

CHAPTER 2.0

ORGANIC CARBON IN AQUATIC ECOSYSTEMS AND PATHWAYS OF DISINFECTION BYPRODUCT FORMATION

Organic carbon, comprising living and non-living fractions, is central to the flow of energy and the trophic structure of aquatic ecosystems (Wetzel, 2001). Although high concentrations of organic carbon are generally undesirable in drinking water sources due to the formation of disinfection byproducts (Amy et al., 1990; Cohn et al., 1999), these concentrations may be beneficial and even essential for aquatic ecosystems. An understanding of the ecosystem processes of organic carbon in the Central Valley is important because any actions to manage the concentrations of organic carbon at drinking water intakes must also consider the potential ecological impacts. Likewise, restoration actions in the Delta to improve habitat quality that change organic carbon concentrations and the quality of the organic carbon must consider the impacts to drinking water. For the purpose of evaluating the role of organic carbon in ecological processes, the division into dissolved and particulate forms, and also bioavailable forms, is critical. However, the formation of THMs and other disinfection byproducts during drinking water treatment is generally not directly related to these forms, but is a function of the chemical structure and reactivity of the organic carbon. General findings from the literature on ecosystem processes and drinking water impacts are briefly reviewed in this chapter. Subsequent chapters present Central Valley and Delta specific data and quantification of the processes described in this chapter.

2.1 ORGANIC CARBON CYCLING AND TRANSPORT

The cycling of organic carbon in terrestrial environments is shown in schematic form in Figure 2-1. Organic carbon is produced from atmospheric carbon dioxide and

water by plants through the many complex reactions of photosynthesis. (in forests, cropland, rangeland, and to a lesser degree on urban land). Organic carbon enters the surface soil pool following senescence and litterfall of plant matter. Microbial populations and fungi break down this organic carbon into smaller, more labile forms and ultimately to carbon dioxide. A fraction of soil organic matter is stored in the terrestrial compartment and a fraction is transported in surface runoff and into groundwater which may enter surface waters as baseflow. Not shown in this schematic are point sources such as wastewater treatment plants that may contain organic carbon originating in the watershed as well as imported organic carbon. The magnitude of organic carbon export is a function of the land use and the level of rainfall and runoff. Literature reports suggest a range of dissolved organic carbon exports from 0.38 tons/km²/yr for cool grasslands to 9.9 tons/km²/yr in swamp forests (Aitkenhead and McDowell, 2000). For most freshwater bodies, watershed sources of organic carbon are a much greater source than internal production (Wetzel, 2001). Other things being equal, dry regions are expected to export a lower amount of organic carbon than wet regions with greater runoff. This is relevant to the Central Valley because it exhibits a variety of precipitation characteristics, with the northern and eastern portions being wetter than the southern and western portions (NRCS, 2006).

