Natural Organic Matter and Disinfectant Byproducts

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The relationship between natural organic matter and disinfection byproducts is important because two disinfection byproducts, total haloacetic acids and total trihalomethanes, are regulated by the EPA under the Safe Drinking Water Act. These disinfection byproducts are created when carbon in water comes into contact with the chlorine disinfectant that is required to remain as residual throughout a water utility's distribution system until the water comes out the tap. The carbon can be from natural sources, human activities, water treatment and the disinfection treatment process. In this chapter we will focus on that fraction of carbon from natural sources and additional inputs that may result from forest management.

The chapter will begin with an overview of natural organic matter in water, its various sources, how it is distinguished between particulate organic matter which is defined

as more than 45 microns in size, and dissolved organic matter, and its effects on the water treatment process. The next section will focus on the chemical characteristics of natural organic matter, how it is analyzed, the size and molecular structure of dissolved organic matter, and the characteristics of particulate organic matter. After this, we will provide an overview of forest management effects on natural organic matter based on the scientific literature review, specifically discussing forest harvesting, forest roads, and natural disturbances such as wildfire and bark beetle infestations. The fourth section will cover the effects of natural organic matter on potable water treatment. The chapter will conclude with an analysis of disinfection byproducts detections in finished water to provide a context to better understand the relationship between natural organic matter in source water and disinfection byproducts in finished, potable water.

7.1. Sources, classification and treatment issues

Natural organic matter is defined as nonliving organic molecules found in the environment in soil, sediments and water. Natural organic matter is a product of mostly plant but also animal tissue decay and plays a pivotal role in the carbon cycle (Nebbioso and Piccolo 2013). Living matter is mostly composed of well-defined molecules such as proteins, nucleic acids, lipids, sugars and cellulose. In contrast, natural organic matter is mostly composed of molecules of unknown structure. The deeper we look into natural organic matter, the more components we find, and therefore complexity increases to a level that entities such as humus, humin, humic acid or fulvic acids become general terms rather than some specific forms of organized matter (Schmidt et al. 2011; Marín-Spiotta et al. 2014). The challenges associated with natural organic matter have been extensively researched because of its ecological and geochemical importance and influences on pollutant fate and transport in the environment.

Key considerations for drinking water providers are identifying sources of, and reducing the quantity of, natural organic matter that arrives at their raw water intakes. Prior to the early 1970s, treatment of natural organic matter in raw water focused on aesthetic issues such as color. Then research demonstrated that natural organic matter is a precursor constituent in the formation of hazardous disinfection byproducts. Natural organic matter from forest detritus is a major precursor to disinfection byproducts in drinking water sources (Bhardwaj 2006). Thus, forest management activities that influence the quantity and mobility of this source of natural organic matter in source waters can influence the potential for disinfection byproducts to form during water treatment (Majidzadeh et al. 2019). In addition, expanded understanding of linkages between natural organic matter and disinfection byproducts continues to spur changes in drinking water treatment and regulation (O'Melia 2006).

Control of environmental processes defining the natural organic matter transformation is achievable if knowledge about its molecular composition is available (Piccolo 2012). Molecular characterization of natural organic matter is a primary research objective in environmental and ecological chemistry (Nebbioso and Piccolo 2011). Recent developments in material sciences and the IT industry, such as nuclear magnetic resonance spectroscopy, or X-ray spectroscopic methods, allow detection and characterization of single organic compounds and, sometimes, homogeneous mixtures. However, because of the heterogeneous composition of natural organic matter, its description is still a challenge.

Natural organic matter in water is either formed in a water body, when it is called *autochthonous*, or is formed outside of the water body then transported into it when it is called *allochthonous* (Wershaw et al. 2005). For a particular water body, the composition

of allochthonous natural organic matter depends on the composition of the living matter compounds from which it originates, and on the natural diagenetic processes (physical and chemical changes that alter the characteristics of sediment after deposition) that alter the composition of the mixture of precursors (Wershaw 2004). As plant and animal tissue degrade in natural systems, soluble organic compounds are leached. These organic compounds are the source of the natural organic matter. Intuitively, the chemical composition of natural organic matter should reflect the composition of the plant and animal tissues from which it is derived (Leenheer et al. 2003; Wershaw et al. 2003; Leenheer et al. 2004). Autochthonous natural organic matter is generally formed by microorganisms living in a water body. However, diagenetic processes in aquifers can also alter the composition of natural organic matter. The most common diagenetic process impacting natural organic matter composition is sorption occurring on mineral surfaces and microbial degradation (Wershaw et al. 2005). Not surprisingly, Wershaw et al. (1995; 1996a; 1996b) found that organic acids in natural organic matter are strongly adsorbed by alumina (aluminum oxide). Furthermore, the natural organic matter components forming complexes with alumina are preferentially adsorbed. Besides sorption of natural organic matter, the microorganisms metabolize plant-derived natural organic matter and produce new types of compounds; such as the colloidal fraction of natural organic matter from the Great Salt Lake (Leenheer et al. 2004).

Operationally, natural organic matter is separated in two components: *dissolved organic matter* and *particulate organic matter* (Thurman 1985). Because it is usually a fine colloidal suspension, dissolved organic matter cannot be regarded as a chemical solution. Dissolved organic matter and its composition are important in natural-water ecosystems because of the number of processes in which it becomes involved. The dissolved organic matter acts as a strong chelating agent for metals, thus affecting their solubility, transport and toxicity (Schnitzer and Khan 1972). Dissolved organic matter is fundamentally involved in the transport of organic pollutants (Carter and Suffet 1982), formation of colloidal particles (Tipping 1986), aqueous photochemical reactions (Zafiriou et al. 1984), nutrient cycling and availability (Sanderman and Kramer 2013; Carlson and Hansell 2015; Wymore et al. 2015), and pH-buffering (Oliver et al. 1983). Dissolved organic matter and particulate organic matter are also important sources of energy in river-water ecosystems (Fisher and Likens 1973).

