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1 **Natural organic matter-cations complexation and its impact on water** 2 **treatment: a critical review**

3
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11 **Abstract**

12 The quality and quantity of natural organic matter (NOM) has been observed to evolve which
13 poses challenges to water treatment facilities. Even though NOM may not be toxic itself, its
14 presence in water has aesthetic effects, enhances biological growth in distribution networks,
15 binds with pollutants and controls the bioavailability of trace metals. Even though NOM has
16 heterogeneous functional groups, the predominant ones are the carboxyl and the phenolic
17 groups, which have high affinities for metals depending on the pH. The properties of both the
18 NOM and the trace elements influence the binding kinetics and preferences. Ca²⁺ prefers to
19 bind with the carboxylic groups especially at a low pH while Zn²⁺ prefers the amine groups
20 though practically, most cations bind to several functions groups. The nature of the chemical
21 environment (neighboring ligands) the ligand finds itself equally influences its preference for a
22 cation. The presence of NOM, cations or a complex of NOM-cations may have significant
23 impact on the efficiency of water processes such as coagulation, adsorption, ion exchange resin
24 and membrane filtration. In coagulation, the complexation between the coagulant salts and
25 NOM helps to remove NOM from solution. This positive influence can further be enhanced by
26 the addition of Ca²⁺. A negative influence is however, observed in lime-softening method as
27 NOM complexes with Ca²⁺. A negative influence is also seen in membrane filtration where

28 divalent cations partially neutralize the carboxyl functional groups of NOM thereby reducing
29 the repulsion effect on NOM and increasing membrane fouling. The formation of disinfection
30 by-products could either be increased or reduced during chlorination, the speciation of products
31 formed is modified with generally the enhancement of haloacetic acid formation observed in
32 presence of metal cations. This current work, presents in details the interactions of cations and
33 NOM in the environment, the preference of cations for each functional group and the possible
34 competition between cations for binding sites, as well as the possible impacts of the presence
35 of cations, NOM, or their complex on water treatment processes.

36

37 **Keywords:** Natural organic matter, Cations, Ligands, water treatment, complexation

38

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60

61 **1. Introduction**

62 The presence of natural organic matter (NOM) in water bodies has recently been observed to
63 increase as well as vary significantly (Eikebrokk et al., 2004). High seasonal variability and
64 elevated concentrations of NOM would pose challenges to water treatment plants in terms of
65 operational optimization and proper process control (Sillanpää, 2015; Sillanpää et al., 2018).
66 Even though NOM may not be toxic itself, it has the tendency of changing both the chemical
67 and physical properties of the water. It may result in colour and odour of the water, influences
68 the concentrations of dissolved O, N, P, and S and serve as a carrier of toxic pollutants like
69 pesticides and radionuclides (Knauer et al., 2017; Santschi et al., 2017) . In addition, NOM
70 serves as both a source and sink for carbon, which may have an indirect climatic effect (Dore,
71 2005; Delpla et al., 2009; Hruška et al., 2009).

72 NOM refers to a complex mixture of different organic compounds that are present in fresh water
73 which is principally formed by the weathering or decay of living material (Stevenson, 1994;
74 Iskrenova-Tchoukova et al., 2010). The different chemical constituents of NOM do not make
75 it practically feasible to characterize it based on individual compounds. There even exists some
76 ambiguity on whether NOM is chemically a true macromolecular entity (Kononova, 1961;
77 LeBoeuf and Weber, 2000) or just an assembly of relatively small molecules held together by
78 relatively weak non-covalent interactions (primary electrostatic and hydrogen bonding) to form
79 a supramolecule (Kalinichev and Kirkpatrick, 2007). Notwithstanding NOM being a complex
80 mixture of organic compounds, there are fractions with distinct chemical formulae such as
81 carbohydrates, fats, waxes, alkanes, peptides, amino acids, proteins, lipids and organic acids.
82 The other fractions, with no distinct chemical formulae and unknown unique identity, are
83 referred to as humic substances. The non humic fractions are easily degraded while the humic
84 fraction, together with soil minerals, can persist for centuries (Pettit, 2004). The elemental

85 analysis of the different components of humic substances reveals that they are primarily
86 composed of carbon (55-57%), oxygen (34-36%), hydrogen (4-6%), nitrogen (0.9-3%), and
87 sulfur (0.4-1.8%) in complex carbon chains (Dixon et al., 1989; Rice and MacCarthy, 1991;
88 Pettit, 2004; Bravo et al., 2017). Very little is known about the nitrogen and sulfur containing
89 functional groups (Filella, 2008). Humic substances can be divided further into three classes
90 based on their solubility and molecular weight (MW). Humin (MW range of approximately
91 100,000 to 10,000,000) is insoluble in aqueous systems at all pH. Humic acid (mixture of weak
92 aliphatic and aromatic organic acids with MW range of approximately 10,000 to 100,000) is
93 soluble at pH >2 and fulvic acid (mixture of weak aliphatic and aromatic organic acids with
94 MW range of approximately 1,000 to 10,000) is soluble at all pH. Fulvic and humic acids are
95 ubiquitous in water systems, and constitute about 10–30% of dissolved NOM in seawater, 70–
96 90% dissolved NOM in wetland water, 40–90% of dissolved NOM in streams and about 50%
97 of dissolved NOM in lake waters, depending on hardness (Xue and Sigg, 1999; Thurman, 2012;
98 Lipczynska-Kochany, 2018a). This is because the presence of hardness cations apparently
99 suppresses the solubility of high molecular weight fulvic acids (Aiken and Malcolm 1987;
100 Breault et al., 1996).

101 NOM could also be defined by its origin, *i.e.* allochthonous or autochthonous. Allochthonous
102 NOM, on the one hand, refers to NOM that originates from a distant place. It may have been
103 transported to the present matrix by agents of erosion and are susceptible to degradation and
104 removal processes during its transport. Allochthonous NOM is typically derived from lignin-
105 containing plants, the degradation of which yields fulvic acids relatively rich in aromatic carbon
106 content and phenolic compounds but low in nitrogen content. Autochthonous NOM, on the
107 other hand, refers to NOM that is indigenous to the matrix and are often algal derived (Luider
108 et al., 2004). Aquatic algal derived NOM has a relatively high nitrogen content, low
109 concentration of aromatic carbon and phenolic compounds (Fabris et al., 2008).