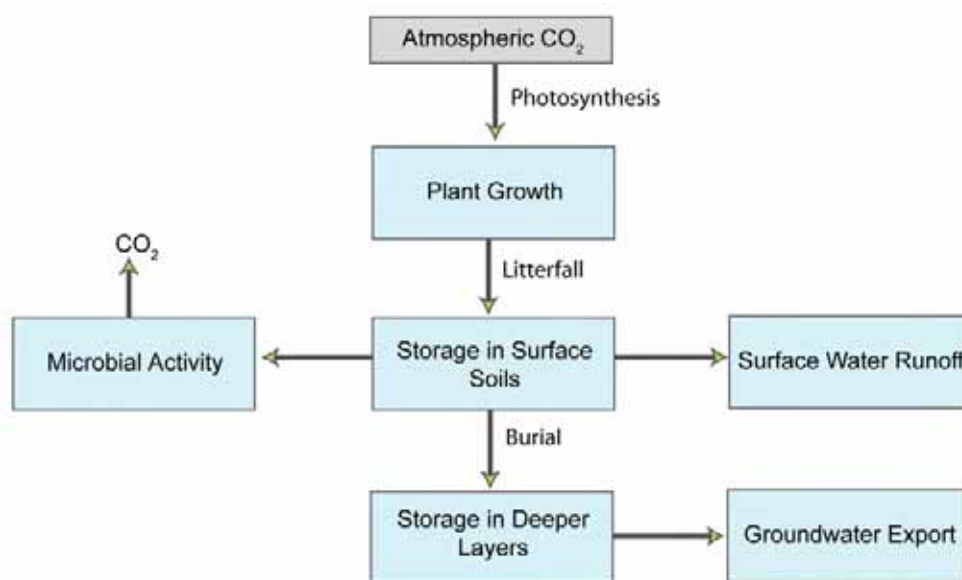


Figure 2-1. Schematic of organic carbon cycling in the terrestrial environment

The cycling of organic carbon in the aquatic environment is shown in schematic form in Figure 2-2. Organic carbon may enter a water body from terrestrial sources in the watershed as shown in Figure 2-1, and it may also be photosynthesized within the water body by benthic and planktonic algae and plants, using atmospheric carbon dioxide or dissolved inorganic carbon as a carbon source. For simplicity, the organic carbon is represented as two pools, particulate and dissolved organic carbon (POC and DOC respectively), although in reality there is a continuum of particle size and molecular weight that influences its metabolism (Wetzel, 2001). A key feature shown

in Figure 2-2 is that DOC, unlike POC, cannot be directly taken up by primary consumers. Bacteria may convert DOC to bacterial biomass which then becomes available for consumption by higher organisms (Wetzel, 2001; Jassby and Cloern, 2000). POC from the watershed and POC from aquatic primary production is generally more accessible to the food web than DOC. In most ecosystems it has been observed that the detrital organic carbon (as DOC and non-living POC) is far more abundant than the organic carbon in living POC (Wetzel, 2001). Bacteria may also metabolize DOC to carbon dioxide that exits the aquatic system. The atmospheric pathway for loss of organic carbon is significant, and in some areas of the Delta, such as the islands, can be far in excess of aqueous export (Deverel and Rojstaczer, 1996). Sediments in water bodies play a key role in the cycling of organic carbon. Generally, POC can settle to the sediments, and provide a source of DOC to the overlying water column through microbial decay. Sediment POC can be stored for long periods, or may be scoured and transported downstream during high flow events. Thus, high flow events in the wet season transport large quantities of organic carbon that may have accumulated in the sediments in preceding months or years.