Leenheer has developed a procedure for the fractionation and description of natural organic matter (Leenheer et al. 2000; Leenheer et al. 2004) into its dissolved organic matter and particulate organic matter components. The definition of dissolved organic matter in this case is any organic matter that passes through a 0.45-μm filter pore whereas the particulate organic matter does not (Figure 7-1). Dissolved organic matter is further distinguished according to polarity. Leenheer's procedure allows isolation and characterization of hydrophilic and colloidal fractions (Leenheer et al. 2000). The identification of hydrophilic and colloidal fractions is important because natural organic matter interacts with all chemical components of natural waters, which in turn alters the behavior of pollutants in surface and groundwater. For example, the solubilities of hydrophobic anthropogenic compounds (i.e., some pesticides) are enhanced by natural organic matter (Wershaw and Hayes 2001), and natural organic matter forms complexes with metal ions that affect the bioavailability and toxicity of the metals to living organisms (Karlsson et al. 2005). Other types of reactions, such as hydrolysis of anthropogenic compounds, are probably also affected by natural organic matter. The isolation and characterization of natural organic matter fractions are of particular importance because each fraction has a unique set of properties. Vignati et al. (2005) showed that the toxicity of contaminants in natural waters is altered by interactions with the colloidal fraction of natural organic matter.
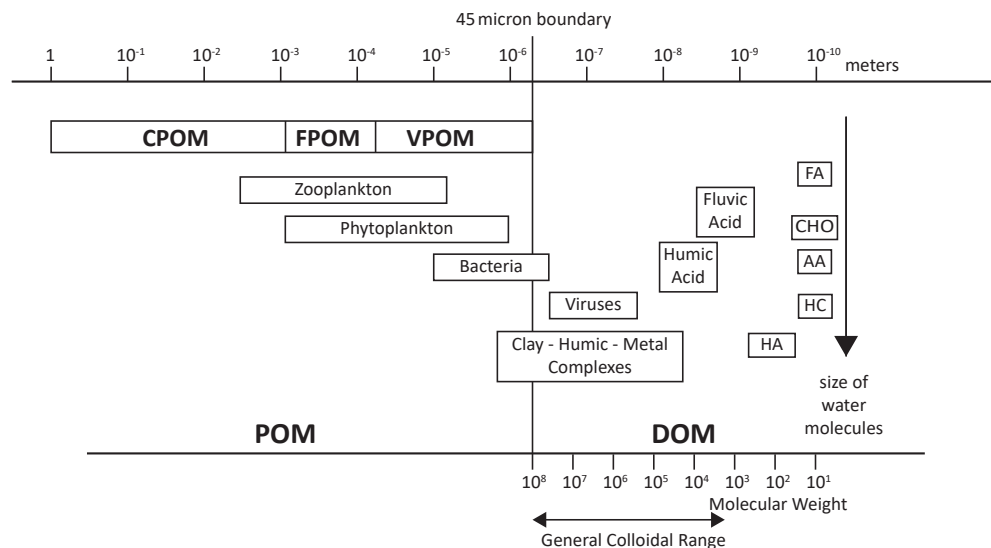
Source: Wershaw *et al*. (2005) AA, amino acids; CHO, carbohydrates; CPOM, coarse particulate organic matter; FA, fatty acids, FPOM, fine particulate organic matter; HA, hydrophilic acids; HC, hydrocarbon; VPOM, very fine particulate organic matter.
Figure 7-1. Size range of particulate organic matter (POM) and dissolved organic matter (DOM) and organic compounds in natural waters.

Terrestrial dissolved organic matter is the result of biological degradation and progressive concentration of organic compounds particularly resistant to degradation. Degradation of vascular plants supplies dissolved organic matter with approximately 10% proteins, 30–50 % carbohydrates (mainly cellulose), some lipids concentrated in the roots and leaf cuticles (Killops and Killops 2004), 15–25% lignin, and other biomacromolecules. Moreover, evidence suggests a correlation between environmental conditions and type of terrestrial dissolved organic matter derived from soil (Christ and David 1996; Nguyen et al. 2019).

Lignin, an important tracer for terrestrial organic matter, consists of multiple phenylpropanoid units that are linked to each other by ether and carbon–carbon bonds that confer chemical stability to lignin, which is assumed to resist extensive microbial degradation (Verma et al. 2009). Proteins and carbohydrates are, in contrast, biolabile compounds, because of the susceptibility of peptide and glycosidic bonds to hydrolysis by a variety of enzymes (Piontek et al. 2010).

There is increasing interest in dissolved organic matter from other sources, such as atmospheric aerosols (Birdwell and Valsaraj 2010). Discovery, characterization and quantitative assessment of such alternative sources is critical for understanding the relevance of dissolved organic matter in global carbon dynamics. This, however, is a challenging task because sampling and analysis of fog-water-derived dissolved organic matter is more difficult than for surface or groundwater. Interest in this subject is increasing. A thorough review of analytical methods for airborne dissolved organic matter aerosols was published by Duarte and Duarte (2011). These authors emphasized the environmental significance of this underestimated source of organic carbon and discussed the use of nuclear magnetic resonance, infrared and mass spectrometry methods for its analysis.

7.2. Chemical characteristics of natural organic matter

Natural organic matter is a complex matrix of various organic chemicals found primarily in surface waters and, to a lesser extent, in groundwater and fog. This section will

provide more background on the chemistry of both dissolved organic matter and particulate organic matter, starting with how dissolved organic matter is analyzed, then discussing its size, molecular architecture and the special case of chromophoric dissolved organic matter. Finally, particulate organic matter will be characterized, particularly its relationship with stream discharge.

7.2.1. Analytical methods for dissolved organic matter

Several challenges can complicate the analysis of natural organic matter, including the difficulty of complete dissolution, lack of proper molecular separation (Schijf and Zoll 2011), extreme heterogeneity of samples, mutual interference from different classes of compound and the tendency of association in complex superstructures (Piccolo 2001). Dissolved organic matter is no exception. However, the introduction of Fourier-transform ion cyclotron mass spectrometry has resulted in substantial analytical improvement (Kujawinski et al. 2002; Kim et al. 2003b). The impact of Fourier-transform ion cyclotron mass spectrometry on natural organic matter analysis has been substantial. The number of masses characterized in dissolved organic matter analysis has increased to such an extent that results can be efficiently reported only in simplified diagrams, such as plots sorting mass-to-change (m/z) ratios by homologous series (such as Kendrick plots), and by oxygen-to-carbon (O/C) and hydrogen-to-carbon (H/C) ratios (such as Van Krevelen diagram) (Kim et al. 2003a; Wu et al. 2004).

Two specific applications of Fourier-transform ion cyclotron mass spectometry are worth mentioning — detection of ions with H/C ratios, which imply a large number of double bond equivalents and thus restricts possible structures to condensed aromatic rings; and ions with heteroatoms, such as nitrogen.

Mass spectrometry methods have become conventional for dissolved organic matter analysis because dissolved organic molecules are readily ionized, especially in negative-ion mode. However, many problems remain unsolved. First, nonionizable compounds cannot be characterized by mass spectrometry. Second, ionization of terrestrial humic substances (HS) and dissolved organic matter is a complex phenomenon prone to irreproducible results because of molecular interferences that result from complex heterogeneous, multi-molecule (called "supramolecular") associations (Peuravuori et al. 2007; Nebbioso et al. 2010; Wickramasekara et al. 2012). These limitations prevent reliance on mass spectrometry methods alone to achieve structural identification of dissolved organic matter molecules.

Nuclear magnetic resonance spectroscopy has become fundamental in complementing dissolved organic matter characterization because ionization is not required for the nuclear magnetic resonance excitation. Both solution and solid-state nuclear magnetic resonance spectroscopy are well established tools in the environmental sciences (Abdulla et al. 2010). Molecular structural information has been obtained from conventional mono-, bi-, and tri-dimensional nuclear magnetic resonance spectra (Simpson et al. 2003), and information about molecular diffusion properties and stacking arrangements of organic matter is obtained by use of diffusion ordered spectroscopy (Šmejkalová and Piccolo 2008).

7.2.2. Size and molecular architecture of dissolved organic matter

A significant amount of fresh water dissolved organic matter is derived from terrestrial soil organic matter that underwent specific transformations that increased its affinity for an aqueous environment. Soil organic matter is traditionally and operationally divided in three categories — fulvic acids, humic acids and humin — according to their

solubility in acids and alkali. These are generally understood to be aggregations of numerous heterogeneous molecules of relatively small molecular mass held together by weak non-covalent bonds that don't involve sharing electrons. There is experimental evidence to show that dissolved organic matter is also arranged in similar supramolecular associations (Peuravuori et al. 2007).