110 NOM can further be classified based on its polarity and hydrophobicity (Sillanpää et al., 2015).
111 The hydrophobic (non-polar) fraction, which, generally constitutes a higher percentage of the
112 NOM fraction, consists of aromatic rings with conjugated double bonds and phenolic structures,
113 while the hydrophilic (polar) fraction is mainly made up of aliphatic carbons and nitrogenous
114 compounds like proteins, sugars and amino acids (Baghoth, 2012). Some functional groups
115 observed in NOM are the substituted alkyl carbons, unsaturated carbons, amides, carboxylic
116 groups, aldehydes and ketones, amino groups, alcohols and phosphate esters, sulfur (Torbjörn
117 et al., 2006; Mopper et al., 2007). Figure 1 gives a summarized scheme of the broad
118 characteristics of NOM.

119 Because of its high reactivity, NOM also controls the bioavailability and biogeochemical
120 cycling of trace elements in the environment (Xia et al., 1997). Considering the fact that it is
121 rare to find a metal un-complexed, 'naked', in the environment, metal-NOM complexation
122 occurs by metal binding to already existing ionized sites or by displacing a proton from its
123 position. This can be due to an increase in the electrostatic interaction between the deprotonated
124 functional groups and the cations as they are deprotonated at higher pH.

125 NOM and climate change affect each other; whereas NOM contributes to climate change
126 through the release of greenhouse gases, climate change influences the quantity, structure and
127 reactivity (biotic and abiotic interactions with aquatic pollutants such as trace elements) of
128 NOM affecting surface and groundwater quality. Climatic conditions that are known to have a
129 positive correlation with DOC concentration in waters include high precipitation, high
130 temperature, storm, floods and runoff (Ågren et al., 2010; Bhurtun et al., 2019). An increase in
131 temperature for instance can increase biological activities and the decomposition of organic
132 matter, which can subsequently be eroded into water bodies during floods or rainfalls.
133 Hurricane Irene alone which occurred in 2011 is estimated to have contributed to 19% of the
134 2011 annual dissolved organic matter (DOM) exports from a forested catchment in Cecil

135 County, Maryland (Dhillon and Inamdar, 2013). Areas of mean temperatures of about 5°C and
136 30°C would have 10% and 3% carbon loss respectively with a temperature increase of 1°C. The
137 change in temperature would also influence the bioavailability and toxicity of pollutants since
138 adsorption processes are temperature dependent (Ripszam et al., 2015). The activity of
139 microbial organism is further enhanced as humic substances act as electron donors acceptors
140 during anaerobic respiration(Lau et al., 2015; Lipczynska-Kochany, 2018b)

141 Available database shows that the increase in DOC quantities started from the early 1980s
142 (Evans et al., 2005). Data on 315 records from across Britain shows that about 69% of the sites
143 studied showed a significant increase in DOC concentration (up to 16% annual percentage
144 change) between 1975 and 2002. A lower proportion (38%) has been found across Europe and
145 northern American countries (189 sites – 11 years) (Skjelkvåle, 2003)

146 Even though underground waters are less sensitive to climate change than surface waters, its
147 quality is also expected to deteriorate due to its exchanges (recharge and discharge) with surface
148 waters (Kjøller et al., 2004) which would have grave consequences on drinking water
149 production and may increase treatment cost. The browning of surface waters by NOM reduces
150 the disinfection capacity as it shield pathogens by absorbing of UV rays (Williamson et al.,
151 2017; Lipczynska-Kochany, 2018a). The formation of disinfection by products (DBPs) in
152 drinking water is expected to rise as well as the release of trace metals into the environment
153 (Lipczynska-Kochany, 2018a). Acidification of groundwater due to acid rains would results in
154 less than 10% NOM-metal complexes making about 90% of trace metals bioavailable (Kjøller
155 et al., 2004).

156 Due to its highly complex structure and heterogeneity, numerous papers and reviews are
157 focused on NOM classification and/or characterization. (Edzwald et al., 1985; Aiken et al.,
158 1992; Bryan et al., 2000; Luider et al., 2004; Sutton et al., 2005; Karlsson et al., 2006;

159 Kalinichev and Kirkpatrick, 2007; Mopper et al., 2007; Fabris et al., 2008; Sillanpää, 2015).
160 The aim of this review is to (1) extensively examine the interactions of cations and NOM in the
161 environment. Much attention is given to the major functional groups as well as cations and the
162 different types of interactions that can exist between them, (2) examine the preference of cations
163 for each functional group and the possible competition between cations for binding sites, (3)
164 assess the impact of the presence of cation, NOM, or their complex on drinking water treatment
165 processes.

166

167 Figure 1

168 **2. Theoretical aspects of complexation of metals to NOM**

169 **2.1. Central atom and ligands**

170 Bonding that occurs through the donation of electron pairs from an orbital of an atom (electron
171 pair donor or ligand) to a partner atom (electron pair acceptor) is referred to as coordinate
172 bonding or coordinate covalent bonding. The ligand can be an ion (possibly an ionic form of
173 the central metal atom) or a molecule. Broadly speaking, the electron pair acceptors are
174 generally referred to as Lewis acids while the electron pair donors, Lewis bases (Lawrance,
175 2010). Once coordination happens, structural properties like the number of bonds, bond angles
176 and bond distances of the new substance formed causes it to have an altered physical property
177 compared to their individual components. Thus, the new physical properties are dependent on
178 the nature of central atom (either same or different atom type) and the ligands involved. The
179 electron pair acceptor, which serves as the central atom, is usually a metal or a metalloid. When
180 there is only one central atom involved, the newly formed structure is called a monomer. When
181 the number of linked units are low, the structure is considered to be an oligomer (Naka, 2014).
182 If several central atoms are involved, they would either be held together by an atom-atom bond
183 or be bridged by a ligand making them a polymer. This linkage can be done through a common

184 donor atom, simultaneously binding to the central metal atoms, or through different donor
185 atoms. The metal atoms can also be encapsulated in a polydentate ligand with each metal
186 coordinating with several donors (Lawrance, 2010).