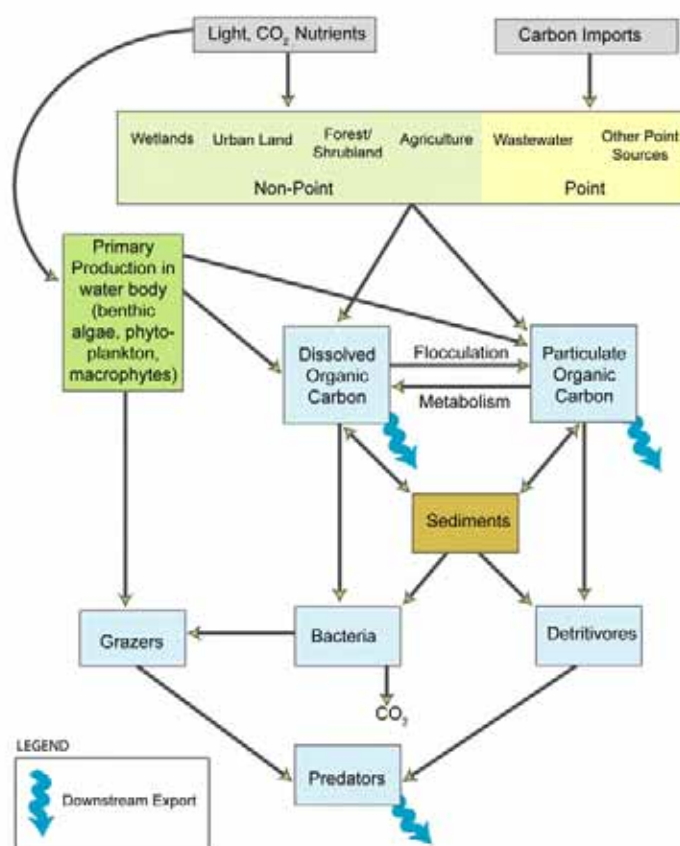


Figure 2-2. Schematic of organic carbon cycling in the aquatic environment (modified from Wetzel, 2001).

The transport processes of organic carbon are shown schematically for the Central Valley - Delta ecosystem in Figure 2-3. Organic carbon, in various stages of decay,

enters water bodies through streams in drainage and runoff and through groundwater flows. Streams play a critical role in organic carbon transport. They act as conduits for organic carbon exported from land surfaces, but may also convert some of the organic carbon into carbon dioxide or store it in sediments. At other times, depending on flow rates, sediment erosion or efflux can be a contribution to the transported load. Further, streams may be an additional source of organic carbon production through algal and macrophyte growth. Organic carbon transport in streams is controlled by flow rates with the greatest loads being transported during high flow events in the wet season. In the wet season, and especially during storm flows, organic carbon stored in the surface layers of various land uses, and also in stream sediments is transported into downstream waters.

The Central Valley is unique in having reservoirs on practically all tributaries, which may play an important role in organic carbon production and export. Reservoirs, by storing water for extended residence times during the warm, dry months of the year, and by providing a large surface area, may provide an environment for algae growth in excess of what would have occurred naturally. Some of the organic carbon produced in reservoirs may be exported downstream. Conversely, reservoirs may act as large settling basins for POC, resulting in less transport of organic carbon downstream.

Tributary organic carbon loads (termed allochthonous loads), which include detrital as well as planktonic organic carbon, reach the Delta where the residence time ranges from days to weeks, depending on season and inflow volume. As shown in Figure 2-3, the Delta is itself a producer of organic carbon due to primary production by benthic and planktonic algae and plants and export from tidal marshes, agriculture, and developed lands (autochthonous loads). A fraction of the internally generated and the tributary organic carbon is exported to San Francisco Bay. Organic carbon is also lost from the Delta by the diversion of water at the drinking water intakes. Additionally, organic carbon is incorporated in sediments and metabolized to carbon dioxide. Because large drinking water intakes are located in the Delta, the quality and quantity of the autochthonous organic carbon is of particular relevance to potential drinking water quality impacts.

Declines in fish species and related food web impacts in San Francisco Bay and the Delta have motivated studies of organic carbon sources and bioavailability independent of drinking water quality-related investigations (e.g., Jassby et al., 1993). Driven by variations in tributary inflows, allochthonous organic carbon loads vary widely from year to year (Jassby et al., 2002). There is also a substantial year-to-year variation in primary production in the Delta with a declining trend in primary production in recent years that has been attributed to various causes including the consumption of phytoplankton by an exotic invading species (the Asian clam *Potamocorbula amurensis*) and other benthic consumers (Jassby et al., 2002).

