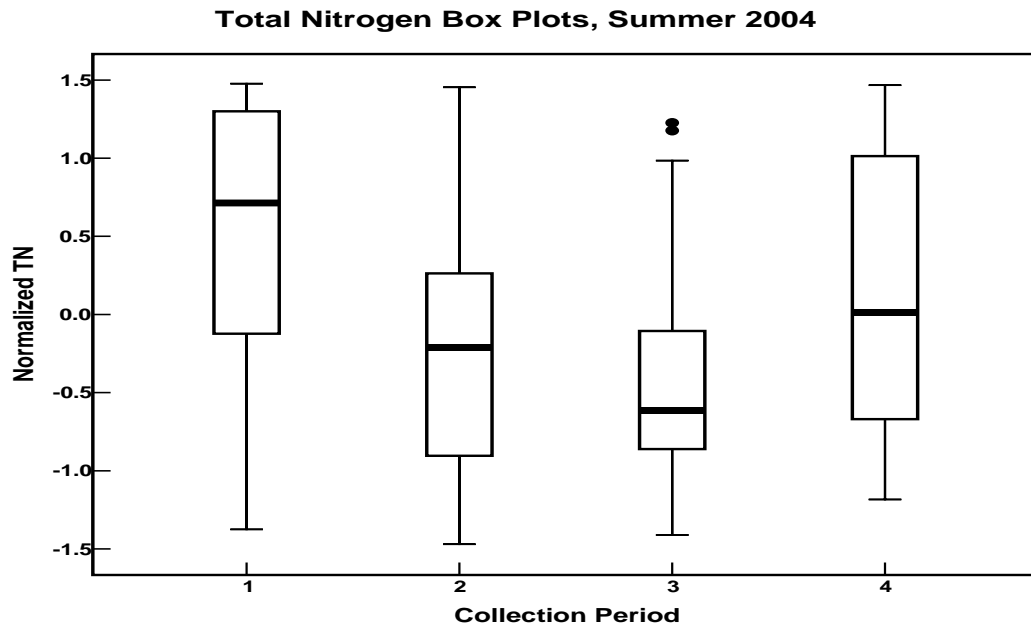


Figure 17. Normalized Total Nitrogen Box Plots for 61 Statewide Missouri Reservoirs, Summer 2004

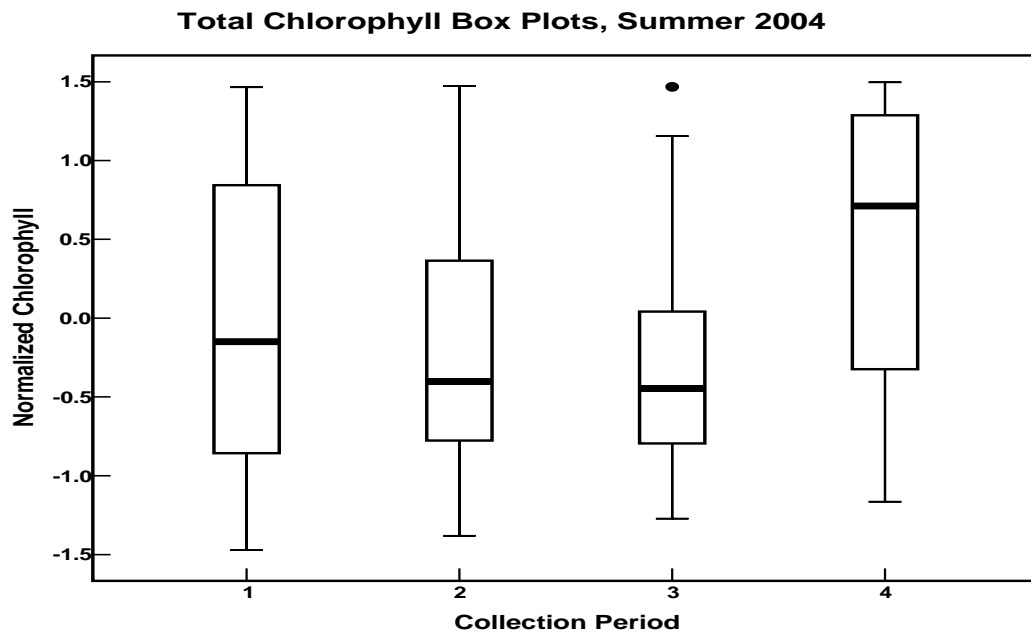


Figure 18. Normalized Total Chlorophyll Box Plots for 61 Statewide Missouri Reservoirs, Summer 2004

In this data set, DOC remained nearly constant across the four summer collection periods (Figure 19). UV₂₅₄ declined dramatically from collection 1 to collection 3 and did not rebound in collection period 4 (Figure 20) as did nutrients and chlorophyll.

This pattern is further illustrated in the SUVA box plots (Figure 21). SUVA (Specific Ultraviolet Absorbance) is UV₂₅₄ absorbance normalized by the DOC content (see Materials and Methods Section) and represents the relative aromaticity of the organic carbon content of the water. The SUVA values for this data set dropped continually from collection 1 through collection 4, suggesting a shift from allochthonous, refractory organic carbon dominance to labile, autochthonous carbon dominance in the epilimnion.

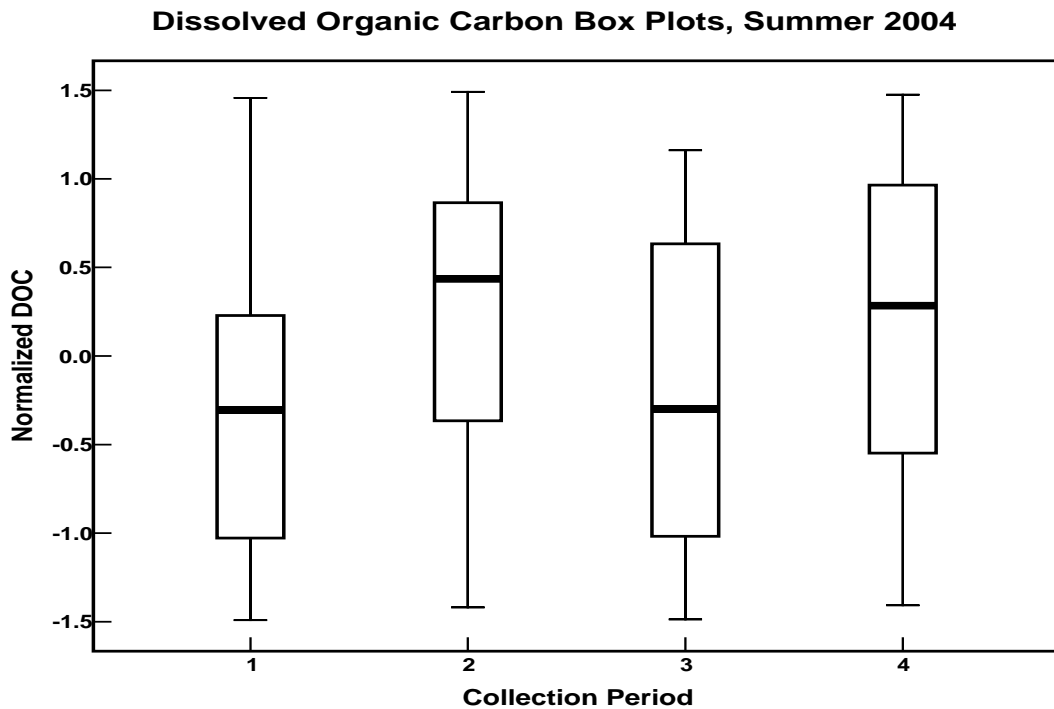


Figure 19. Normalized DOC Box Plots for 61 Statewide Missouri Reservoirs, Summer 2004