187 Ligands can be grouped into two main classes; simple and heterogeneous ligands according to
188 their structural properties and the ability to chemically define their structures and metal
189 complexation chemistry. In the case of a simple ligand like EDTA, its molecular structure
190 (composition and geometry), concentration (activity) of itself and its complexes,
191 stoichiometry of its complexation with metals, metal-ligand formation free energy or
192 thermodynamic equilibrium constant are known or can be known. However, heterogeneous
193 ligands like humic substances may exhibit characteristics that are opposite to that of the
194 simple ligands; poly-functionality which results in high electrical charge density, structural
195 modification as a function of *e.g.* pH, ionic strength, metal binding, and variation in molecular
196 weights (Buffle et al., 1990; Filella, 2008). Thus, the ligand can present either a single or
197 multiple donor atoms; if only one donor atom is coordinated, it is referred to as a monodentate
198 ligand. If multiple donor atoms are involved, it is referred to as polydentate ligands. The
199 ‘denticity’ therefore defines the number of donor atoms or groups that are available or used in
200 bonding. For polydentate ligands, the subsequent lone pair after the first coordination is
201 oriented in a way that prevents them from coordinating with the same central atom. In an
202 instance where the existing covalent bond is deformed, two lone pairs from a ligand can be
203 attached to the same metal forming a cyclic compound referred to as a chelate. Even though
204 the shape of the ligand influences the strength of the complex formed and the coordination,
205 there are no rules to really predict a particular shape to be formed by a ligand in complex
206 structure. In general, chelate rings exhibit an enhanced stability compared to monodentate
207 ligand since the size of the stability constant is almost invariably proportional to the number

208 of coordinated donor atoms in a ligand (Lawrance, 2010). Figure 2 shows various possible
209 coordination of a central metal atom to a ligand.

210 Figure 2

211 Carbon can act as a ligand (*e.g.* carbanion (H_3C^-)) and effectively donate electrons to coordinate
212 a metal. This type of coordination can occur either by σ covalent bonds or π covalent bonds
213 when side of carbons equidistance from the central metal are involved. The d_z^2 and $d_{x^2-y^2}$
214 orbitals of the transition metals are also often involved in σ bonding while the other three more
215 stable orbitals d_{xy} , d_{xz} , d_{yz} are mostly involved in π bonding. They have incomplete d-orbital
216 and an electronic configuration of ns , $(n-1)d$, np with varied oxidation numbers (Lawrance,
217 2010). The oxidation number indicates the number of available spaces that have been created
218 because of loss or gain of electrons, which influences the tendency to coordinate with ligands
219 to make up for this loss. For metals with different oxidations states, the chemistry of each state
220 distinctively differs from the others. The effect of ionic interactions on the valence electrons (p
221 orbitals for main group, d orbitals for transition group and f orbitals for lanthanides) influences
222 its bonding and coordination. The valence shell of a d -block element can be considered as
223 having a total of 9 orbitals (18 electrons) which comprises, 5 nd orbitals, $(n+1)s$ and $(n+1)p$
224 orbitals respectively. To achieve stable oxidation state, elements in the d -block (transition
225 metals) of the periodic table ought to have a partially filled nd subshell. The five d (d_{xy} , d_{xz} , d_{yz} ,
226 d_z^2 and $d_{x^2-y^2}$) orbitals occupy different spatial orientations and presents two different shapes.
227 Two of the five orbitals lie along the axes while the other three lie between the axes of the
228 coordinate system. This is however different for elements in the main block which require either
229 a fully occupied or empty subshell to attain oxidation stability.

230 When there is a direct linkage between the metal atom and the ligand, it is referred to as a
231 direct or inner sphere complexation. If however the metal atom is bridged to the ligand by
232 water molecule, it is referred to as indirect or outer sphere complexation. For carboxylic

233 group, the metal atom can be directly linked to one of the oxygen atoms of the carboxylate
234 (monodentate) or both oxygen atoms (bidentate) as shown in Figure 3. However, this behavior
235 depends on the metal ion involved as *e.g.* in the case of Ca^{2+} as the central atom, there can be
236 a proton transfer from water to the carboxylic group at lower water content (Aquino et al.,
237 2011). Small ions preferentially form monodentate outer sphere complexes to avoid steric
238 hindrance (Falck, 1989; Allen, 1993; Dudev and Lim, 2004; Kunhi Mouvenchery et al.,
239 2012). An increase in the number of water molecules in the coordination shell of the cations
240 favours more monodentate coordination than bidentate coordination.

241 Figure 3

242 **2.2. Preferential binding sites**

243 Two major types of functional groups, usually indicated as being of greatest importance with
244 respect to NOM-cation binding, are carboxyl and phenolic groups (Kalinichev and Kirkpatrick,
245 2007; Chappaz and Curtis 2013), phenolic groups are much less abundant than carboxylic
246 groups. In accessing the composition of these two main functional groups in 14 IHSS standards,
247 (Ritchie and Perdue, 2003) concluded that carboxyl groups constitute 78% to 90% of the total
248 acidity for fulvic acids and 69% to 82% for humic acids. Thus, the average of phenolic-to-
249 carboxyl groups for the IHSS samples studies is about 21: 79. . The high affinity of these two
250 groups to cations compared to other minor groups (ester, amine, alcohols, aldehydes and
251 ketones) is highly dependent on the pH (Nederlof et al., 1993; Mota et al., 1996). At high pH,
252 there is an increase in deprotonation, which increases the available binding sites of ligands. A
253 lower pH, however, increases protonation reducing the available binding sites.