The composition of fresh water dissolved organic matter is believed to depend on the transformation of plant and decomposed animal compounds into humic-like substances. Investigation of river and lake dissolved organic matter composition supports the hypothesis of plant genesis. In particular, nuclear magnetic resonance spectroscopy using two-dimensional, long-range correlation techniques has enabled characterization of compounds directly related to decay of terpenes — such as carboxyl-rich alicyclic molecules and material derived from linear terpenoids — is consistent with previous dissolved organic matter literature (Leenheer et al. 2003). The same nuclear magnetic resonance techniques also enabled detection of hexopolysaccharides and aromatic structures, possibly of lignin origin.

Chemical properties of compounds are bound to affect their distribution in water. Lignins are regarded as refractory substances, i.e., those resistant to decomposition by heat, pressure, or chemical action. In fact, lignins contribution to total dissolved organic matter increases along riverine paths, owing to slower mineralization, and was found in the greatest concentration in oceans. In contrast, the contribution of lipids is expected to be smaller because of their limited aqueous solubility; they are nevertheless found in lacustrine dissolved organic matter. This suggests that the supramolecular structure of dissolved organic matter enhances the solubility of specific hydrophobic molecules by forming complex associations with them. The dynamics of hydrophobic compounds in natural bodies are complex, because they are also important components of particulate organic matter. Although it is well established that hydrophobic organic matter is an abundant component of particulate organic matter and sedimentary matter, it is not yet clear whether hydrophobic dissolved organic matter and particulate organic matter are related to each other.

Because of the further complexity introduced by the tendency of dissolved organic matter molecules in solution to associate, assessment of the size of dissolved organic matter particles is not straightforward. Interestingly, whereas mass spectrometry of dissolved organic matter indicates molecular masses lower than 1,000 Daltons (Daltons are defined as 1/12th the mass of an unbound carbon atom) for most compounds, size-exclusion chromatography (SEC) profiles of the same sample suggests a much larger hydrodynamic volume. This discrepancy confirms that single molecules are prone to spontaneous association, but more evidence should be gathered on how this structure is organized.

Nebbioso and Piccolo (2013) argue that a plausible structure for fresh water dissolved organic matter is an aggregation of spontaneous self-associated superstructures formed by plant-derived products of natural decay, such as lipids, amino sugars, sugars, terpene derivatives, aromatic condensed structures, and lignin-derived compounds.

7.2.3. Chromophoric dissolved organic matter

Chromophoric dissolved organic matter is the light absorbing fraction of dissolved organic carbon (Rochelle-Newall and Fisher 2002). Interaction with solar radiation is a fundamental property of fresh water dissolved organic matter and is very relevant in freshwater environmental interactions. The mechanism of formation of chromophoric dissolved organic matter (CDOM) is still debated, but experimental evidence over

the last decade suggests that organic matter derived from phytoplankton, initially colorless, is processed by microbial flora into fluorescent dissolved organic matter. In fact, CDOM isolated after incubation of algae was found to grow concomitantly with microbial mass (Rochelle-Newall and Fisher 2002). Further evidence of the involvement of phytoplankton in the formation of lacustrine dissolved organic matter came from quantitative assessment of average and daily rates of in-situ production (Zhang et al. 2009). It has also recently been reported that fluorescence absorption peaks for humic and fulvic acids increased proportionally with the amount of dissolved organic matter. These acids are probably formed under terrestrial conditions and then transported in natural water bodies, thereby affecting fluorescence response (DePalma et al. 2011). The different chemical composition of autochthonous and humic dissolved organic matter in fresh water necessitated more systematic description. Hence, the humification index and the index of recent autochthonous contribution were created (Huguet et al. 2009).

The chemical origin of the colloidal properties of CDOM have also been investigated by flow-field flow fractionation (Stolpe et al. 2010), assuming differentiation between humic and/or fulvic-like and protein-like compounds. Whereas the origin of the latter was attributed to fresh-water autochthonous life, the sources of the former materials are believed to be terrestrial. Furthermore, it seems there is a strict correlation between the size fraction and the composition of the colloidal phase, with protein-like materials occurring primarily in the smaller size fraction and humic-type materials in the larger (Boehme and Wells 2006).

7.2.4. Characterization of dissolved organic matter

The molecular composition of fresh water dissolved organic matter has been studied less than that of marine dissolved organic matter, probably owing to the greater effect of oceanic dissolved organic matter on the geochemical carbon balance. Nevertheless, several studies have tried to remedy this and characterize fresh water dissolved organic matter substances in detail. The nuclear magnetic resonance spectroscopy experiment of Lam et al. (2007) performed on lacustrine dissolved organic matter showed the potential of this technique in recognizing and quantifying functional groups even in such a complex dissolved organic matter system. Lam et al. (2007) succeeded in differentiating aliphatic, carbohydrate, aromatic, and carboxyl-rich alicyclic molecules as well as characterizing specific regions assignable to well-known organic species. They also differentiated terpene-derived carboxyl-rich alicyclic molecules from the material derived from linear terpenoids; therefore, allowing further analysis of terpene metabolism in dissolved organic matter. However, the conventional technique for molecular investigation of dissolved organic matter is, again, FT-ICR MS (Fourier Transform – Ion Cyclotron Resonance Mass Spectrometry), because of its resolving power, which is capable of revealing hundreds of empirical formulae and furnishing plausible molecular structures for each unknown compound.

7.2.5. Characteristics of particulate organic matter

To understand the movement of particulate organic matter from small mountainous river systems to the ocean, several studies were focused on the concentration and composition of suspended particles from rivers draining into the Pacific Ocean (Hood et al. 2006; Hatten et al. 2012; Goñi et al. 2013). The studies investigated watersheds covered a wide range of sizes, from less than 1 km^2 (Hood et al. 2006) to 10,000 km^2 (Goñi et al. 2013) with a discharge rates from 42 m^3/s to 208 m^3/s and variability from 65 m^3/s to 517 m^3/s, respectively. Even in these differently-sized basins the findings were similar, that "concentrations of all measured constituents in both rivers increased as a function of discharge, resulting in their export being dominated by short-lived,
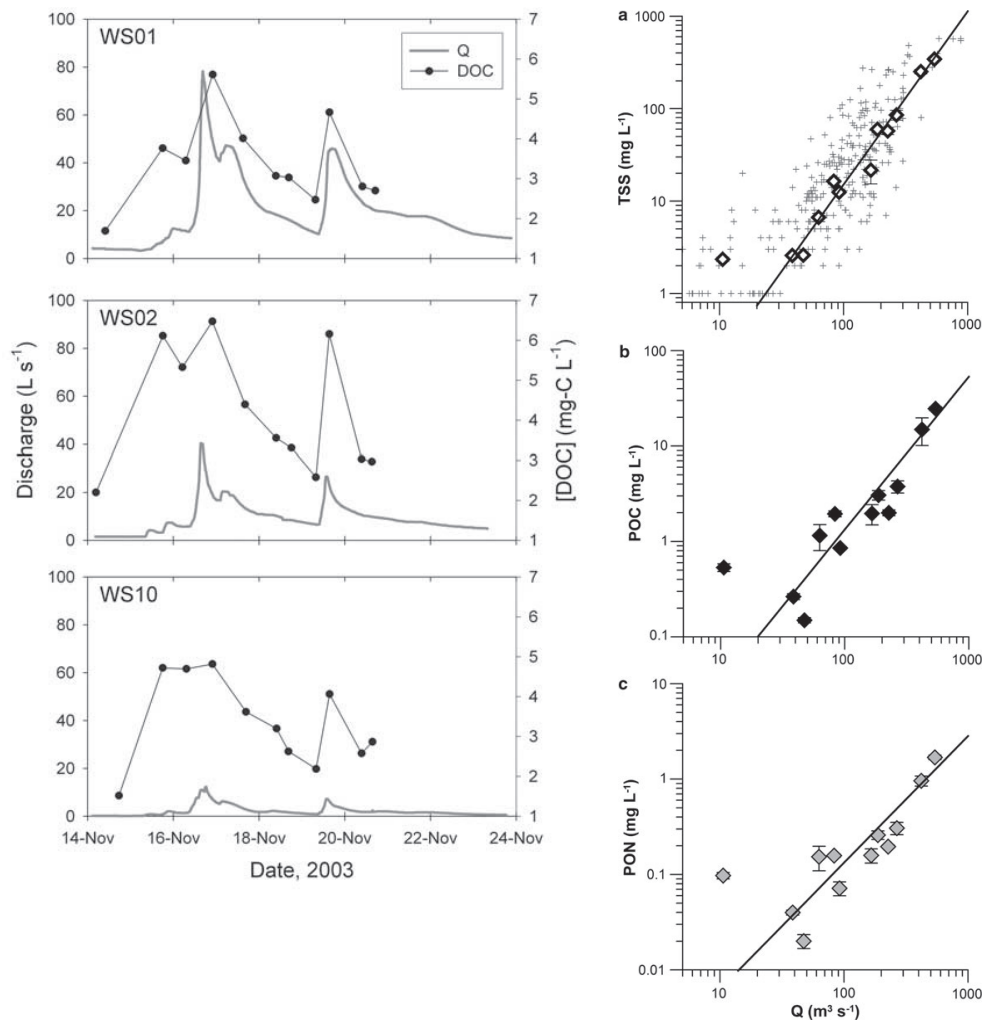
Figure 7-2. Time series of fluorescence index (FI), dissolved organic carbon concentrations and discharge in (A) watershed 1, (B) watershed 2 and (C) watershed 10, as presented by Hood et al. (2006) and the concentrations of a total suspended sediment (TSS), (B) total particulate organic carbon (POC) and (C) total particulate organic nitrogen (PON) plotted versus discharge (Q, m3 s–1) from the study Hatten et al. (2012).