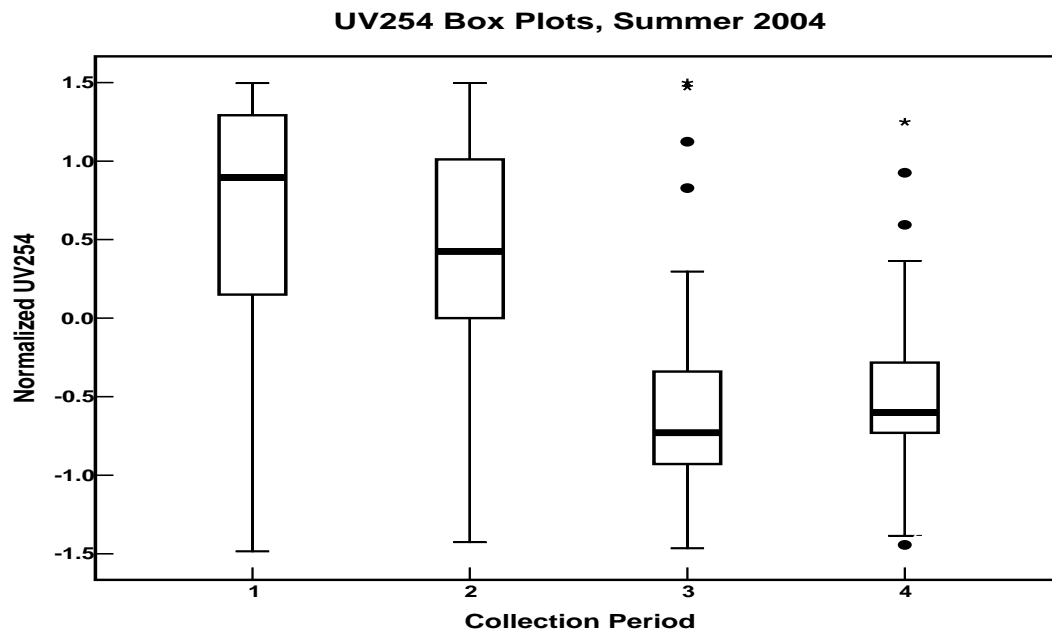


Figure 20. Normalized UV₂₅₄ Box Plots for 61 Statewide Missouri Reservoirs, Summer 2004

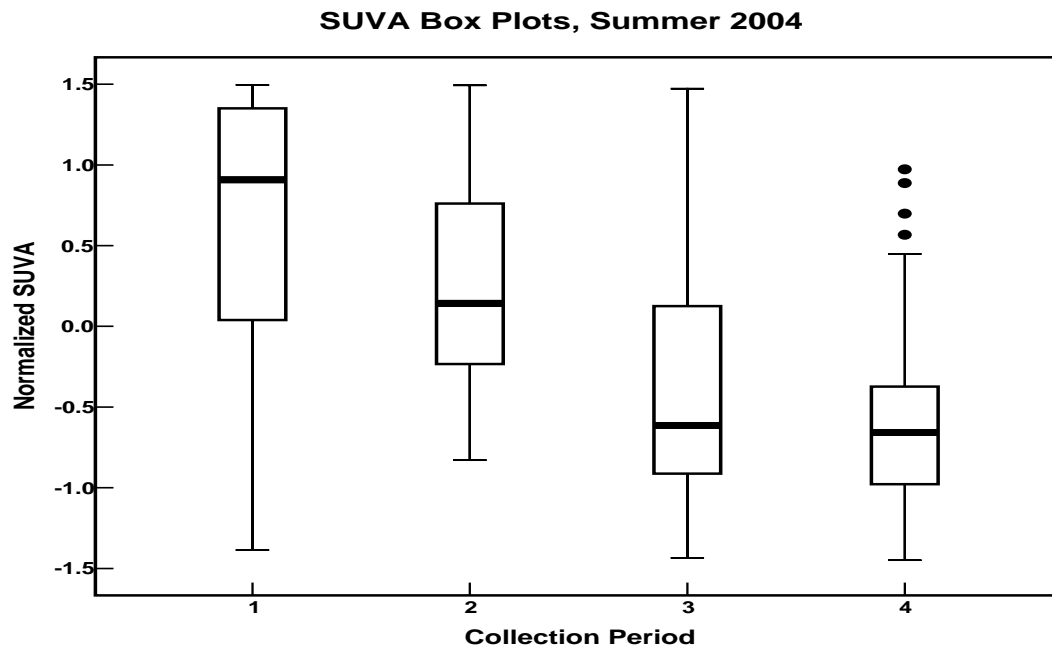


Figure 21. Normalized SUVA Box Plots for 61 Statewide Missouri Reservoirs, Summer 2004

Fall (September - November)

Fall models were developed for TTHMFP, CD, UV_{254} and DOC using weekly data from 15 northern Missouri reservoirs. TTHMFP ranged from a minimum of 154 $\mu\text{g/L}$ in Brookfield Reservoir to a maximum of 625 $\mu\text{g/L}$ in Harrison County Reservoir. Chlorine demand ranged from 5.7 mg/L in Nehai Tonkyea Reservoir to 14.4 mg/L in Harrison County Reservoir. UV_{254} ranged from 58 to 384 while DOC ranged from 3.94 mg/L to 11.14 mg/L (Table 17). Modeling un-aggregated fall data (Table 18), 70% of the cross-system variation in TTHMFP was explained by DOC. Sixty-four percent of the variation in chlorine demand was accounted for by TN, TP and hydraulic flushing rate ($R^2 = 0.64$) while 84% of the variation in UV absorbance was explained by DOC, TP and hydraulic flushing rate. DOC was modeled using TN and TP with hydraulic flushing rate ($R^2 = 0.71$, Table 18).

The 15 northern Missouri reservoirs were also modeled using fall reservoir means (Table 17). Sixty-eight percent of the variation in TTHMFP was explained by flushing rate while 82% of the variation was explained by DOC and flushing rate. Eighty percent of the variation in chlorine demand was explained by DOC alone while 78% was explained by TN and flushing rate. UV_{254} was best modeled using DOC and flushing rate ($R^2 = 0.90$) or TN and flushing rate ($R^2 = 0.88$). DOC was modeled with TN and flushing rate ($R^2 = 0.86$).

Minimum, Maximum and Median Fall Values for 15 N-MO Reservoirs

Variable	Min.	Date	Reservoir	Max.	Date	Reservoir	Median	n
TTHMFP	154	Oct. 19	Brookfield	625	Sept. 7	Harrison	268	120
CD	5.7	Sept. 8	Nehai	14.4	Sept. 13	Harrison	7.9	120
UV ₂₅₄	58	Oct. 27	Nehai	384	Sept. 8	Marceline-1	128	188
DOC	3.94	Nov. 2	Nehai	11.14	Sept. 7	Harrison	6.00	188
TN	0.21	Oct. 19	Nehai	1.96	Sept. 7	Harrison	0.84	188
TP	4.5	Nov. 23	Nehai	162.3	Nov. 16	Sterling	36.0	188
Chl	0.9	Nov. 30	Nehai	122.5	Sept. 7	Harrison	14.6	188

Table 17. Maximum, minimum and median fall values for all 15 reservoirs in 2004. TTHMFP = Total Trihalomethane Formation Potential (µg/L). CD = Chlorine Demand (mg/L). UV₂₅₄ Ultraviolet Absorbance at 254 nm/cm*1000. DOC = Dissolved Organic Carbon (mg/L). TN = Total Nitrogen (mg/L). TP = Total Phosphorus (µg/L). Chl = Total Chlorophyll (µg/L).

Fall Models for 15 N-MO Reservoirs: Un-aggregated Data	R ²	n
$TTHMFP = 68.0 [DOC] - 146.5$	0.70	120
$\log CD = 0.66 + 0.162 \log [TP] + 0.18 \log [TN] + 0.08 \text{ sqrt HFR}$	0.64	120
$\text{sqrt UV}_{254} = 0.95 [DOC] + 3.618 \log [TP] + 1.19 \text{ sqrt HFR} - 0.09$	0.84	188
$DOC = 5.32 + 5.26 \log [TN] + 1.065 \log [TP] + 0.77 \text{ sqrt HFR}$	0.71	188

Table 18. Models developed using un-aggregated fall data collected from 15 northern Missouri reservoirs in 2004. TTHMFP = Total Trihalomethane Formation Potential (µg/L). CD = Chlorine Demand (mg/L). UV₂₅₄ = Ultraviolet Absorbance at 254 nm/cm*1000. HFR = Hydraulic Flushing Rate = Rainfall (ft) * Watershed Area (ac) / Volume (ac-ft). TP = Total Phosphorus (µg/L). TN = Total Nitrogen (mg/L). DOC = Dissolved Organic Carbon (mg/L).