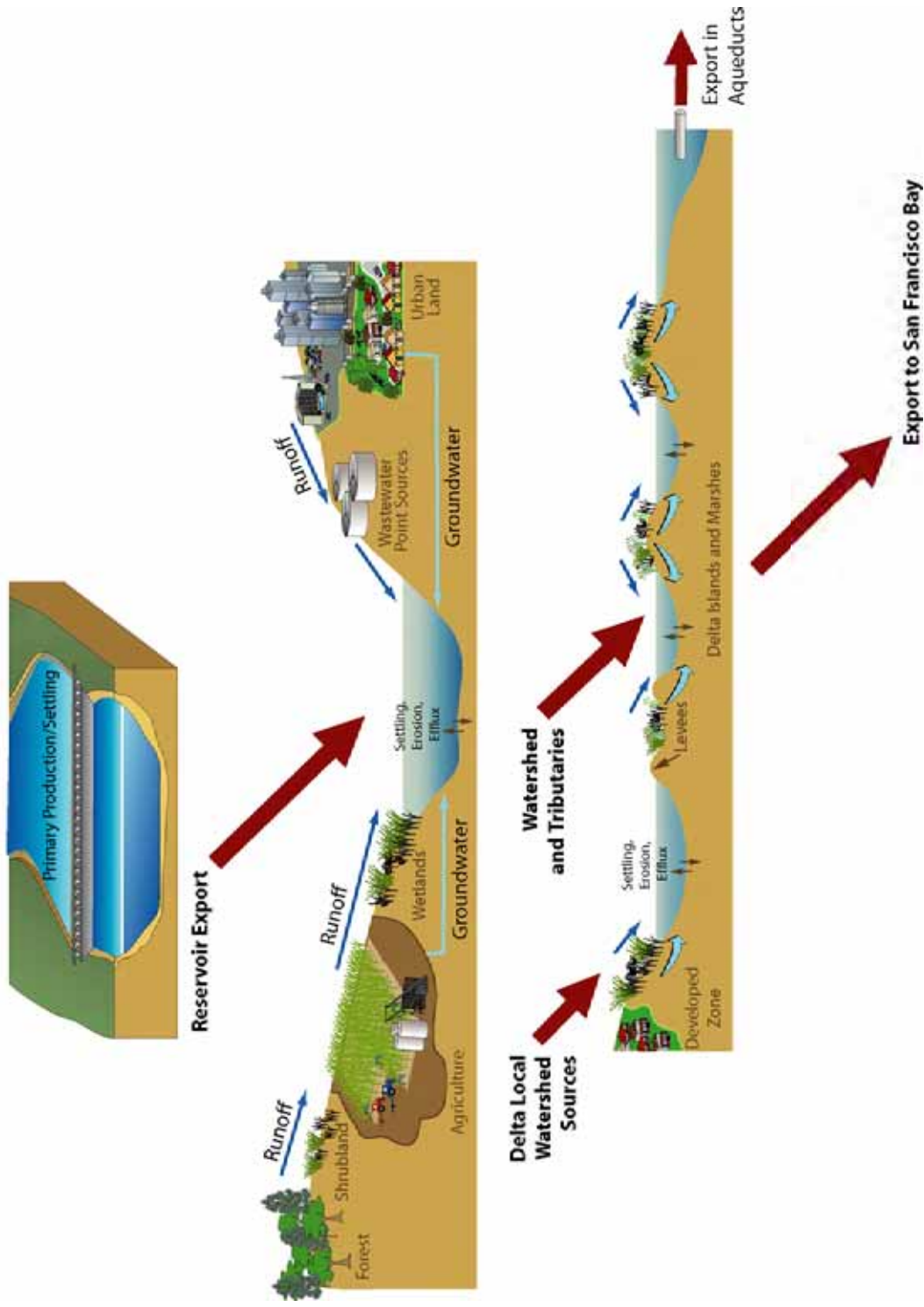


Figure 2-3. Schematic representation of organic carbon transport in the Central Valley-Delta system. Organic carbon originates in upstream natural sources, and is released from reservoirs to the lower watershed, where there are additional contributions from point and non-point sources. The organic carbon from the tributaries enters the Delta, where there are additional point and non-point sources in its immediate watershed, as well as production within the Delta. A fraction of the organic carbon is exported in aqueducts, but in most seasons, a large fraction is exported downstream to San Francisco Bay.