wintertime high-discharge events" (Goñi et al. 2013). The same pattern was observed in Figure 7-2 for three small watersheds from the H.J. Andrews Long-Term Ecological Research (Hood et al. 2006).

Hatten et al. (2012) found significant differences in the particle compositions collected at low and high discharges, even though the watershed studied had similar ^{14}C ages with other small mountainous river systems. The low flows contained primarily organic detritus from non-vegetation sources (e.g., algal cells) while particles with vegetation and soil-derived particulate organic matter dominated the high flows. Biomarker compositions indicate that a significant portion of the particulate organic matter originated from areas affected by shallow landslides and riparian zones, which could be caused by the steep hillslopes in combination with high net primary production and relatively thick soils. According to Hood et al. (2006), during storms the dissolved organic carbon gained more humic material, which increased between 9 and 22 % in the study watersheds. The humic content of dissolved organic carbon decreased after the storm but was still elevated compared with the pre-storm samples.

Similar to Hood et al. (2006), Goñi et al. (2013) found that concentration of all constituents increased with discharge, indicating that mobilized materials comes from the watershed exhibiting shallow landslides. The composition of the discharge, namely the lignin phenols and cutin acids, suggest the source was conifer-dominated forest vegetation but with significant inputs of nonwoody angiosperms. The results support previous findings that areas manifesting frequent landslides are commonly covered by a mixture of gymnosperms (e.g., Douglas-fir and hemlock) and angiosperms (bigleaf maple, red alder, vine maple) (Roering et al. 2003). Based on their dual carbon isotope signatures (radiocarbon Δ^{14}C and stable carbon isotope δ^{13}C), the biogenic particulate organic matter seems to have a mean residence time of a few hundred years that characterizes the transit times of mobilized silts and clays from headwater valleys. It is possible that most of the particulate organic matter transported during the high-discharge events of 2007 - 2009 from the Umpqua watershed came from soils mobilized during shallow landslides, as there was no evidence to support significant amount of materials from deeper soils and/or bedrock.

7.3. Forest management effects on natural organic matter

The present review used more than 100 studies regarding natural organic matter, out of which 30 were pertinent to Oregon. The studies are either observational, which basically test some hypotheses, or modeling, which aim to predict stream behavior following various agents of change, natural or human triggered. The papers of Nieminen et al. (2017) and Leenheer (2009) are notable because they are review studies, with the limitation that the former is focused on the Scandinavian peninsula and the latter is addressed to researchers. Nevertheless, Leenheer (2009) sets the stage for natural organic matter study, by stating that "obtaining pure natural organic matter compounds that can be identified by conventional analyses is not yet possible, and the most homogeneous of natural organic matter fractions still contain hundreds to thousands of compounds." He goes even further, by saying that "natural organic matter structures derived from analytical data are models of average data sets, and these models are only approximations." While some studies aimed at understanding the dynamics of natural organic matter in relatively undisturbed forests, understood as reduced active forest management in the last 40 years (Lee and Lajtha 2016), other were focused on the impact of natural events on natural organic matter, such as fire (Abdelnour et al. 2013; Wang et al. 2015a, 2015b, 2016) or bark beetle (Kraus et al. 2010; Beggs and Summers 2011; Brouillard et al. 2016). Multiple studies were concentrated on impact of human

activities on natural organic matter, particularly forest harvesting (Nieminen et al. 2017), but only one was carried out in the Pacific Northwest in the last two decades (Kelliher et al. 2004). Another Oregon study, a reconnaissance study of the Clackamas River by the U.S. Geological Survey (Carpenter et al. 2013), evaluated sources of dissolved organic carbon and disinfection by-product precursors from different land uses within the watershed; additionally, they evaluated treatment efficacy to remove these constituents. An interesting series of three papers was dedicated to streams meandering within Fanno Creek in Washington County, Oregon, an urban watershed (Goldman et al. 2014; Keith et al. 2014; Sobieszczyk et al. 2014). The modeling studies were focused either on dissolved organic carbon and total mercury concentrations in small watersheds following clearcutting (Zhang et al. 2016) or on the effects of forest harvest on catchment carbon and nitrogen dynamics (Abdelnour et al. 2013).

7.3.1. Timber harvesting

The impact of forest management on dissolved organic matter was studied by Lee and Lajtha (2016) using the parallel factor analysis (PARAFAC) model of Stedmon and Bro (2008). They found that the proportion of protein-like dissolved organic matter — which is inversely related to dissolved organic carbon — increases during low-flow, whereas for shallow subsurface flow it decreases. Their study confirmed the importance of the antecedent soil moisture on dissolved organic carbon, and consequently on dissolved organic matter (van Verseveld et al. 2009). Lee and Lajtha (2016) pointed towards a relatively reduced dissolved organic matter source from microbial-processes. They predicted that basins on which younger stands are growing would have larger contributions of protein-like and microbial-like components in stream water than basins with old growth because it seems that dissolved organic carbon still has relatively lower values in streams from harvested watersheds even after a half century (Lajtha and Jones 2018). They argue that the reason for reduced dissolved organic carbon, and consequently dissolved organic matter, is the reduced amount of coarse woody debris, which was diminished during the harvesting and regeneration process by site preparation, slash removal, burning or both burning and slash removal. Their inference is supported by local evidence from the H.J. Andrews Experimental Forest as well as by other studies carried out in the Hubbard Brook Experimental Forest in New Hampshire (Cawley et al. 2014), and in the Coweeta Hydrologic Laboratory in North Carolina (Yamashita et al. 2011). Their main finding is that the impact of forest harvest is long-lasting; many decades after harvesting, the metabolism of dissolved organic matter is still being affected. One can argue that the complexity of the hydrological systems is another factor responsible for a change in dissolved organic matter concentrations even after 50 years. The system followed another path after being triggered by an event(s) — such as harvesting, wind throw or fire — that significantly altered the species composition (Prigogine 1997; Sprott 2003; Phillips 2004; Freire and DaCamara 2019). From the nonlinear perspective, it can be argued that any change would position the watershed behavior on a different dissolved organic matter concentration trajectory . Therefore, changes in dissolved organic matter would have occurred with or without harvesting.