Fall Models for 15 N-MO Reservoirs: Lake Means	R²	n
$TTHMFP = 44.47 [DOC] + 166.5 \text{ sqrt HFR} - 112.4$	0.82	15
$TTHMFP = 63.4 + 320.5 \text{ sqrt HFR}$	0.68	15
$\log CD = 0.51 + 0.06 [DOC]$	0.80	15
$\log CD = 0.83 + 0.32 \log [TN] + 0.15 \text{ sqrt HFR}$	0.78	15
$\text{sqrt UV}_{254} = 2.96 + 0.90 [DOC] + 4.16 \text{ sqrt HFR}$	0.90	15
$\text{sqrt UV}_{254} = 8.57 + 6.13 \log [TN] + 5.35 \text{ sqrt HFR}$	0.88	15
$DOC = 6.0 + 6.09 \log [TN] + 1.56 \text{ sqrt HFR}$	0.86	15

Table 19. Models developed using arithmetic means of aggregated fall data collected from 15 northern Missouri reservoirs in 2004. TTHMFP = Total Trihalomethane Formation Potential ($\mu\text{g/L}$). CD = Chlorine Demand (mg/L). UV_{254} = Ultraviolet Absorbance at 254 nm/cm*1000. HFR = Hydraulic Flushing Rate = Rainfall (ft) * Watershed Area (ac) / Volume (ac-ft). TP = Total Phosphorus ($\mu\text{g/L}$). TN = Total Nitrogen (mg/L). DOC = Dissolved Organic Carbon (mg/L).

Aggregated Seasonal Means

Arithmetic seasonal means for winter, spring, summer and fall from the 15 northern Missouri reservoirs were combined and models were developed for TTHMFP, chlorine demand, UV absorbance and DOC. TTHMFP models used summer and fall data only. Chlorine demand models used spring, summer and fall data. DOC and UV_{254} models contained means from all four seasons. DOC, TP, TN and hydraulic flushing rate best explained the variability in all four response variables (Table 20). TTHMFP was modeled using DOC ($R^2 = 0.80$) and flushing rate ($R^2 = 0.58$). Eighty percent of the cross-system variation in chlorine demand was explained by DOC while TP and flushing rate together explained 68% of the variation. UV_{254} was best modeled with DOC and TP ($R^2 = 0.86$) or

TP alone ($R^2 = 0.76$). DOC was best described using flushing rate in conjunction with either of the nutrients TN ($R^2 = 0.78$) or TP ($R^2 = 0.72$).

Models for 15 N-MO Reservoirs: Seasonal Lake Means	R²	n
TTHMFP = 72.56 [DOC] – 183.4	0.80	30
TTHMFP = 93.9 + 224. sqrt HFR	0.58	30
log CD = 0.48 + 0.06 [DOC]	0.80	45
log CD = 0.48 + 0.234 log [TP] + 0.07 sqrt HFR	0.68	45
sqrt UV ₂₅₄ = 0.939 [DOC] + 3.923 log [TP] – 0.39	0.86	60
sqrt UV ₂₅₄ = 7.980 log [TP] - 0.53	0.76	60
DOC = 5.6 + 4.82 log [TN] + 1.47 sqrt HFR	0.78	60
DOC = 0.74 + 3.150 log [TP] + 1.08 sqrt HFR	0.72	60

Table 20. Models developed using aggregated seasonal means from 15 northern Missouri reservoirs in 2004. TTHMFP = Total Trihalomethane Formation Potential ($\mu\text{g/L}$). CD = Chlorine Demand (mg/L). UV₂₅₄ = Ultraviolet Absorbance at 254 nm/cm*1000. HFR = Hydraulic Flushing Rate = Rainfall (ft) * Watershed Area (ac) / Volume (ac-ft). TP = Total Phosphorus ($\mu\text{g/L}$). TN = Total Nitrogen (mg/L). DOC = Dissolved Organic Carbon (mg/L).

Annual Means

Arithmetic seasonal means from winter, spring, summer and fall were averaged for each of the 15 northern Missouri reservoirs into an annual mean. Models were developed for TTHFP, chlorine demand, UV absorbance and DOC concentration. DOC, TP, TN and hydraulic flushing rate best explained the variability in all four DBP response variables (Table 21). TTHMFP was best described using DOC ($R^2 = 0.82$) or flushing rate ($R^2 = 0.70$). Chlorine demand was modeled using DOC and TP ($R^2 = 0.97$) or TP and flushing rate ($R^2 = 0.88$). Eighty-four percent of the variability in UV₂₅₄ was explained by DOC.

DOC was best modeled by flushing rate ($R^2 = 0.77$) or by TN and flushing rate together ($R^2 = 0.86$).

Models for 15 N-MO Reservoirs: Annual Lake Means	R²	n
TTHMFP = 86.59 [DOC] – 250.9	0.82	15
TTHMFP = 27.4 + 158.2 sqrt HFR	0.70	15
log CD = 0.4 + 0.05 [DOC] + 0.102 log [TP]	0.97	15
log CD = 0.5 + 0.184 log [TP] + 0.06 sqrt HFR	0.88	15
sqrt UV ₂₅₄ = 1.4 + 1.59 [DOC]	0.84	15
DOC = 4.9 + 3.68 log [TN] + 1.07 sqrt HFR	0.86	15
DOC = 3.38 + 1.73 sqrt HFR	0.77	15

Table 21. Models developed using aggregated annual data collected from 15 Missouri reservoirs in 2004. TTHMFP = Total Trihalomethane Formation Potential ($\mu\text{g/L}$). CD = Chlorine Demand (mg/L). UV₂₅₄ = Ultraviolet Absorbance at 254 nm/cm*1000. HFR = Hydraulic Flushing Rate = Rainfall (ft) * Watershed Area (ac) / Volume (ac-ft). TP = Total Phosphorus ($\mu\text{g/L}$). TN = Total Nitrogen (mg/L). DOC = Dissolved Organic Carbon (mg/L).

Chlorophyll

Chlorophyll is generally considered a good indicator of DBP formation potential because algal biomass often contributes a large fraction of DOC to the precursor pool (Hoehn et al. 1980, Chapra et al. 1997). Autochthonous carbon, however, is more labile in nature and less reactive with chlorine than allochthonous carbon (Hoehn 1983). In this 2004 study of Missouri reservoirs, the relationships between chlorophyll and THM surrogates (TTHMFP, chlorine demand, UV₂₅₄ and DOC) were weak ($R^2 = 0.10$ to 0.48 for seasonal models and $R^2 = 0.31$ to 0.62 for annual means, Table 22). All DBP surrogates were highly variable for any given level of chlorophyll, but the relationships were positive. For

TTHMFP and chlorine demand, the relationship with chlorophyll remained fairly consistent across seasons while UV₂₅₄ and DOC showed dramatically stronger relationships from winter to spring and spring to summer. This trend represents the increase in autochthonous productivity in the summer. These relationships, however, were weak compared to other environmental variables. In a cross-system analysis of annual reservoir means, the relationships between chlorophyll and the DBP variables were also weak compared to other variables ($R^2 = 0.31 - 0.62$, Table 22).