Recent studies have concluded that tributary inputs of organic carbon several times larger than in-Delta primary productivity and agricultural drainage (Jassby and Cloern, 2000). A fraction of the tributary and internal loads are exported in the water supply intakes, while the remainder flows into San Francisco Bay. Evaluation of bacterial communities in the Delta using DNA fingerprints showed seasonal, but not spatial variation, in the bacterial communities. Bacterial communities associated with local primary production-derived organic carbon were dominant in summer/fall, and communities associated with terrestrial sources were dominant in winter (Stepanauskas et al., 2003).

The bioavailability, and therefore the ecological significance, of different components of organic carbon in the Delta are variable. Although a fraction of the DOC is available for bacterial metabolism, it appears to be a less important food source at the base of the food web than organic carbon derived from primary production within the Delta (Jassby and Cloern, 2000; Sobczak et al., 2002, 2004). Further, much of the natural POC load in the tributaries is a much poorer food source than natural phytoplankton. In controlled experimental studies with a zooplankton, *Daphnia magna*, total detrital organic carbon concentrations were found to be weakly related to growth, although chlorophyll *a* concentrations were found to be a good predictor for growth (Müeller-Solger et al., 2002). This study indicates that in a system like the Delta with an abundance of detrital organic carbon, much of it from tributary sources, some consuming organisms exhibit a preference for organic carbon freshly derived from primary production. In laboratory studies on water samples from the Delta, it has been shown that a relatively small fraction of the DOC and POC is available for bacterial metabolism (operationally defined as a 21-day incubation), and the bioavailable fraction is well correlated with primary production (Sobczak et al., 2004). If these results are corroborated by further research, potential reductions in tributary loads of organic carbon are less likely to have adverse ecological impacts, and it may be found that water quality objectives for drinking water supply and ecosystem health are not necessarily in conflict.

2.2 ORGANIC CARBON CHEMISTRY AND DRINKING WATER QUALITY

As shown schematically in Figure 2-2, organic matter in the water column of a water body consists of materials from plant, animal, and bacterial origins in various stages of decay, with fragments of variable molecular weight, functional group, and chemical reactivity. This organic carbon can exist as both POC and DOC, although DOC is generally considered the more important fraction for the production of disinfection byproducts because of its greater abundance and reactivity during chlorination (e.g., Chow and Gao, 2003; Chow et al., 2003). Organic carbon can broadly be divided into two groups, humic and non-humic substances (Thurman, 1985). Humic substances are high molecular weight compounds largely formed as a result of bacterial and fungal action on plant material and include humic acids (that precipitate at $\text{pH} < 2$), fulvic acids (soluble at any pH), and humin (insoluble materials). Non-humic substances include proteins, carbohydrates, and other lower molecular weight substances that are more available to bacterial degradation than humic substances.

Several studies in the literature have shown the link between TOC or DOC levels and THM formation. For example, using data from 133 lakes, rivers, and reservoirs across the US, Chapra et al. (1997) showed that TOC levels were a good predictor of THM formation potential (THMFP) with a non-linear relationship ($\text{THMFP} = 43.8 \cdot \text{TOC}^{1.248}$, $r^2 = 0.94$). It was also noted that higher TOC waters, possibly with a higher proportion of humic acids, produced more THMs per unit weight of carbon than lower TOC waters. In general, simple measures of organic carbon (such as DOC or TOC) work best as a predictor for THM formation if the carbon originates from one type of source. When organic carbon in a water sample originates from multiple sources, or when waters from different locations are compared, the predictive ability is likely to be weaker. Thus, for samples from a single Delta island, Fujii et al (1998) found a strong correlation between DOC and THMFP, although this relationship may be weaker when multiple locations are compared together (Weishaar et al., 2003) or when rivers with multiple sources are considered (Amy et al., 1990). A considerable amount of recent research has focused on relating organic matter compositional information to THM formation, and on identifying the origins of organic carbon near water intakes in the Delta. Much of this work has confirmed that organic carbon in water from different locations varies considerably with respect to the formation of THMs during chlorination (Bergamaschi et al., undated; Fujii et al., 1998; Fram et al., 1999; Weishaar et al., 2003). Although the relationship between organic carbon sources and concentrations at individual water supply intakes is complex, these studies suggest that management of organic carbon sources for drinking water quality should consider both quality and quantity, with greater emphasis on sources with the highest THMFP.