An excellent review of the effects of forest harvest on natural organic matter (Nieminen et al. (2017) focused on peatlands. Researchers argued that soil characteristics contribute to nutrient exports following harvesting, but the contribution of soil characteristics to the export of the other nutrients and dissolved organic carbon from harvested peatland forests is not necessarily well documented. The studies — focused on sediment reduction and nutrient exports from drained peatland forests — have assessed either the impacts of sedimentation ponds (Joensuu et al. 1999) or natural and restored wetland buffers (Vikman et al. 2010; O'Driscoll et al. 2014). Researchers found that sedimentation ponds

are effective only in retaining the exports of particles, whereas wetland buffers not only retain particles but also decrease the export of dissolved elements (Vikman et al. 2010; O'Driscoll et al. 2014).

Nieminen et al. (2017) found that the main factors affecting the export of elements after forest harvesting in drained peat wetlands are soil characteristics, nutrient uptake by vegetation, management of forest residues, and drainage and site preparation. Soil characteristics, particularly phosphorus (P) adsorption capacity and iron (Fe) content, may have a strong impact on the exports of dissolved organic carbon for high water table conditions following harvesting. Reduction of Fe in anoxic soils reduces the number of protons. This increases soil water pH, which results in a breakup of Radical–Ferric Iron–Radical associations, leading to an increase in electronegativity of the organic complexes (Grybos et al. 2009). In these conditions, the exports of Fe and dissolved organic carbon may increase for soils with high Fe content (Nieminen et al. 2015; Kaila et al. 2016). Nitrogen (N) exports after forest harvest seem to be higher from minerotrophic sites — soils and vegetation getting their water from streams or springs flowing over or through rocks —() than from ombrotrophic sites where rainfall is the predominate source of water(Kaila et al. 2015; Nieminen 2003). A possible reason is that organic substances contain organic N, which increase mobilization and leaching under anoxic conditions in Fe-rich minerotrophic peats.

In the last two decades, the impact of forest harvest on natural organic matter has been studied using complex models, such as the Visualizing Ecosystems for Land Management Assessments, or VELMA (Abdelnour et al. 2013). VELMA is a spatially distributed ecohydrology model that simulates changes in soil water infiltration and redistribution, evapotranspiration, surface and subsurface runoff, carbon and nitrogen cycling in plants and soils, and the transport of dissolved carbon and nitrogen into streams. The model combines watershed level and soil column level frameworks. The multilayered soil column, which consists of n soil layers, is the fundamental hydrologic and ecological unit. The soil column framework is placed within the catchment framework using catchment topography, which is gridded into pixels, each pixel consisting of one coupled soil column. The neighboring soil columns communicate through downslope lateral transport of water and nutrients. The model computes the surface and subsurface runoff responsible for the lateral transport and feeds the uphill soil column to the surrounding downslope soil columns. Nutrients transported downslope from one soil column to another soil column are processed through submodels that ensure the discharge of water and nutrients into the stream from all soil columns.

The watershed framework contains a submodel for lateral transport of nutrients, the equations for which are detailed in Abdelnour et al. (2011). The model uses climatic data for the watershed 10 of the H.J. Andrews Long-Term Ecological Research from Jan. 1, 1969 to December 31, 2008. Input data for the model are daily temperature; precipitation; atmospheric nitrogen deposition; daily streamflow; and NO3, NH4, dissolved organic nitrogen (DON), and dissolved organic carbon (DOC) losses to the stream, overlaid on a 30-meter resolution digital terrain model. Results supplied by the model theorize that losses of dissolved nutrients in the pre-harvest old-growth forest were generally low and contained primarily organic nitrogen and carbon. After harvest, however, the carbon and nitrogen losses from the terrestrial system to the stream and atmosphere increased, following the reduced plant nitrogen uptake, increased soil organic matter decomposition and high soil moisture. Finally, the modeling exercise suggests that the rate of forest regrowth following harvest was lower than that after fire because post-clear-cut stocks and turnover of detritus nitrogen were substantially lower than after fire.
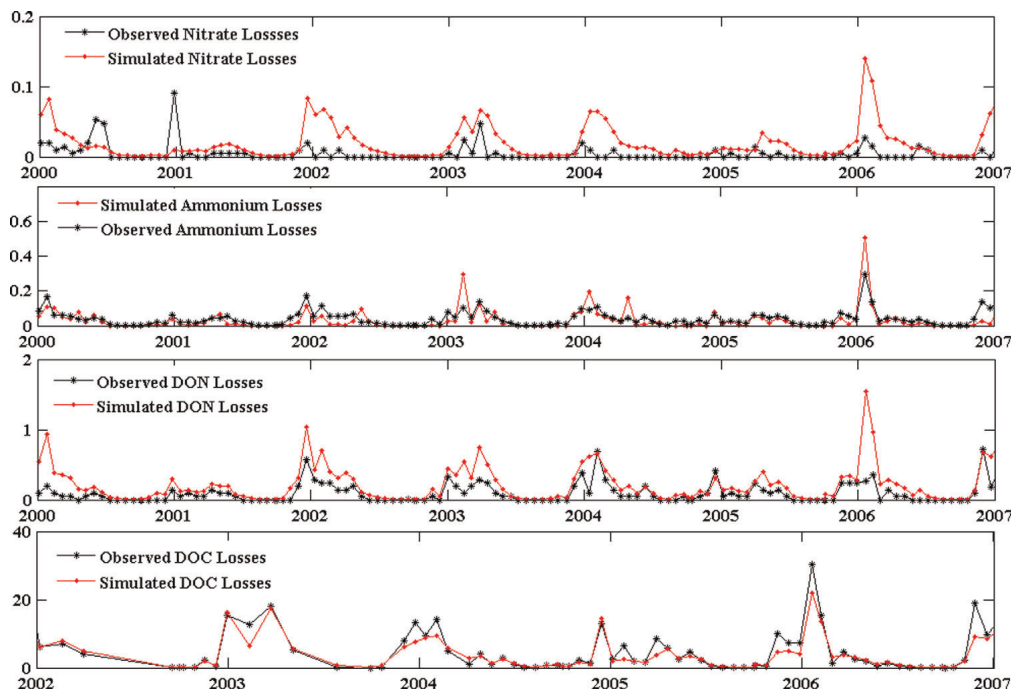
Figure 7.3. The simulated (red dots) versus observed (black dots) NO_3 (mg N/m²), NH_4 (mg N/m²), DON (mg N/m²) and dissolved organic carbon losses (mg C/m²) to the stream after the 1975 clearcut of WS10 in the H.J. Andrews, according to Abdelnour et al. (2013). The x axis represents the selected data between 2000 and 2007 for NO_3, NH4 and DON losses and between 2002 and 2007 for dissolved organic carbon losses, while the y axis represents the amount of daily losses that reaches the stream.