R² Values for Total Chlorophyll Data and DBP Surrogates

Variable	Winter	Spring	Summer	Fall	All Data	Annual Means
TTHMFP	No Data	No Data	0.28	0.23	0.26	0.31
CD	No Data	0.39	0.37	0.38	0.37	0.62
UV ₂₅₄	0.11	0.32	0.42	0.27	0.32	0.54
DOC	0.10	0.29	0.48	0.26	0.33	0.56

Table 22. R² values for log-transformed total chlorophyll and DBP surrogates. TTHMFP = Total Trihalomethane Formation Potential (µg/L). CD = Chlorine Demand (mg/L). UV₂₅₄ = Ultraviolet Absorbance at 254 nm/cm*1000. DOC = Dissolved Organic Carbon (mg/L). Data is from 15 northern Missouri reservoirs sampled weekly in 2004.

Total Phosphorus

Total phosphorus exhibited a strong relationship with both chlorine demand and UV₂₅₄ at all levels of aggregation (Figures 22 - 24). Fifty-one percent of the cross-system variability in chlorine demand was explained by total phosphorus among un-aggregated data (Figure 22), 64% was explained among seasonal means (Figure 23) and 83% was

explained among annual lake means (Figure 24). A strong, non-linear relationship between TP and UV_{254} existed at all levels of aggregation (Figures 25 - 27). Seventy-one percent of the variation in UV_{254} was explained by TP among un-aggregated data (Figure 25), 79% among seasonal means (Figure 26) and 83% among annual means (Figure 27)

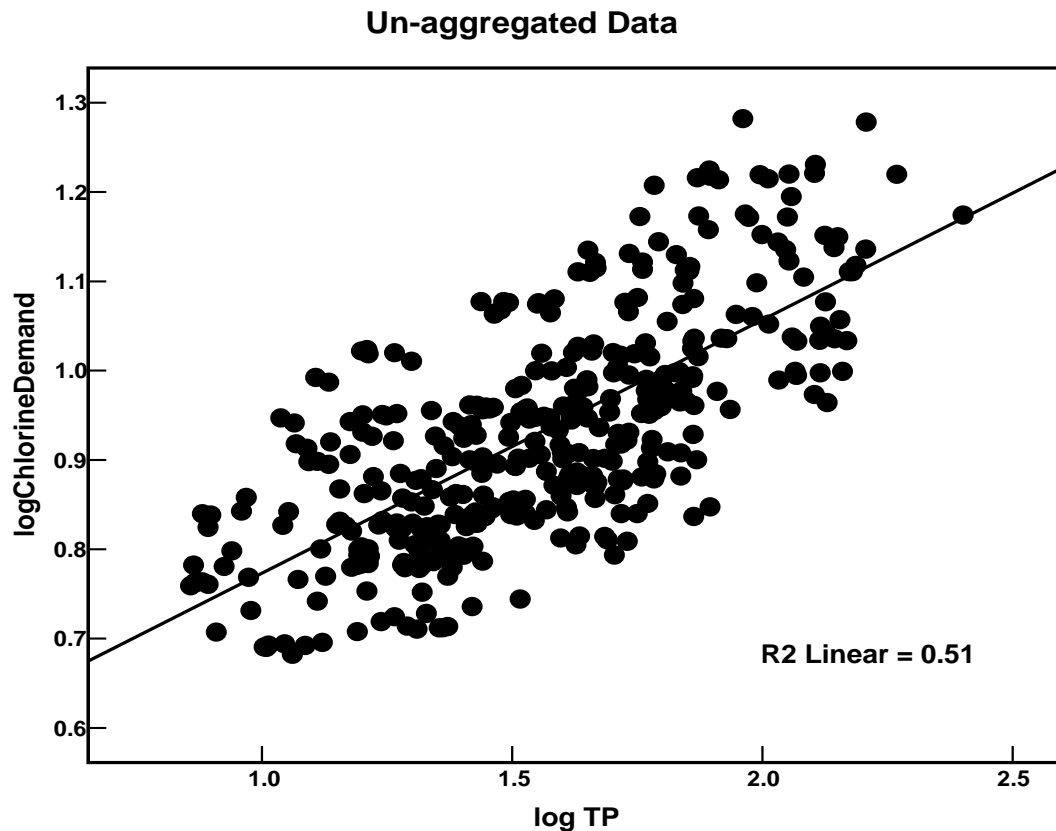


Figure 22. Scatter plot of log-transformed total phosphorus and log-transformed chlorine demand using un-aggregated weekly data from 15 northern Missouri reservoirs sampled in 2004.

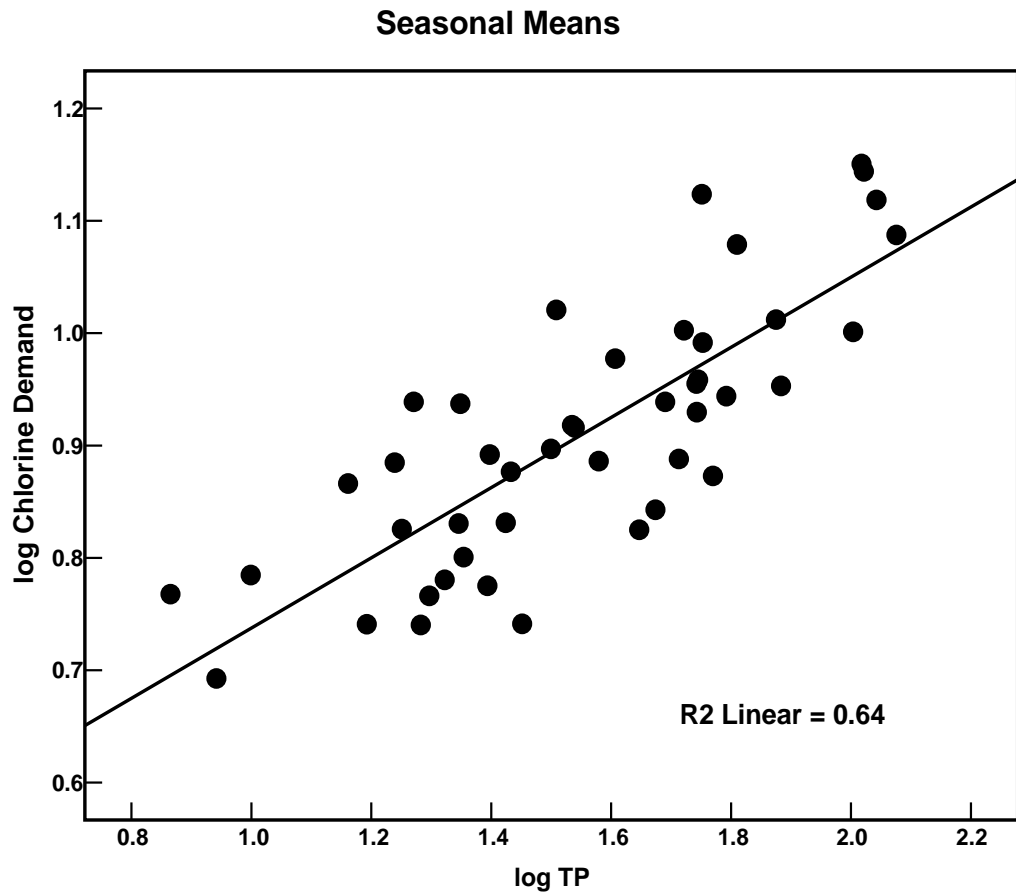


Figure 23. Scatter plot of log-transformed total phosphorus and log-transformed chlorine demand using aggregated seasonal means from 15 northern Missouri reservoirs sampled in 2004.