254 Figure 4, gives a summary of preference for the two main functional groups of NOM and their
255 characteristic paths in complexation

256 Figure 4

257

258 **2.2.1. Carboxylic group**

259 The carboxylic group which is more acidic than the phenolic group starts to dissociate at pH >
260 4.4; *e.g.* the dissociation of the carboxylic group of Suwanee river humic substance occurs at
261 pH of 4.42 (Baalousha et al., 2006) making it responsible for the formation of negative sites on
262 DOM (Aquino et al., 2011). During dissociation, a net negative charge is created which causes
263 the production of large potentials at the surface of humic substance, and the formation of a
264 double layer in their surrounding (Bryan et al., 2000). For humic substance to achieve steric
265 stability there has to be a repulsion of like charges. This repulsion of the negative charges causes
266 an electrical double layer to be formed at each interface, which in effect increases the surface
267 area for smaller sized particles as well as their binding affinities with cations. Figure 5 shows
268 some of the different carboxylic structures likely to be found in humic substances. As counter
269 ions approach the locality of macro ions such as humic substances, they electrostatically interact
270 with any available site (non-specific) or a targeted site (specific). The choice of which site can
271 be quite challenging to determine. Some surface complexation models that have sought to
272 improve the prediction of metal behavior and their speciation in the environment are the NICA
273 and Donnan Models. While the NICA model describes specific association, the Donnan model
274 rather describes non-specific association (Kinniburgh et al., 1996). However for all models, one
275 of the basic requirements is that both the functional groups and the humic substance should be
276 simplified (Zhao, 2008).

277 Figure 5

278 Aside the affinities of the individual ligands, the nature of the environment in which they find
279 themselves cannot be ignored. Thus carboxylate binding, depends on both the availability and
280 type of interactions between the central metal atom and the carboxylate O atom, as well as
281 between the carboxylate O atoms and its neighboring ligands (Dudev and Lim, 2004). The
282 presence of functional groups containing heteroatoms in the close vicinity of COOH groups

283 affects their ionization efficiency due to inductive effects. Electron withdrawing substituents
284 on C atoms in α position to the COOH groups, decreases the electron density leading to an
285 increase in the asymmetric vibrational modes, enhance their acidity, and may also participate
286 in chelation reactions (Hay and Myneni, 2007). Additionally, in macro ions such as humic
287 molecules, where multiple ionizable groups are in close proximity, electrostatic effects result
288 in transmission of polarization through the solvent medium. This may affect the carboxylic
289 group pKa values, which are a measure of their reactivity (Deshmukh et al., 2007).

290 ***2.2.2. Phenolic group***

291 Phenols are considered as one of the most important groups for complexation with metal atoms
292 (Chappaz and Curtis, 2013). Phenolic compounds are naturally leached from plant materials
293 into the soil and water matrix and constitute about 60% of the plant dry mass (Cates and
294 Rhoades 1977). Figure 6 shows some phenolic structures that can be found in humic substances.
295 If two hydroxyl groups are positioned ortho to each other, they can bidentatively complex with
296 a metal atom (Guan et al., 2006). At higher pH (> 9.5), the phenolic group involves more in
297 complexation as it is easily deprotonated at this pH. The dissociation of phenolic groups of
298 Suwanee river humic substance occurs at pH of 9.68 (Benedetti et al., 1995; Baalousha et al.,
299 2006). When molecules get larger in size, they tend to become less soluble and so its tendency
300 to be coordinated to a metal ion is limited even though the rules of coordination do not change
301 (Lawrance, 2010). The presence of phenolic groups enhances the complexation capacity of
302 carboxylic groups especially when it is located at the ortho position and at lower pH. This is
303 because the ortho-phenolic-oxygen increases the electron density of the carboxylic group,
304 which subsequently favors inner sphere complexation between the carboxylic group and the
305 metal hydroxide even though aromatic carboxylic acids usually form outer sphere complexes
306 with metal hydroxides (Nordin et al., 1998; Guan et al., 2006).

307 Figure 6

2.2.3. *Other functional groups*

308
309 Amines, a derivative of ammonia that has one or more of its hydrogen atoms substituted by an
310 alkyl or aryl group constitutes a nitrogen atom with a lone pair of electrons. While Ammine, is
311 a complex compound that contains ammonia molecule. This difference is important because
312 the substitution of the hydrogen atom alters the electronic effect and polarity as well as the size
313 of the molecule, which subsequently redefines the preferences of the ligands. At higher pH, a
314 monodentate ammonia ligand already coordinated to a metal atom can deprotonate (NH_2^-) to
315 increase its lone pairs of electrons to two and forms a bridge with a second metal atom. Thus,
316 ligands can coordinate to two metals either by using a lone pair from each of the two donor
317 atoms or using two lone pairs from the same donor atom. Amines are less 'sterically efficient'
318 than carboxylate because the size of amine causes it to bump into other ligands when occupying
319 coordination sites around a metal which often leads to lower stability (Lawrance, 2010).

320 Aldehydes and ketones although not abundant, are known to serve as ligands in transition metal
321 complexes (Huang and Gladysz 1988). They consist of a carbonyl functional group ($\text{C}=\text{O}$)
322 where the tetravalent carbon atom has two available sites for bonding. Aldehydes and ketones
323 species are produced as by-products during ozonation in drinking water treatment (Shilov and
324 Shul'pin, 1997; Choi et al., 1998; Świetlik et al., 2004). Figure 7 gives some of ketones and
325 aldehydes found in humic substances or in drinking waters as by-products. Ketonyl metal
326 complexes can be formed either through trans-metalation (transfer of ligands from one metals
327 to another), oxidative addition or by the interaction of electrophilic metal centers with ketones
328 in their enol or enolate form. When the central metal atom is softly electrophilic during keto-
329 enol equilibrium, a complex with a π -bonded enol can be formed which can evolve into a
330 ketonyl complex (Barone et al., 2012). The absorbance and emission properties (especially at
331 visible wavelengths) of humic substances, can be greatly influenced by the presence of ketones

332 and aldehydes, because they act as the primary acceptors in charge-transfer transitions within
333 these samples (Vecchio et al., 2017).

334 Figure 7

335 Esters, which are mostly formed by the replacement of a hydrogen of an acid with an alkyl or
336 any organic group are known to form partial bonds with transition metals (Verkade et al., 1965).
337 The presence of metals ions can increase the hydrolysis of amino esters. Hence, in the absence
338 of a suitable metal ion, the hydrolysis of amino esters is very slow, but upon addition of metal
339 ion, a rapid reaction is observed due to the cleavage of the metallic complex and pH. Upon
340 further increase in the metal concentration, a 1:1 ester-metal complex formation is observed
341 (Kroll, 1952). Phosphate di-esters, on the one hand, do not exhibit a chelating mode of
342 coordination but rather prefers bridging to two adjacent metal ions. Phosphate monoesters, on
343 the other hand, are likely to attract more metal ions around them and form larger aggregates
344 due to the presence of two acidic protons and one phosphoryl oxygen (Murugavel et al., 2008).
345 Sulfur functional groups, although present in humic substances in various oxidation states as
346 thiol, thiophene or disulfide, sulfoxide, sulfone, sulfonate and sulfate esters are considered as
347 minor functional groups (Filella, 2008). Figure 8 shows some Sulfur moieties that could be
348 present in NOM.