The soil column framework includes four submodels: soil temperature model, soil plant model, nitrification and denitrification (Abdelnour et al. 2013). The soil plant model is the only model that combines multiple submodels, namely atmospheric nitrogen deposition, Michaelis-Menten enzyme kinetics, plant mortality, plant uptake, water stress function, biomass root function, vertical transport of nutrients and soil organic carbon decomposition.

A similar, process-based model was used by Zhang et al. (2016), to project the impact of forest management (clearcut, regeneration and growth) on dissolved organic carbon and total mercury export from the forest-dominated Pine Marten Brook and Moose Pit Brook watersheds of Kejimkujik National Park in Nova Scotia, Canada. Zhang et al. (2016) suggest that during a forest rotation, dissolved organic carbon and total mercury concentrations decrease after clearcut to a minimum at approximately 15 years after regeneration and then increase with age. They found that large debris pools left on-site after clearcutting can provide significant pulses in dissolved organic carbon and within-watershed total mercury export during the first two to three years after harvest. The model suggests a sinusoidal variation of the dissolved organic carbon concentration and total mercury concentration, with a maximum in autumn followed by a minimum in the spring, another maximum in June and the second minimum before leaf fall. The field data used to calibrate the model indicated that conifer species and wetland-dominated watersheds are prone to transferring more dissolved organic carbon and total mercury to aquatic ecosystems than deciduous and dryland-dominated watersheds.
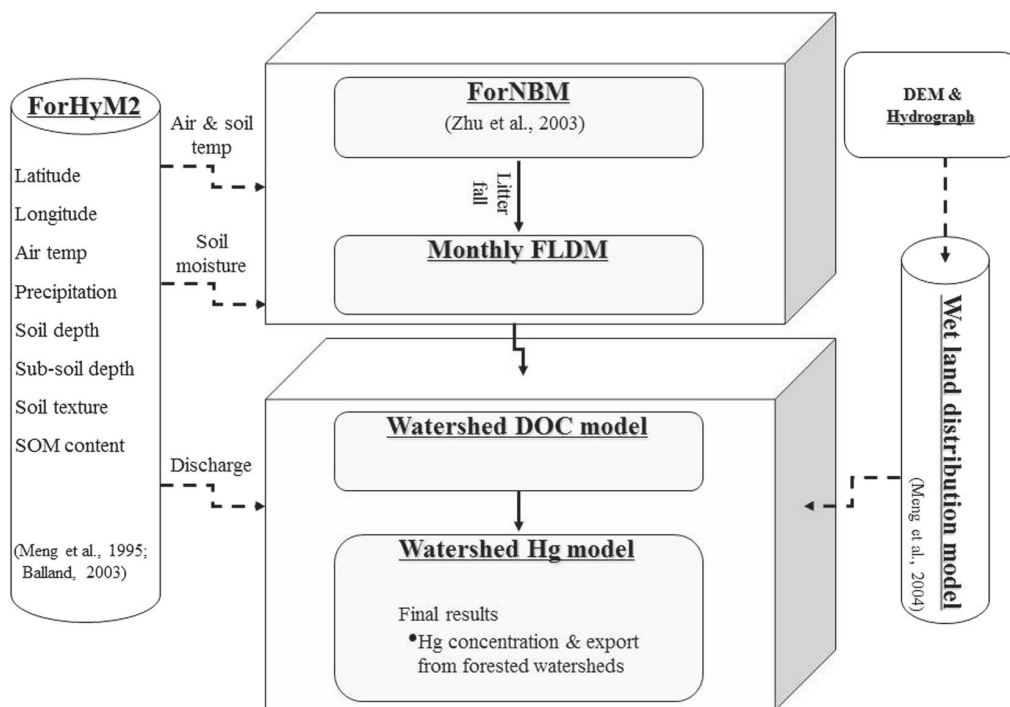
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Figure 7-4. Structure of the in-stream dissolved organic carbon - and Hg-concentration model according to Zhang *et al.* (2016). ForHyM2 is used to simulate variation in soil temperature and moisture and stream discharge. ForNBM is used to simulate forest growth and litter production. Monthly FLDM is used to simulate monthly litter decomposition. Output from FLDM is used as input to the dissolved organic carbon production and export model component.

7.3.2. Forest roads

Based on the study of Yanai et al. (2003), Abdelnour et al. (2013) argued that it is difficult to separate the effects on natural organic matter of plant biomass removal from the effects of roads. Typically, models are used to reduce impacts resulting from the failure to differentiate biomass removals from road effects.(Yanai et al. 2003; Abdelnour et al. 2013; Zhang et al. 2016). To model such complex systems, researchers rarely develop ad-hoc models. They most likely use either existing models or build one for preexisting modules that fit the objectives, data availability and methodology (Yanai et al. 2003; Zhang et al. 2016). As such, in the last 20 years only few papers were dedicated to the relationship between natural organic matter and forest roads (Deljouei et al. 2015; Abdi et al. 2018). The only study since 2000 pertinent to Pacific Northwest that we found is Abdi et al. (2018), which assessed the relationship between the amount of organic matter and the behavior of forest soil as road material, which is not the focus of this review. Evidence for the Pacific Northwest area found that the main export of natural organic matter and disinfection byproducts is triggered by the first major rain event occurring in the fall (Kraus et al. 2010).

7.3.3. Natural disturbances: wildfire and beetles

Whereas forest roads' impact on natural organic matter is difficult to quantify and separate from other sources, the story is different for natural catastrophic events, specifically wildfire and mountain pine beetles, on which there has been a significant amount of research (Beggs and Summers 2011; Wang et al. 2015a, 2015b, 2016; Brouillard et al. 2016).

Wildfires are increasing in frequency and severity in the United States, which is likely altering the chemistry and quantity of natural organic matter and disinfection byproducts traveling outside forested watersheds. Wang et al. (2015a) claim that we have mostly speculative understanding on the effects of the fire triangle (heat, oxygen and fuel) on dissolved organic matter alteration. A similar statement was made by Wang et al. (2015b), who assert that the effects of wildfire on drinking water quality are limited, especially in terms of natural organic matter and natural organic matter-associated formation of disinfection byproducts. Considering that forest floor is a major source of terrestrial dissolved organic matter, they investigated characteristics and disinfection byproducts formation of water extractable organic matter from unburned detritus and two types of burned detritus (i.e., black ash, suggesting moderate fire severity, and white ash, suggesting high fire severity) associated with the 2013 Rim Fire in California. A similar laboratory study aiming to answer analogous questions on dissolved organic matter and disinfection byproducts was carried out using detritus from *Pinus ponderosa* (ponderosa pine) and *Abies concolor* (white fir). Spectroscopic results suggest that burned-detritus extracts had lower molecular weight and divergent aromaticity depending on oxygen availability. The laboratory findings show that disinfection byproducts' precursors in fire-affected forest detritus are highly dependent on temperature and oxygen availability. The 2013 Rim Fire revealed that wildfire consumed a large portion of organic matter from the detritus layer, which led to lower yields of water extractable organic carbon and organic nitrogen. Therefore, the wildfire triggers an overall reduction in water extractable terrestrial precursors of disinfection byproducts in forest detritus (Wang et al. 2015b).