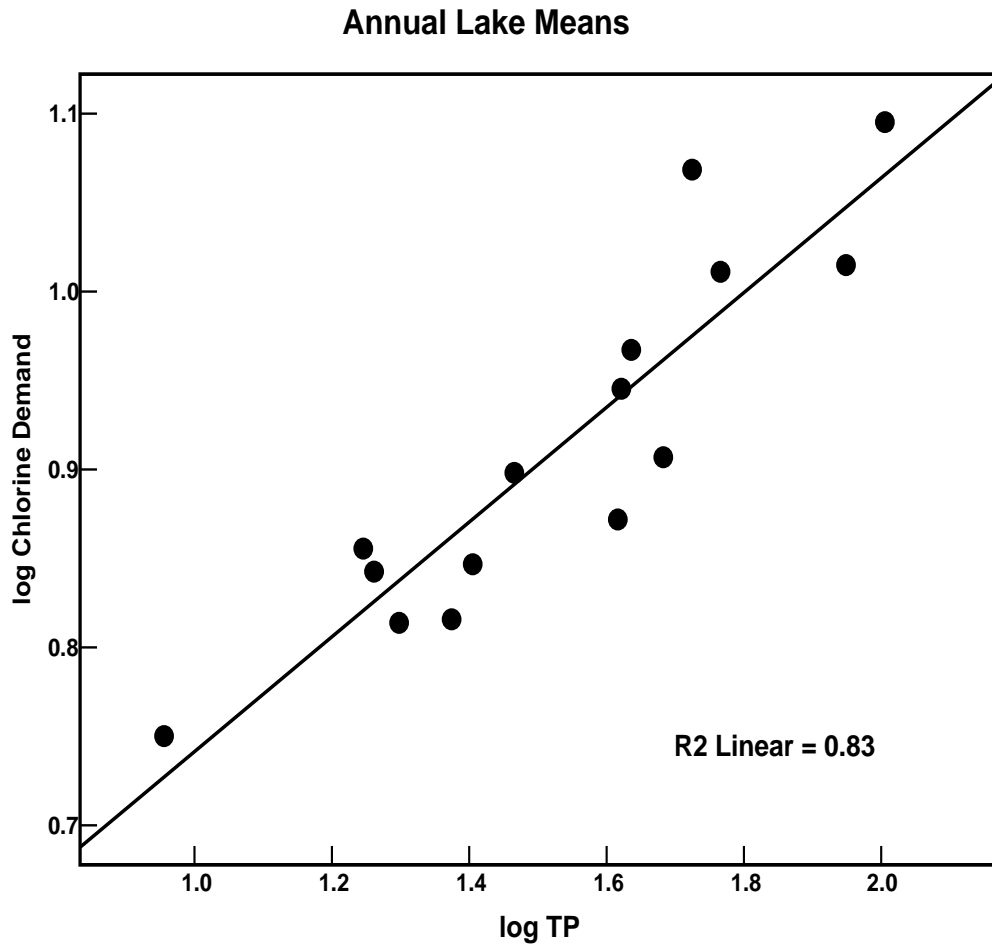


Figure 24. Scatter plot of log-transformed total phosphorus and log-transformed chlorine demand using aggregated annual means from 15 northern Missouri reservoirs sampled in 2004.

Un-aggregated Data

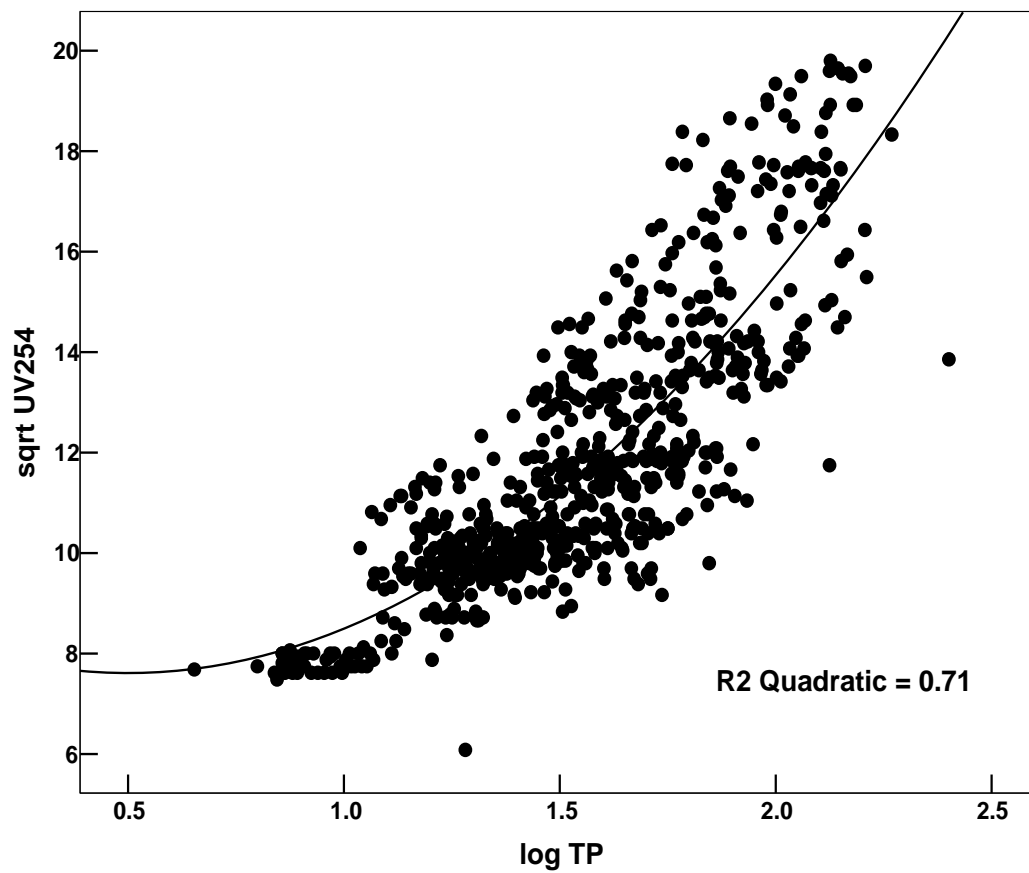


Figure 25. Scatter plot of log- transformed total phosphorus and square root-transformed UV₂₅₄ [Ultraviolet Absorbance at 254 nm/cm*1000] using un-aggregated weekly data from 15 northern Missouri reservoirs sampled in 2004. Equation: $\text{sqrt UV}_{254} = 3.51 [\text{logTP}]^2 - 3.50 [\text{logTP}] + 8.48$ ($R^2 = 0.71$).