349 Figure 8

350 According to Bloom et al. (2001), a humic acid (HA) containing 0.2% of reduced sulfur has 63
351 μmolg^{-1} of thiol sites. In peatland, sulfate reduction leads to the formation of sulfur which then
352 reacts with metal(oid)s like antimony (Sb) or arsenic to form complexed precipitate at low or
353 neutral pH values (Rittle et al., 1995; Dijkstra et al., 2004). The high affinity of Sb(III) for thiol
354 can result in up to 44% of total Sb forming a 3-fold coordination to sulfur at a distance of 2.46
355 Å (Xia et al., 1999). (Besold et al., 2019), however recently found that sulfur-reacted peat
356 increases sorption of antimonite to as high as 98%. Carboxylic and phenolic groups are likely

357 to make available additional sorption sites for antimonite in this particular matrix only when
358 the amount of reduced sulfur is low no metal (oxyhydr)oxides are available. In the case of low
359 Hg concentration, thiols groups are seen to be the most preferred binding sites and likewise
360 responsible for the binding of methylmercury (CH_3Hg^+) (Skylberg et al., 2003).

361 **2.3. Preferences of central atoms (cations) for ligands**

362 Protons are present in aqueous systems and originally occupy most of the binding sites of NOM.
363 Thus, metal ions must compete with the protons for binding sites. When a metal (M) reacts with
364 equimolar amounts of ligands L_A and L_B , the amounts of ML_A and ML_B , will depend on the
365 cation preference and are rarely equivalent. This section looks at some S, D and P block cations
366 that are present in the environment at significant concentrations and their preference for ligands.

367 **2.3.1. s-block (calcium, magnesium, sodium)**

368 Even though calcium (Ca^{2+}) exhibits a relatively weak bonding with humic acids, compared
369 to trivalent cations, they cannot be ignored considering their high concentration in most fresh
370 waters. Ca^{2+} predominantly binds with carboxylic sites at low pH but would equally bind with
371 phenolic sites at high pH (Kinniburgh et al., 1999). Amine moieties show the same binding
372 preference as carboxylic acid towards calcium. However calcium has a preference for binding
373 to larger and more negatively charged molecules because they generally have large ligand
374 groups (Cabaniss, 2011). In calculating the potential mean force for the interaction of cations
375 and carboxylic groups of NOM in aqueous solutions, Iskrenova-Tchoukova et al. (2010),
376 found that, Ca^{2+} binding depended on the distance between the Ca^{2+} and the carbon atom of
377 the carboxylic moieties. The presence of Ca^{2+} also results in competition with other cations
378 for available binding sites (Cao et al., 2006) and the modification of redox transformation of
379 some competing cations like Fe (Jiang et al., 2017). Iglesias et al. (2003), concludes that at
380 concentration above 2.5 mM, calcium can significantly compete with copper of concentration
381 $1\mu\text{M}$ for adsorption sites on NOM. The presence of Ca^{2+} further causes relatively small NOM

382 to aggregate and form larger colloidal particles of supramolecular structure (Kalinichev and
383 Kirkpatrick, 2007). This role (probably specific to Ca^{2+} , as the same observations were not
384 made for other cations studied, Na^+ and Mg^{2+}), can be explained in two main geometrical
385 paths (Iskrenova-Tchoukova et al., 2010);

386 1. Directly, by cationic bridging between carboxylic groups from different NOM
387 molecules. Generally metal bridging can occur at a monodentate or bidentate
388 configuration through inner and outer sphere coordination depending on the ion charge
389 and the local ligand environment (Tipping and Hurley, 1992; Kalinichev and
390 Kirkpatrick, 2007). Bidentate complexes can occur only if the two functional groups
391 involved are close enough to undergo interaction with the same cation otherwise
392 monodentate complexes may be formed (Mouvenchery et al., 2012).

393 2. Indirectly, by Ca^{2+} simultaneously complexing with two or more carboxylic groups of
394 the same NOM molecules. This coordination reduces the net charge and repulsion of
395 the complex, thus allowing the complexes to approach each other more readily.

396
397 Magnesium (Mg^{2+}) is with calcium, the primary cation responsible for the hardness of water.
398 When dissolved in water, magnesium interacts with NOM present and results in the formation
399 of soluble and sorbed complexes, and a variety of solid phases. Mg^{2+} equally competes with
400 other cations for binding sites. (Kalinichev and Kirkpatrick, 2007), suggest that, the strongly
401 held hydration shell makes Mg^{2+} interact little with NOM. This is however, contradicted by
402 Yan et al. (2015), who in studying Mg^{2+} -NOM interaction using differential absorbance
403 spectroscopy confirms the existence of strong interactions between Mg^{2+} and NOM. This is
404 however dependent on pH and the ability of Mg^{2+} to deprotonate phenolic and carboxylic
405 groups of NOM. While there was an increase in differential absorbance with increase in Mg^{2+}
406 concentration, an increase in pH (5 to 11), increases the concentration of Mg bound onto SRHA

407 and SRFA although the effect of pH was more pronounced for SRHA. This noticeable effect in
408 humic acid is probably because it has about 2/3 less of carboxyl group content compared to
409 fulvic acids. The phenolic content in fulvic and humic acids are statistically similar (Ritchie
410 and Perdue, 2003). An explanation to the supposed minimal interaction could be due to the
411 bond between Mg^{2+} and NOM which is mainly by nonspecific Donnan electrostatic interaction
412 and so the quantity of Mg^{2+} that is bonded to NOM is minimal (Li and Elimelech 2004). The
413 carboxylic group, forms strong association with Mg^{2+} compared to the phenolic group (Ahn et
414 al., 2008). Even at higher pH, Mg^{2+} shares similar properties to Ca^{2+} and can still bond to the
415 carboxylic groups and to a lesser extent to the phenolic groups of the NOM (Lu and Allen,
416 2002; Iglesias et al., 2003; Yan et al., 2015). This binding was accompanied by the replacement
417 of protons in the protonation-active phenolic and carboxylic groups (Korshin et al., 2009).