In contrast to wildfires, 15 years of bark beetle infestation in the northern Rocky Mountains of Colorado had a significant impact on drinking water quality as a result of increased organic carbon release and hydrologic shifts induced by the tree dieback. Brouillard et al. (2016) analyzed 10 years of municipal data, from 2004 to 2014, across six water treatment facilities which cover the extent of beetle impact. The study revealed a significant increasing trend in total organic carbon and total trihalomethane production within the beetle-infested watersheds, while no or insignificant trends were found in watersheds with lower impact. Alarmingly, the total trihalomethane concentration trend in the watersheds that experienced high bark beetle impact exceeded regulatory maximum contaminant levels during 2013 and 2014.

Brouillard et al. (2016) found that about 50% of the forest affected by beetles was the threshold for enhanced needle drop for the high impact watersheds, and between 25% and 30% areal infestation for moderate impact watersheds. They found that surface water from high impact watersheds exhibited significantly higher total organic carbon, aromatic signatures, and disinfection byproducts formation than watersheds with lower infestation levels. Furthermore, the spectroscopic analyses of surface water suggest that heightened disinfection byproducts precursor levels are a function of both total organic carbon and aromatic character, and the areal infestation in the watershed. The relationship between total organic carbon and aromatic character was heightened during precipitation and runoff events. In these situations, the altered hydrologic flow paths resulting from tree mortality seem to mobilize organic carbon and elevate disinfection byproducts formation potential for months after runoff. Brouillard et al. (2016) found that water quality is impacted nearly one decade after bark beetle infestation, but significant increases in total organic carbon mobilization and disinfection byproducts precursors are limited to areas that experience massive tree mortality.
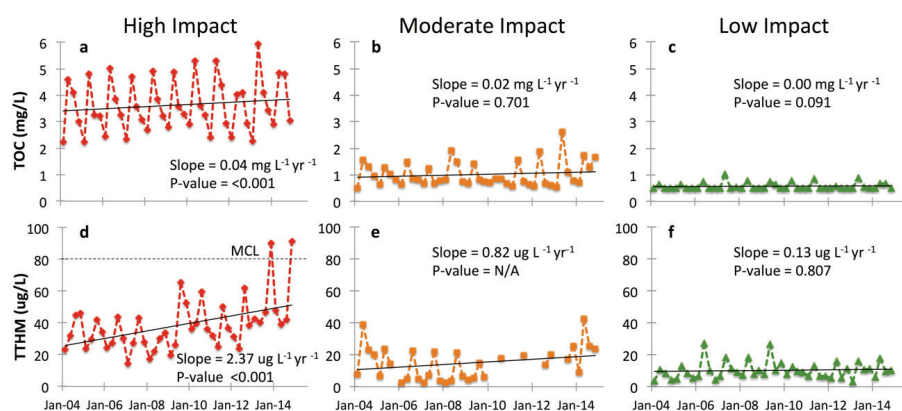
Figure 7-5. Analysis of compiled water quality data obtained from six water treatment facilities from Brouillard et al. (2016). The results shows an increasing trend in high-impact watersheds compared to lower impacted watersheds. Panels depict water quality data from 2004 to 2014 where a–c display binned total organic carbon (TOC) concentrations and d–f portray binned total trihalomethane (TTHM) concentrations in high- (red diamonds), moderate- (orange squares) and low-impact (green triangles) watersheds with a regulatory total trihalomethane maximum contaminant level (MCL) of 80 ppb.

7.4. Effects of natural organic matter on potable water treatment

Standard water treatment processes involving coagulation with alum and ACH typically remove dissolved organic carbon by 30% to 39%, depending upon the source concentrations, with preferential removal of higher molecular-weight, aromatic carbon (Carpenter et al. 2013). Powdered activated carbon (PAC) as a supplement to the coagulants further reduced dissolved organic carbon and disinfection by-product precursors by an additional 4% to 10% (Carpenter et al. 2013). Reduction is particularly effective for lower aromatic and lower molecular-weight substances that typically come from tributaries draining agricultural, rural residential, and urban areas in the watershed. The higher aromatic content water containing humic and fulvic acids from upper watershed, forested regions provided the bulk of the disinfection by-product precursors (Carpenter et al. 2013).

Ultrafiltration has been used to move large volumes of water through membrane pores, which are restrictive for dissolved organic matter but not for water molecules and small ions. It is a formidable desalting method that is also used to purify water from excessive dissolved organic matter content. Ultrafiltration is also affected by incomplete recovery of organic carbon, but to a lesser extent.

Reverse osmosis is an improvement of ultrafiltration, as it operates similarly by allowing water through membranes but restricting cut-off for dissolved organic matter. However, in reverse osmosis the solution is forced by a pressure gradient to flow against osmotic flow (hence reverse osmosis). Different and more restrictive membranes are used for reverse osmosis than for ultrafiltration, resulting in greater retention of ions in dissolved organic matter samples. Such retention consists mainly of ions derived from silicic acid (H_4SiO_4) and sulfuric acid (H_2SO_4). Development of methods such as reverse osmosis, coupled with electrodialysis and pulsed electrodialysis, was, in fact, intended to minimize these inorganic impurities. These processes are now rapidly becoming conventional for dissolved organic matter purification and are in constant development, optimization and standardization.

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7.5. Prevalence of standards exceedances

There are 63 chemicals that were found in samples of finished water that meet or exceed USEPA standards for "alerts" or "exceedance." The trigger value for alerts varies according to the chemical. In some cases, it is any presence. For the ones we're concerned with, an alert is issued if the concentration is greater than or equal to 50% of the maximum contaminant level. Our primary concern is the two disinfection byproducts, total haloacetic acids and total trihalomethanes, and thus it is useful to understand how frequent these two contaminants are compared to others sampled.

The data records show alerts or exceedances for these 63 chemicals, divided into eight categories: Inorganic chemicals, volatile organic chemicals, synthetic organic chemical, radiological agents, nitrate, nitrite, arsenic and asbestos. There were 5,813 "detections" of these 63 chemicals from 697 public water supplies over the nearly 20-year period. For two disinfection byproducts, haloacetic acid is the fourth most commonly detected (5.9%), while total trihalomethanes is the fifth most common (5.0%). In comparison, nitrate (nitrogen) is the most commonly detected contaminant (44.2%); arsenic is the second most common (16.3%); and tetrachloroethylene is the third (6.3%).

Based on an examination of the data, the disinfection byproducts are only found in water samples from the utilities' distribution system, and according to the incident reports, these samples are often taken at the end of long pipe runs. Most detections and exceedances of disinfection byproducts are from utilities that utilize surface water sources, including produced, purchased and groundwater under the influence of surface water. For haloacetic acid, it is 97%, and for total trihalomethanes it is 83%. If a disinfection byproduct is found, most often it exceeds the maximum contaminant level standard (89% for haloacetic acid; 93% for total trihalomethanes) rather than just the lower detection level that triggers an alert. Figure 7-6 shows the wide variation in the numbers of yearly detections from 2004 to 2019. The numbers range from a high of 80 for HAA5 in 2004 to a low of 8 for total trihalomethanes in 2017. On average, there are about 30 detections of total haloacetic acid statewide, and 25 of total trihalomethanes annually.
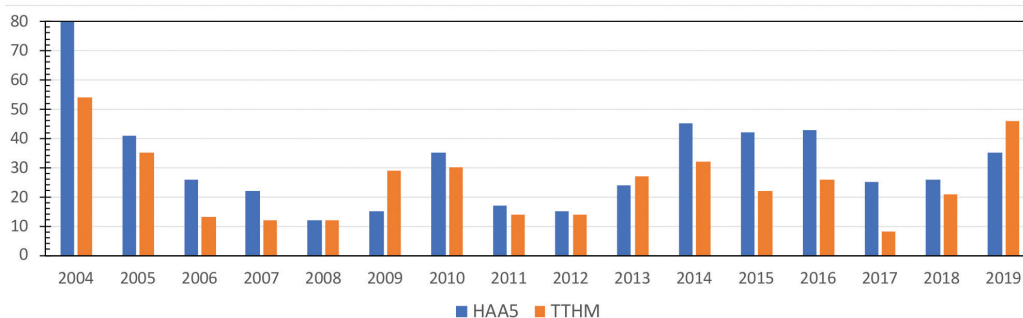

Figure 7-6. Yearly detections of total haloacetic acids (HAA5) and total trihalomethanes (TTHM).