Seasonal Lake Means

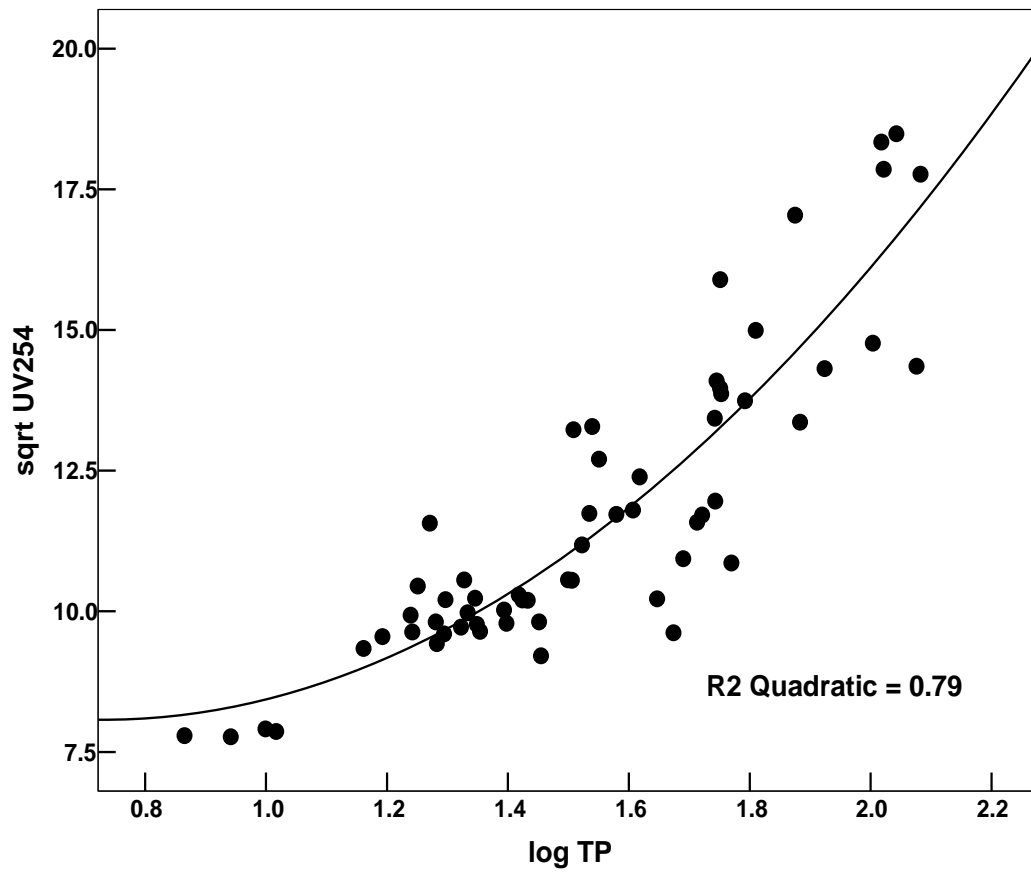


Figure 26. Scatter plot of log-transformed total phosphorus and square root-transformed UV₂₅₄ [Ultraviolet Absorbance at 254 nm/cm*1000] using aggregated seasonal means from 15 northern Missouri reservoirs sampled in 2004. Equation: $\text{sqrt UV}_{254} = 4.98 [\text{logTP}]^2 - 7.28 [\text{logTP}] + 10.73$ ($R^2 = 0.79$).

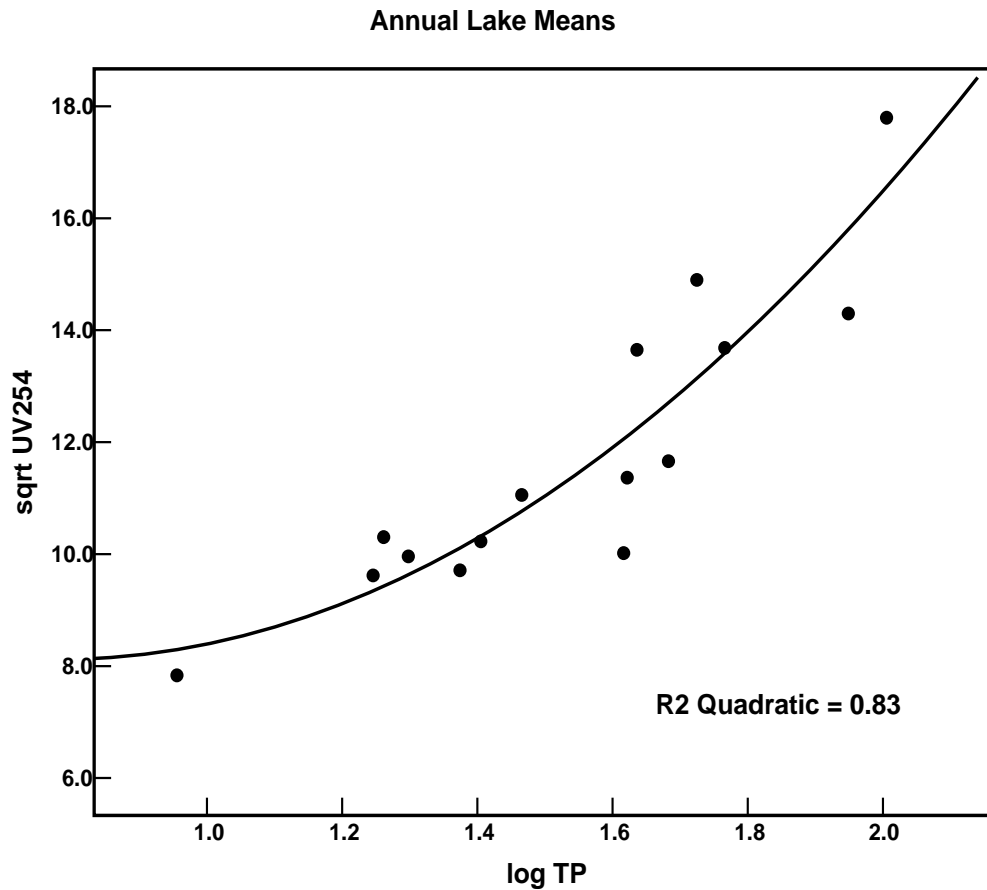


Figure 27. Scatter plot of total phosphorus and UV₂₅₄ [Ultraviolet Absorbance at 254 nm/cm*1000] using aggregated annual means from all 15 reservoirs sampled in 2004. Equation: $\text{sqrt UV}_{254} = 5.61 [\text{logTP}]^2 - 8.73 [\text{logTP}] + 11.52$ ($R^2 = 0.83$).

Hydraulic Flushing Rate

In this study, reservoirs with higher flushing rates had higher DOC content and increased chlorine demand (Figures 28 & 29). Missouri reservoirs are artificial impoundments and have higher watershed to surface area (or volume) ratios than natural lakes, resulting in

higher flushing rates. This hydraulic feature magnifies the importance of allochthonous organic carbon inputs in Missouri reservoirs.

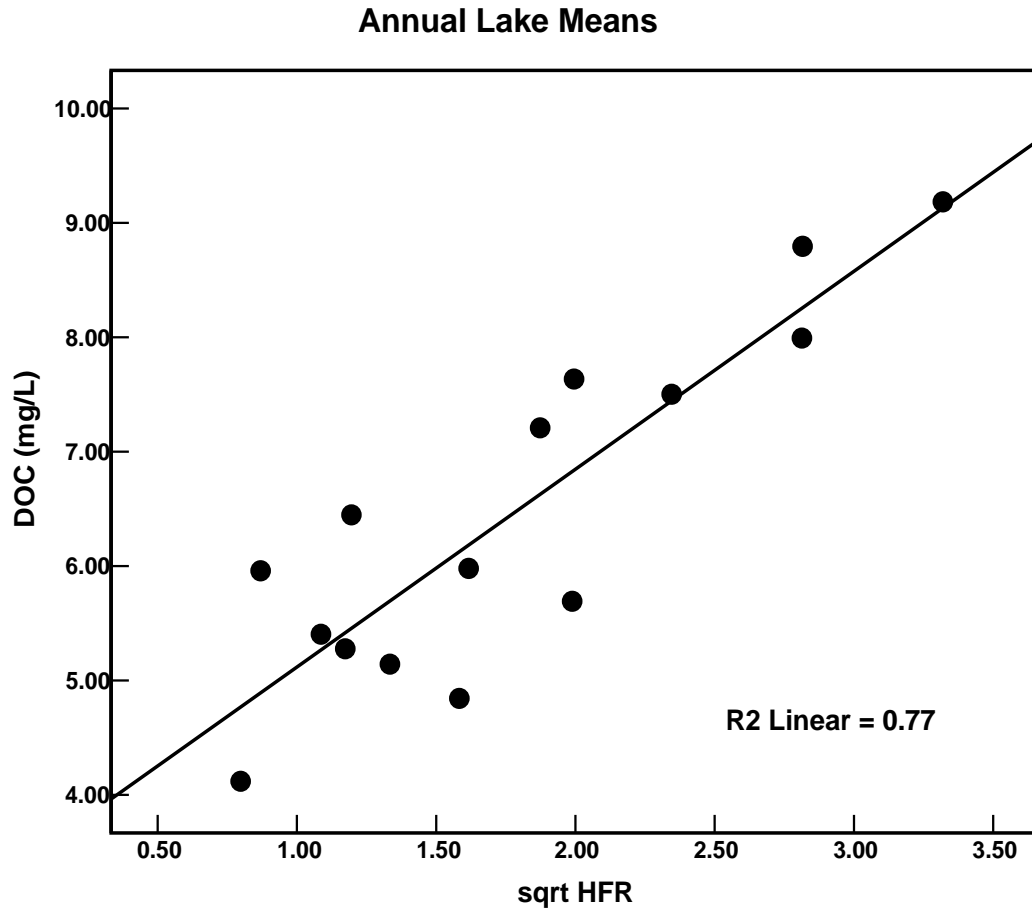


Figure 28. Scatter plot of annual hydraulic flushing rate and mean annual DOC from 15 northern Missouri reservoirs in 2004