418

419 Regarding sodium (Na^+), on the one hand, it is considered that this cation forms only very weak
420 outer-sphere complexes with NOM and the ions remain almost entirely in the solution to be
421 hydrated by the water molecules. Therefore, Na^+ does not bind to NOM and even its outer-
422 sphere coordination to the carboxylate groups is statistically weak (Kalinichev and Kirkpatrick,
423 2007). On the other hand, it is considered that Na^+ could act as relatively effective cross-linker
424 for NOM (Aquino et al., 2011). An increase in the cation charge density increases equally the
425 tendency to form a contact ion pair (Kalinichev and Kirkpatrick, 2007). Iskrenova-Tchoukova
426 et al. (2010), however, has disagreed with the conclusion of (Kalinichev and Kirkpatrick, 2007)
427 that Na^+ does not bind to NOM, and states that Na^+ , like Ca^{2+} , rather shows a strong preference
428 for bidentate carboxylate groups even though the bond for the latter may be weak.

429 **2.3.2. d-block (cadmium, copper, iron, zinc)**

430 Cadmium (Cd^{2+}) complexes with NOM under natural water conditions (Hertkorn et al., 2004).
431 Cd^{2+} shows, a relatively weak binding, even though they prefer amine-containing sites to pure

432 carboxylates and bind to smaller, less aromatic molecules (Cabaniss, 2009, 2011). Li et al.
433 (1998), however, have stated that Cd^{2+} is rather primarily coordinated to O donor atoms
434 (carboxyl groups) and would be coordinated to N donor atoms only at high pH with no observed
435 coordination with S. In disagreement, Hertkorn et al. (2004), have stated that the coordination
436 with S is possible. This has been evidenced in the case of soil organic matter where Cd^{2+} at a
437 concentration of below 1000 $\mu\text{g/g}$ is exclusively bonded to the reduced organic sulfur ligands
438 (thiols). Cd^{2+} forms inner-sphere complexes with two S groups in an octahedral geometry (Xia
439 et al., 1997; Karlsson et al., 2005). At higher concentration, however, there is contribution from
440 the organic O and N containing ligands (Karlsson et al., 2005; 2007). According to the bond
441 distances and coordination numbers, in soil organic matter, Cd^{2+} is complexed to a mixture of
442 a 4-coordination with S (thiols) and 4- and 6-coordinations with O and N containing ligands
443 respectively (Karlsson et al., 2005).

444 In the environment, Copper (Cu^{2+}) can exist in four different oxidation states (0, +1, +2 and
445 +3), with the most abundant speciation found in pure water being Cu^{2+} . The speciation of
446 copper is influenced by pH and available oxygen (WHO 2003). The type of coordination it
447 undergoes is determined by several factors, the most important being the ligand-to-metal ratio
448 (Carrera et al., 2004). Cu^{2+} is very strongly bounded to humic acids even though this
449 interaction is pH dependent, especially at trace concentrations. At a pH between 4 and 8, most
450 of the binding can be attributed to the phenolic sites (Kinniburgh et al., 1999). However,
451 Cabaniss (2011) has suggested that at pH below 7, the largest reactive sites in NOM are the
452 carboxylate fractions and can form a vast number of coordination complexes with Cu^{2+} . In
453 terms of strength, the strongest bonds are expected to be formed with carboxyl ligands. Cu^{2+}
454 also shows high affinity for amine containing sites which are often located on small (MW <
455 1000 Da) lower aromaticity molecules (Cabaniss 2011). Cu^{2+} is complexed by O and N

456 functional groups in NOM, forming a structure involving one or two five-membered chelate
457 rings (Karlsson et al., 2006).

458 The remarkable affinity of Cu^{2+} towards NOM, compared to other cations, may probably be due
459 to the excellent match in size between the cupric ion and one or several ligands (*e.g.* oxygen and
460 sulfur) (Kinniburgh et al., 1999; Manceau and Matynia, 2010). Thus NOM has a high sorption
461 capacity and selectivity for Cu^{2+} over a large concentration range (Gao et al., 1997). The size-
462 match fit (strain energy), is a function of the bond-length and bond-angle deformation, the
463 torsional strain of the chelate, and van der Waals interactions among non-bonded atoms
464 (Manceau and Matynia, 2010). Considering the poly-functional nature of NOM, Cu^{2+} is likely
465 bonded to more than one functional group in proportions that may vary with the metal
466 concentration, the pH and the chemical composition of the organic matter. In the presence of
467 other cations however, Cu^{2+} would have to compete for binding sites. Chappaz and Curtis
468 (2013), in studying the simultaneous interaction of Cu-Al-DOM, observed that Cu is strongly
469 complexed with the high molecular weight fraction of NOM than the low molecular weight
470 fractions. Due to the availability of relative sensitive and inexpensive electrochemical methods
471 for the measurement of Cu^{2+} in Cu-NOM complexation, copper complexation has been the
472 model choice of many studies (Filella, 2008).

473

474 Iron (Fe) mainly forms complexes with NOM as Fe^{2+} or Fe^{3+} with the speciation being highly
475 influenced by pH. The presence of humic substances, however, slows down the oxidation of
476 Fe^{2+} as well as the aggregation of the Fe particles (Pédrot et al., 2011). Even though hydroxide
477 and oxide forms of Fe have low solubility in water, it is still possible to find high concentrations
478 of such Fe speciation associated with organic colloids in water rich in organic matter
479 (Pokrovsky et al., 2005; Pédrot et al., 2011). Humic substances equally inhibit the
480 crystallization of iron hydroxide and iron oxides, by forming Fe nano-(hydr)oxides coated with

481 DOM and Fe(III)-DOM complexes (Pédrot et al., 2011). At pH lower than 3 and higher than 6,
482 Fe species bind to humic acids thereby indicating that it has the same relative affinity for
483 carboxylic and phenolic humic acid sites (Dudev and Lim, 2004; Marsac et al., 2013).
484 In the presence of EDTA in wastewater, transition metals especially Fe³⁺ because of its
485 increased valence electrons interacts strongly with the nitrogen groups of EDTA (Muñoz and
486 von Sonntag, 2000).