One hundred-forty-two Oregon public water systems had detections of disinfection byproducts from 2002 through 2020. There are three general patterns in these detections. First, most of these public water systems (77%) have occasional and infrequent detections (i.e., less than one every two years). The second pattern is that a particular utility will have a cluster of detections before resolving the problem (i.e., detections in fewer than nine years from 2003–2019) but will have more than eight total detections. This pattern represents about 17%, or 24, of the utilities with detections. Finally, a small number of utilities have chronic detections year-in and year-out; there are
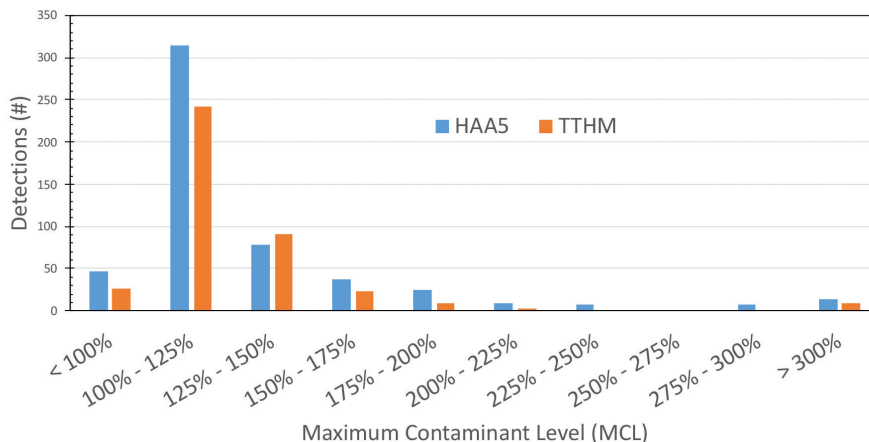
Figure 7-7. DBP detection sample concentrations compared to the maximum contaminant level (MCL).

seven utilities representing 5% of the utilities with detections, and less than 5% of all public water suppliers.

Most detections, and thus most disinfection byproducts exceedances, are within 125% of the maximum contaminant level (Figure 7-7). Most detections of haloacetic acid and total trihalomethanes exceed the maximum contaminant level threshold, 91% and 93%, respectively. Almost 60% of haloacetic acid and total trihalomethanes detections are within 125% of the maximum contaminant level, with the majority of the remainder within 150% of the maximum contaminant level, 15% and 23% respectively. There are relatively few detections that are over 200% of the maximum contaminant level, and the highest of these may be sampling errors.

The two regulated disinfection byproducts, total haloacetic acids and total trihalomethanes, are respectively the fourth- and fifth-most frequent contaminant alerts and exceedances in the Oregon Health Authority's database. Disinfection byproduct detections in finished drinking water show that in most cases the utility relies on surface water as their primary source. Most detections are isolated events, but 17% of water utilities have clusters of detections with absences in intervening years, while 5% have chronic, annual detections of disinfection byproducts in their water systems. Further, most exceedances are within 150% of the maximum contaminant level.

7.6. Summary and findings

The relationship between natural organic matter and disinfection byproducts is important because two disinfection byproducts — total haloacetic acids (HAA5) and total trihalomethanes (TTHM) — are regulated by the EPA under the Safe Drinking Water Act. These disinfection byproducts are created when carbon in water comes into contact with the chlorine disinfectant that is required to remain as residual throughout a water utility's distribution system until the water comes out the tap. The carbon can be from natural sources, can result from human activities, may be added during water treatment and may be formed through the disinfection process in the treatment plant.

The two regulated disinfection byproducts — total haloacetic acids and total trihalomethanes — are respectively the fourth- and fifth-most frequent contaminant alerts and exceedances in the Oregon Health Authority's database. Disinfection byproduct detections in finished drinking water show that in most cases the utility relies on surface water as its primary source, and these samples are often taken at the end of

long pipe runs. Most detections are isolated events, but a subset of water utilities (17%) have clusters of detections with absences in intervening years, while a smaller set (5%) have chronic, annual detections of disinfection byproducts in their water systems. Most exceedances are within 150% of the maximum contaminant level.

Today, natural organic matter is the raw water constituent that most often influences the design, operation and performance of water treatment systems. In addition to its role in the formation of disinfection byproducts, natural organic matter can overwhelm activated carbon beds used in water treatment and reduce their ability to remove organic micropollutants. Natural organic matter also contributes significantly to the fouling of membranes in all membrane technologies used in water treatment, and can promote microbial fouling and regrowth in water distribution systems.

Operationally, natural organic matter is separated in two components: dissolved organic matter and particulate organic matter. A significant amount of fresh water dissolved organic matter is derived from terrestrial soil organic matter that underwent specific transformations that increased its affinity for an aqueous environment. The composition of fresh water dissolved organic matter is believed to depend on the transformation of plant and decomposed animal compounds into humic-like substances. Freshwater dissolved organic matter is an aggregation of spontaneous self-associated superstructures formed by plant-derived products of natural decay, such as lipids, amino sugars, sugars, terpene derivatives, aromatic condensed structures and lignin-derived compounds.

Concentrations of constituents increase as a function of stream discharge, with their export being dominated by short-lived, wintertime high-discharge events. Low flows contain primarily organic detritus from nonvegetation sources (e.g., algal cells) while particles with vegetation and soil-derived particulate organic matter dominated the high flows.

- Modeling indicates that many decades after harvesting, the metabolism of dissolved organic matter is still being affected. This is because carbon and nitrogen losses from the terrestrial system to waterways and the atmosphere increase due to reduced plant nitrogen uptake, increased soil organic matter decomposition and high soil moisture.

- During and after harvesting, if slash is removed or burned, dissolved organic carbon and dissolved organic matter are reduced due to the diminished amount of coarse woody debris remaining.

- Evidence for the Pacific Northwest area indicates that the main export of natural organic matter and disinfection byproducts is triggered by the first major rain event occurring in the fall.

- Wildfires are increasing in frequency and severity in the United States, which is likely altering the chemistry and quantity of natural organic matter and disinfection byproducts traveling outside forested watersheds. Wildfires consume a large portion of organic matter from the detritus layer, which leads to lower yields of water extractable organic carbon and organic nitrogen. Therefore, wildfires appear to trigger an overall reduction in water extractable terrestrial disinfection byproducts precursor yield from detritus.

- The last 15 years of bark beetle infestation had a significant impact on water quality as a result of increased organic carbon release and hydrologic shifts induced by the tree dieback. Water quality is impacted nearly one decade after bark beetle

infestation, but significant increases in total organic carbon mobilization and disinfection byproducts precursors are limited to areas that experience massive tree mortality.

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