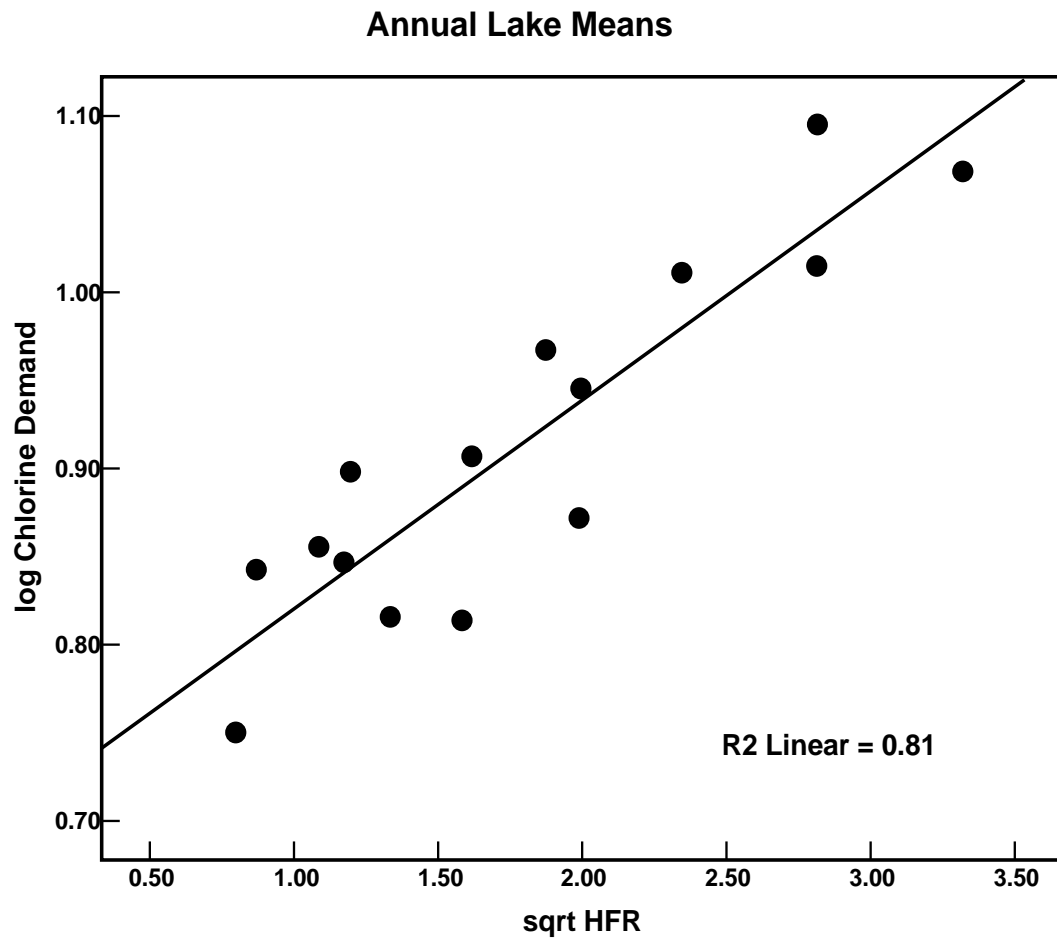


Figure 29. Scatter plot of annual hydraulic flushing rate and mean annual chlorine demand from 15 northern Missouri reservoirs in 2004.

DISCUSSION

The source and sink processes for DBP precursors vary both among reservoir systems and within reservoir systems. Each reservoir possesses a unique biogeochemistry that affects the precursor load, composition, distribution and reactivity in the system (Edzwald et al. 1985, Canale et al. 1997, Cooke and Kennedy 2001, Sachse et al. 2001). The relative proportion of allochthonous and autochthonous organic carbon depends on watershed characteristics and autochthonous productivity, which vary both annually and seasonally within reservoirs (Rasmussen et al. 1989, del Giorgio and Peters 1994, Gergel et al. 1999, Sachse et al. 2001) as well as globally and regionally (Kalff 2002, Pace and Cole 2002, Xenopoulos et al. 2003). Lake and watershed morphology, and hence hydraulic flushing rate, may control carbon loading in some systems while algal productivity may dominate in other systems or at different times within the same system (Chapra et al. 1997). Identifying the relative influence of allochthonous and autochthonous carbon inputs and the temporal variation in DBP formation potential was the goal of this cross-system study of Missouri reservoirs.

Although DOC is the single most important precursor of DBP, the mechanisms of formation can not be modeled directly after DOC dynamics (Amy et al. 1990), and thus DOC is often a poor estimator of DBP or its surrogates at any given time period (White et al. 2003). Essentially, DBP formation potential depends on two factors: DOC concentration and DOC reactivity. Increased DOC concentration does not always equate to higher DBP formation potential due to differences in reactivity (Rook 1977, Amy et al.

1990, Chang et al 2000, Sachse et al. 2001). In this study, however, the cross-system relationships using annual means of DOC and TTHMFP ($R^2 = 0.82$); DOC, TP and chlorine demand ($R^2 = 0.97$); DOC and UV_{254} ($R^2 = 0.84$) and DOC and HFR ($R^2 = 0.77$) were quite strong (Table 21), suggesting that these surrogate measures work well as predictors of DBP formation potential in Missouri reservoirs.

DOC was not the only useful predictor of DBP using annual means. Watershed hydrology and water age are known to influence the relative importance of allochthonous and autochthonous carbon in aquatic systems (Gergel et al. 1999, Pace and Cole 2002, Hein et al. 2003). In this study, HFR explained 70% of the variation in TTHM, HFR and TP together explained 88% of the variation in chlorine demand and TN together with HFR explained 86% of the variation in DOC (Table 21). These findings suggest that using DOC and nutrient data in conjunction with reservoir HFR may provide a good proxy of THM formation potential in Missouri reservoirs and also suggest that allochthonous inputs may be the dominant DBP precursors in Missouri reservoirs. Although algal extra-cellular products are known contributors to DBP precursors (Plummer and Edzwald 1998), chlorophyll was not an important explanatory variable in any of the models developed during the cross-system analysis. Care should be exercised, however, when using a single year's data to characterize lakes over the long-term due to inherent year-to-year variability in lakes (Knowlton et al. 1984) and precipitation (USGS 2005). The strong link between precipitation and DOC concentrations (Pace and Cole 2002) could lead to dramatically different precursor pools from year to year.

The models describing DBP surrogates using reservoir means utilized the same set of key environmental variables across seasons. Explanatory models for TTHMFP during summer and fall included DOC and HFR and accounted for 68 to 86% of the cross-system variation. Chlorine demand models were strongest in spring and summer when allochthonous and autochthonous organics are increasing, with 82 – 96% of the variation explained by DOC, TP or both. UV₂₅₄ models were less consistent from season to season illustrating the fluctuation in allochthonous inputs and the added effects of autochthonous productivity in the summer. Ninety percent of the variation in UV₂₅₄ was explained by TP in winter, DOC in summer and DOC in combination with HFR in fall. Spring UV₂₅₄ models were not as strong, with only 66 – 78% of the variation explained by nutrients or HFR combined. Again, chlorophyll was not an explanatory variable in any of the best seasonal models. UV₂₅₄ peaks coincided very well, however, with USGS stream discharge data. The strong linkage between UV absorbance and the stream hydrograph exemplifies the importance of allochthonous inputs in Missouri in 2004.