487 Zinc (Zn) in the aquatic environment can either be linked to the organic or inorganic phases. At
488 low concentrations, the sorption of Zn²⁺ occurs mostly on pH-dependent binding sites of
489 oxyhydroxides competing with its binding to organic matter. Zn could sorb to clay minerals by
490 ion exchange processes (Mertens and Smolders, 2013). Zn²⁺ generally show a weaker binding
491 compared to other transition metals like Cu²⁺ and Ni²⁺, and prefers to bind rather to amine
492 groups and smaller less aromatic molecules instead of carboxylates (Cabaniss, 2011, 2009).
493 Zinc is most likely to be involved in inner sphere complexation and can be coordinated to four
494 or six O atoms and also form 4 coordination with N and S ligands (Karlsson et al., 2007).

495 **2.3.3. p-block (aluminium, lead)**

496 In the aquatic environment, aluminium (Al³⁺) complexes with NOM, which subsequently
497 modifies its speciation and influences its toxicity. The exchange reaction between Al³⁺ and H⁺
498 and the hydrolysis of Al³⁺ on organic matter exchange sites are important factors to buffer pH
499 and control the activity of Al³⁺. In the presence of other competing cations like Cd²⁺ and Pb²⁺,
500 Al³⁺ can reduce the amount of Pb²⁺ ions bound to the carboxylic functional group by a factor
501 of 2 to 3 especially at lower pH of 3 to 5.5 (Pinheiro et al., 2000). This competition effect is
502 solely dependent on its affinity for carboxylic, phenolic or chelate ligands, which is pH
503 dependent. Al³⁺ like Fe³⁺ strongly influences the speciation of rare earth element in organic rich
504 waters. At pH ≥ 3, Al³⁺ competes with rare earth elements/lanthanides suggesting that Al³⁺ is
505 bound to carboxylic sites rather than phenolic sites. At neutral pH such as in natural waters,

506 Al^{3+} is expected to bond to weak carboxylic groups (Dudev and Lim, 2004; Marsac et al.,
507 2012). Other studies observed that Al^{3+} has a unique preference for phenol-containing sites and
508 larger, more aromatic molecules (Cabaniss, 2011).

509 In the natural aquatic environment, Lead (Pb) may exist in two oxidation forms (+2 and +4)
510 with the +2 being dominate. Pb^{2+} exhibits a binding strength which is similar to that of Cu^{2+} and
511 form strong binding with amines dominated NOM. It equally binds with other groups such as
512 phenols, alcohols, ether groups and larger molecules but forms slightly weaker bonds with
513 carboxylate (Cabaniss, 2009, 2011). The large ionic radius of Pb^{2+} (1.19Å) makes it possible
514 for it to form complexes with varied coordination numbers (2-15) of central atom. The
515 complexation of Pb^{2+} , with oxygen donor atoms, forms products with two different bond
516 lengths. While the primary bond exhibit a predominate covalent property, the secondary bonds
517 are to a larger extent ionic and in most cases serving as a bridge for molecules (Davidovich et
518 al., 2009).

519 Table 1 gives a summary of the cation preference for each of the main functional groups.

520 When there are contradictory results from different researchers, both results are presented.

521 Table 1

522 **2.4. Complexation equilibrium of NOM**

523 Metals (s, p and d) as well as ligands have their preferences that are largely determined by their
524 electronegativity, a factor of both the size of the atom and number of valence electrons.
525 Generally, p-block and d-block elements have higher affinities compared to s-block elements.
526 Hence, very electronegative ligands prefer less electronegative metals (and vice versa). Further,
527 there is a stronger adsorption between metal cations and acidic functional groups when the acid
528 is weaker and cation valence is higher. The complexation strength for lighter metals increases
529 with charge to size ratio of the binding ion (Skylberg and Magnusson, 1995; Kalinichev and
530 Kirkpatrick, 2007). Metal ions can be bound either as counterions (due to electrostatic forces),

531 or bound specifically to reactive groups. The competition between metal ions may be largely
532 due to the chemical nature of the bound ions. Depending on the deprotonation state and type of
533 cation, the cation-NOM interaction can be specific or unspecific which may be indirectly
534 influenced by the non-polar moieties (Tipping and Hurley, 1992). Unlike cation exchange
535 mechanism where there is a fixed and permanent negative charge, the ion exchange behaviour
536 shown by humic substances is not in general charge equivalent (Kinniburgh et al., 1999). The
537 cation-proton exchange depends on the polyelectrolyte structural charge density, the degree of
538 ionization, the type of cation and the total cation concentration in solution. The release of
539 protons during dissociation can either be due to competition from cations for the same binding
540 sites or a decrease in the intrinsic deprotonation constant of non-dissociated groups due to the
541 binding of cations at neighbouring polymeric sites (Mota et al., 1996).

542 The low ionic charge and relatively large size makes alkali metal ions form complexes faster
543 than other ions on the periodic table, though formed complexes are generally weak. When they
544 react with multidentate ligands, the rate of reaction depends to some extent on the nature of the
545 chelating agent and the differences in the stabilities of the complexes are seen in its dissociation
546 rate. Alkaline earth ions however demonstrate considerable variation in reaction rate depending
547 on the element involved. For example, the greater charge density on Mg^{2+} makes its bonding
548 considerably faster and stronger compared to Ca^{2+} . The rate of reaction is therefore dependent
549 largely on ionic size. The rate of Ni^{2+} is however, about a power of 10 slower than that of Mg^{2+}
550 although they have similar ionic radii. Likewise is the rate of Cu^{2+} adhesion much higher than
551 that of Ni^{2+} . The rate of reactions for trivalent metal ion reaction is slower compared to divalent
552 ions but they form stronger bonds (McAuley and Hill, 1969).