Organic carbon quality is characterized in a few different ways in routine monitoring and specialized research studies. The data most commonly reported in the Delta and vicinity include dissolved, particulate, and total organic carbon, ultraviolet (UV) absorbance at 254 nm, specific UV absorbance (or SUVA, which is absorbance in units of cm^{-1} divided by the DOC concentration in mg/l). To a limited extent, data are also available on the THMFP through equilibrations of water samples with gaseous chlorine in a protocol to mimic the disinfection process in water treatment plants (California Department of Water Resources, 1994). Specialized, limited-duration research studies have performed considerably more detailed analysis of the structure of natural organic matter to estimate reactivity and identify sources. These analyses have included separation into various fractions (hydrophilic and hydrophobic, humic and fulvic acids, etc.), ^{13}C -NMR spectroscopy to identify chemical structures and carbon:nitrogen ratios and stable isotope ($\delta^{13}\text{C}$, $\delta^{15}\text{N}$) signatures to identify sources. The variety of analyses of aquatic organic carbon samples and the information derived from them is summarized in Table 2-1. An important goal of these studies is to establish the link between various structural moieties of organic carbon and THMFP. When certain chemical characteristics of organic carbon associated with THM formation can be related to specific sources, the information can be used to improve management of source water quality by targeting the most reactive forms of

organic carbon. Key findings from recent research on organic carbon chemistry are summarized below.

Table 2-1
DOC-related measurements.

Measurement	Information Provided
TOC and DOC	Direct measure of total quantity of organic carbon present
UV absorbance (254 nm)	Surrogate for DOC concentration
Specific UV absorbance (SUVA)	Indicative of DOC aromaticity
Fluorescence	Indicative of aromatic structures
Separation by nonionic resins	Distribution by apparent molecular weight; indicative of acidic and non-acidic fractions and of hydrophilic/hydrophobic portions; separation into humic and fulvic acids
DBP formation potential	Direct measure of drinking water quality impact
¹³ C NMR Spectra	DOM chemical structure, specific functional groups
Isotopic composition of N and C in natural organic matter	Identification of source

A significant quantity of the initial work on organic carbon characterization was focused on UV absorbance (and SUVA), because this parameter was related to the aromaticity of organic carbon, a property identified to be related to general organic matter reactivity and THM formation (Reckhow et al., 1990). More recent work in the Delta and other locations shows that the correlation between SUVA and THM formation potential is weak (Fujii et al., 1998; Fram et al., 1999; Weishaar et al., 2003). SUVA, while confirmed to be a good predictor of aromaticity by ¹³C-NMR spectroscopy, is a weak predictor of THM formation because non-aromatic fractions of organic carbon also play an important role and all aromatic fractions are not highly reactive (Weishaar et al., 2003; Fleck et al., 2004). In Delta waters, the percentage of organic carbon was not shown to correlate with the THM formation (Fram et al., 1999). In a study with water with from a relatively homogeneous source (Twitchell Island agricultural drainage), the correlation between SUVA and specific THMFP was considerably weaker than that between DOC and THMFP (Fujii et al., 1998). SUVA has also been shown to be influenced by interferences such as pH, nitrate, and iron in water samples, although these may not be significant at the ranges of these parameters in surface waters (Weishaar et al., 2003). SUVA is used to determine the level of TOC removal required in raw water samples (US EPA, 1998) and continues to be a widely used measure of organic carbon reactivity. In fact, at most organic carbon sampling locations in the Delta and Central Valley, SUVA (or UVA) is the only other additional chemical characterization that is reported.