The strong correlation between TP and DBP surrogates suggest there is a relationship between DBP and trophic state, but a causal relationship is still ambiguous (Walker 1983, Chapra et al. 1997, Cooke and Kennedy 2001). External phosphorus and nitrogen loading is linked to sediment transport from the watershed and hence hydraulic flushing rate (Hein et al. 2003, Jones and Knowlton 2005). The high flushing rates of artificial Missouri reservoirs are in effect loading reservoir systems with TP and TN while at the same time introducing hydrophobic, reactive allochthonous carbon. This finding implies a synergistic relationship between hydrology, trophic state and the resultant DBP

precursor pool (Canale et al. 1997, Cooke and Kenndy 2001). This large-scale relationship, however, may not apply on smaller spatial or temporal scales such as in individual reservoirs or at any given time period, as is often seen in limnological studies where empirical relationships are generated using cross-system data (Jones et al. 1998). As stated earlier, 2004 was a particularly wet year for Missouri with overall higher than normal precipitation and stream discharge following nine dry years (USGS 2005).

Chlorophyll concentration, a measure of autochthonous productivity, was only weakly related to THMFP using summer data ($R^2 = 0.28$), fall data ($R^2 = 0.23$) or annual reservoir means ($R^2 = 0.31$, Table 22), illustrating the dominating role of allochthonous over autochthonous carbon inputs. Consistently weak relationships between chlorophyll and the DBP surrogate measures chlorine demand, UV_{254} and DOC were also found both seasonally and when compared as annual reservoir means (Table 22). This, however, may be the result of algal species composition shifts over the summer. Nguyen et al., 2005, found that despite nearly equivalent DOC excretion and POC biomass in three algal species, chlorophyll production varied dramatically. This indicates that chlorophyll may not be a good measure of autochthonous DOC production.

As expected, summer data demonstrated the strongest relationships with chlorophyll ($R^2 = 0.37 - 0.48$), when algal productivity is the highest (Scully et al. 1988, Gergel et al. 1999, Royer and David 2005), while winter data had the weakest relationships ($R^2 = 0.10 - 0.11$, Table 22). Based in these positive but weak relationships between chlorophyll and

DBP surrogates, we conclude that while autochthonously produced carbon influenced DBP formation potential, it was not the controlling factor in Missouri reservoirs in 2004.

UV₂₅₄ is a good surrogate measure for chlorine reactivity and thus DBP formation potential (Kitis et al. 2001, White et al. 2003). UV₂₅₄ absorbance can be used to monitor changes in DOC concentration and composition (Edwards and Cresser 1987, Rasmussen et al. 1989). Algal-derived autochthonous carbon is more labile in nature (Sachse et al. 2001), less reactive with chlorine and does not exhibit strong absorbance peaks in the UV₂₅₄ range. It generally consists of colorless extra-cellular products released by phytoplankton such as carbohydrates and amino acids. Allochthonous organic carbon, however, is highly colored and consists of the breakdown products of lignin and cellulose which absorb highly at 254 nm (Wetzel 1983, Gergel et al. 1999). The supply of this highly colored DOC is a function of hydrology and varies temporally with precipitation and runoff (Rasmussen et al. 1989, Jansson et al. 2000, Pace and Cole 2002). The decline in UV₂₅₄ during summer (Figure 20) can be attributed to declining precipitation, stratification, settling and plunging inflows; all factors that also influence nutrient concentrations in the epilimnion. Most Missouri reservoirs stratify in summer, isolating the epilimnion from the hypolimnion, resulting in plunging density inflows of allochthonous material that bypass the epilimnion (Jones and Knowlton 2005). Additionally, stream discharge and precipitation declined over the summer (Figures 11 – 14) with a concomitant decline in UV₂₅₄. These processes affect the relative influence of allochthonous and autochthonous carbon in the epilimnion, favoring allochthonous carbon in early summer shifting toward algal contributions in late summer.

The failure of UV_{254} to rebound in Collection Period 4 (Figure 20) when nutrients and chlorophyll had increased (Figures 8-10) may be due to the labile nature of autochthonous carbon and the reduction of allochthonous inputs through reduced precipitation and runoff. This is further exemplified by the steady decline in SUVA values over summer from Collection Period 1 through 4 (Figure 21). SUVA represents UV_{254} absorption normalized by DOC, and increased SUVA values represent DOC enrichment in refractory DBP precursors (White et al. 2003). The steady decline in SUVA values seen in this study indicates that although DOC values remained fairly constant over the summer (Figure 19), the reactivity per unit carbon declined, again indicating the decreasing influence of allochthonous carbon over the summer.

The relationship between nutrients and chlorophyll has been firmly established (Jones and Bachmann 1976, Chapra et al. 1997, Jones et al. 1998, Kalff 2002, Xenopoulos 2002, Xenopoulos and Frost 2003). Algal productivity depends on nutrient loading, light availability and temperature (Cooke and Kennedy 2001, Kalff 2002, Xenopoulos 2002, Xenopoulos and Frost 2003). Strong relationships between TP, TN and the DBP surrogates are due to the synergistic effects of allochthonous inputs and stimulated autochthonous productivity. Loading from allochthonous runoff stimulates autochthonous productivity thereby increasing the organic carbon pool both directly and indirectly. The control and/or reduction of TP inputs to a reservoir via erosion control reduce THMFP by virtue of reducing both the allochthonous and autochthonous carbon load in the system. Although chlorophyll is correlated with increased DBP formation potential in many

studies (Chapra et al 1997, Plummer and Edzwald 1998), this study demonstrated that chlorophyll, while influencing DBP formation potential, does not always control DBP formation potential, also noted by Canale et al. (1997).

Algal contributions, as represented by chlorophyll, are important in DBP formation potential but played a secondary role in this study. In effect, autochthonous carbon inputs influenced but did not control DBP formation potential in Missouri in 2004. In artificial reservoirs dominated by a high watershed to surface area ratio (Kalff 2002), HFR may control the DBP precursor pool both directly through refractory carbon inputs and indirectly through stimulation of autochthonous carbon, particularly in wet years. On a global scale, specific catchment features can not successfully model or predict DOC concentrations, however, on smaller regional scales such as used in this study, catchment variables become important and their predictive power becomes significant (Xenopoulos et al. 2003). In this cross-system analysis, HFR explained 77% of the variation in DOC concentration and 81% of the chlorine demand (Figures 28 & 29), suggesting that HFR can provide a rough indicator of DBP precursor loading and subsequently DBP formation potential in Missouri.

Watershed dynamics are complex and involve the synergistic interaction of several variables over time and space. Water quality can be considered a reflection of the impact of both land use and land cover, particularly for artificially constructed reservoirs where these impacts are magnified. Improving drinking water quality through source water protection is a direct application of this research; reducing nutrient rich and sediment

laden runoff will reduce the allochthonous input of DBP precursors, reduce the autochthonous production of DBP precursors and improve drinking water quality. Additionally, proper siting and construction of reservoirs (placing dams higher in the watershed and constructing deeper reservoirs) could reduce watershed impacts and extend the life of the reservoir by reducing HFR. Aside from the health benefits of safe drinking water, watershed and source water management is ecologically, aesthetically and economically beneficial to the community. The hydrologic cycle is complex and dynamic and a better understanding of organic carbon cycling through aquatic systems will allow us to better protect our source waters.

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GLOSSARY OF ACRONYMS

AWWA	American Water Works Association
CD	Chlorine Demand
Chl	Chlorophyll
DBP	Disinfection By-Products
DBPFP	Disinfection By-Product Formation Potential
DIUF	Deionized Ultra-Filtered
DOC	Dissolved Organic Carbon
DOH	Department of Health
ECP	Extracellular Products
EPA	Environmental Protection Agency
GC	Gas Chromatograph
HAA	Halogenated Acetic Acids
MCL	Maximum Contaminant Level
NDIR	Non-Dispersive Infrared
NOM	Natural Organic Matter
POC	Particulate Organic Carbon
THM	Trihalogenated Methane
THMFP	Trihalogenated Methane Formation Potential
TOX	Total Organohalides
TTHM	Total Trihalogenated Methane
TTHMFP	Total Trihalogenated Methane Formation Potential

UFC	Uniform Formation Conditions
UV ₂₅₄	Ultraviolet Absorbance at 254nm
SDWA	Safe Drinking Water Act
SUVA	Specific Ultraviolet Absorbance