The most direct measure of the chemical functional groups of natural organic matter is through ^{13}C -NMR spectroscopy, a method that is complicated and expensive to apply on a routine basis. However, reports of organic matter characterization with this approach continue to grow in the literature. A major finding from the application of ^{13}C -NMR spectroscopy is that aromaticity is not a good predictor of THMFP (Weishaar et al., 2003), although the role of other functional groups has not been clearly identified (Chow and Gao, 2003).

Fractionation evaluations on organic carbon in water samples using nonionic resins, followed by tests for THMFP, have been performed by several researchers (e.g., reviewed by Chow and Gao, 2003). Fractionation of organic matter into hydrophobic and hydrophilic acids has shown that hydrophobic acids more readily form THMs than hydrophilic acids at many locations (Krasner et al., 1996), and specifically in the Central Valley and Delta (Bergamaschi et al., 2000). Fractionation into apparent molecular weight (AMW) has not shown a strong correlation between AMW and THMFP and there is no consensus in the literature on the link between the two parameters (Chow and Gao, 2003). In some instances in the Delta, lower AMW fractions were found to be more reactive than the larger AMW fractions (Amy et al., 1990). Organic carbon from different sources in the Delta was found to have different propensities to form THMs, with the limited data currently available indicating that tributary organic carbon was more reactive than that released from Delta agricultural islands (Bergamaschi et al., 2000).

Carbon:Nitrogen ratios and stable isotope chemistry in bulk organic matter ($\delta^{13}\text{C}$, $\delta^{15}\text{N}$) and in THMs ($\delta^{13}\text{C}$) formed in test samples can be used to elucidate the source of organic matter, and to identify the relative reactivity of the different organic carbon fractions (e.g., Bergamaschi et al., 1999). Organic matter from tributary sources (originating in surface runoff and groundwater flow) has much lower nitrogen contents (C:N of about 50:1) compared with organic matter derived from primary production within water bodies (C:N of about 12:1) (Wetzel, 2001). Data from the Delta show relatively small differences across different sites in all of these parameters. Organic carbon at most tributary and Delta locations sampled appears to be dominated by detrital material, with C:N ratios in most cases 30 or greater. In general, the stable isotope data are consistent with a small addition of organic matter due to primary production in the Delta, with much of the organic matter originating in the tributaries (Bergamaschi et al., undated). The limited spatial and temporal detail in the data currently available precludes a more detailed assessment using these analytical approaches.

It is important to note that published research on disinfectant byproduct formation has largely focused on the potential for THM formation, and not on potential for formation of haloacetic acids and other organic halides. An exception is work by the Municipal Water Quality Investigations Program (MWQI, 2003) where a limited amount of haloacetic acid formation was also studied. THMs are generally the most abundant disinfection byproduct in tests for disinfectant byproduct formation

potential, and haloacetic acids are no more than 50% of the total concentration of THMs.

2.3 MAJOR FINDINGS

Organic carbon in the dissolved form (DOC) is the form considered to be more likely to react during chlorination and form disinfection byproduct compounds. DOC is generally less bioavailable to the base of the food web compared with particulate organic carbon and/or organic carbon freshly derived from primary production. Thus, efforts in the Central Valley and Delta to control or manage DOC levels for drinking water quality may not have direct adverse effects on the food web, although this is a subject that needs to be studied further.

There is general agreement in the literature that THM formation is correlated to DOC concentrations, although the relationship is more complex when a specific structural characteristic of DOC is compared with THMFP. A commonly used measure of DOC aromaticity, SUVA at 254 nm, was found to be poorly correlated to THM formation in Delta waters.

Characterization of organic matter through sophisticated analytical tools such as stable isotope signatures is an active area of research. Published information that was available at this time, however, is limited to a small number of locations near the Delta, and with limited temporal resolution. The data are indicative of a contribution due to in-Delta primary production, although the variability of this contribution as a function of time is not known. There is limited knowledge on the relative propensity of different sources to form THMs, although it appears that Delta island drainage is somewhat less reactive than tributary sources.