553 From the sections 2.3, it can be established that the complex and ill-defined nature of NOM
554 place a huge limitation on our ability to measure and interpret the complexation equilibria of
555 NOM (Filella, 2008). In particular, Town and Filella (2000), in a review of trace metal

556 complexation parameters for natural waters highlighted the variation in results of each work,
557 which was probably, due to the different experimental conditions and techniques used for each
558 study. The use of varied methods for the determination of cation complex with functional
559 groups makes it challenging to quantify and assign a unique definition to ‘strong’ or ‘weak’
560 affinity. For instance, while on the one hand, Cabaniss (2011), used *a priori* model to define
561 binding strength/affinity (“weak” $\log K_{ML} < 5$, “moderate” $5 < \log K_{ML} < 10$, and ‘strong’ \log
562 $K_{ML} > 10$), based on the conditional formation constant (K_{ML}) for complex ‘ML’ from ‘M’ and
563 ‘L’, Iskrenova-Tchoukov et al. (2010), on the other hand, used bond angles and lengths (radial
564 distribution functions and potential mean force), to define the strength of affinity.

565 **3. Impact of complexation on physico-chemical characterization of NOM**

566 Complexation reactions modify the basic fractioning constituents of the NOM; concentration,
567 polarity, size, solubility, absorbance properties and acid, base, and neutral characteristics (Yan
568 and Korshin, 2014). This session highlights some of the possible modifications due to NOM-
569 metal complexation and their impact on NOM characterization.

570 **3.1. Morphology (size, hydrophobicity, charges)**

571 Factors that are influenced by the cation-NOM binding include molecular size, composition
572 and configuration of the organic matter, pH and ionic strength of the solution and chemical
573 properties of cation and cation/NOM composition (Ritchie and Perdue, 2003; Kalinichev and
574 Kirkpatrick, 2007). In analyzing the effective MW distribution of the different fractions of
575 NOM in the presence and absence of ions using light scattering techniques and high
576 performance size exclusion chromatography (HPSEC), it can be observed that the size of NOM
577 is significantly reduced when the ionic strength (for Na^+) of the solution is increased. This is
578 probably due to coil-to-globule conversion and polyelectrolyte interaction that caused the NOM
579 conformation to change from linear to spherical. However, the effect on the size would also be
580 dependent on the cation involved, since the size of NOM is rather increased when the cation

581 under consideration is Ca^{2+} instead of Na^+ . This is possibly due to the aggregation or chelating
582 between humic acids and Ca^{2+} (Xi et al., 2004).
583 Bowers et al. (2015), in using ^{43}Ca NMR, X-ray diffraction and helium ion microscopy to study
584 cation binding and dynamics in flocculated NOM, however observed no changes in the flocculation
585 morphologies with the type of NOM fraction, solution pH, or solution ionic strength, though
586 admittedly certain pH and ionic strength were needed to induce flocculation.
587 In varying the pH at which NOM complexes with cations, Ritchie and Perdue (2003), observed
588 a downwards drift in pH above 6.5 even when aliquots of NaOH was added. This suggests that
589 the slow reactions of some ligands generate additional acidity. Proton association and
590 dissociation from a ligand is influenced by its molecular structure through polar substituents
591 and resonance effects. In comparing formic acid (HCOOH) to acetic acid (CH_3COOH), though
592 they both have an $-\text{OH}$ group, the former is seen as a stronger acid because the ability of the
593 hydrogen atoms to attract electrons more strongly by displacing electrons from the $-\text{OH}$ group
594 in the direction of the O atom. An increase in the distance from the acid group decreases the
595 influence of polar constituents present. Likewise, saturated hydrocarbons groups are electron-
596 repelling while unsaturated ones are electron-withdrawing (Tipping, 2002).

597 **3.2. Electronic spectral changes**

598 The optical properties (absorbance and fluorescence) of DOM have been greatly explored in
599 studying its characteristics. This is because of the presence of chromophores and/or
600 fluorophores in the ligands of NOM. Optical properties of DOM are highly variable and
601 controlled by different physico-chemical parameters (pH, photoreactivity, redox conditions)
602 and biological processes (Jaffé et al., 2008). When chromophores or fluorophores absorb light
603 in the UV-vis region, electrons in the ground state are excited to higher energy states. The nature
604 of the transition is mainly $\pi\pi^*$ and $n\pi^*$. The molecular structure therefore determines the
605 absorption maximum and intensity. As conjugation increases in a structure, the maximum

606 wavelength moves to longer wavelength. Classical optical spectroscopy techniques are widely
607 used to study DOM and its interaction with metal cations. Indeed, absorbance or fluorescence
608 measurements are inexpensive, easy, relatively rapid and do not require sophisticate
609 pretreatment.

610 UV-vis spectroscopy can provide some structural information about the organic matter in water.
611 Spectral features obtained for a complex mixture of molecules can be generally considered as
612 the average of individual compounds that form the solution. Specific UV absorbance (SUVA),
613 ascertained as the UV absorbance of a solution at a given wavelength normalized for DOC
614 concentration, is strongly correlated with the degree of aromaticity of DOM (Weishaar et al.,
615 2003). This indicator of DOM aromaticity is often calculated at 254 nm (SUVA₂₅₄) (Kim et
616 al., 2018; Lee et al., 2018). Numerous studies have shown that the variation of the SUVA₂₅₄
617 descriptor is directly bound to metal complexation. Studies on copper, zinc, cadmium and nickel
618 complexation with DOM on surface waters, isolated using reverse osmosis, have highlighted
619 important positive correlation between the absorbance indices and the metal binding affinity
620 pointing out that in those waters, aromatic humic substances are the predominant metal
621 chelators (Baken et al., 2011). This result was also confirmed for iron in naturel fresh water
622 (Fujii et al., 2014; Kikuchi et al., 2017). In anthropogenically influenced waters however, nickel
623 is mainly complexed to EDTA and can account for about 87% of all EDTA sites bonded. (Baken
624 et al. 2011). The complexation of Na⁺ and Mg²⁺ with tocopheroxyl radicals results in an increase
625 in UV-absorbance (Mukai et al., 2012). Trivalent cations (Al, Fe, Cr) complexes with
626 anthocyanins and its derivatives resulted in a stronger decrease in absorbance than Mg²⁺
627 (Sigurdson et al., 2016). While an increase in absorbance intensity could be due to band
628 broadening resulting from the superposition of un-associated and chelate form of the NOM, a
629 decrease in absorbance intensity could also be due to a decrease in the energy needed to cause
630 light-induced electron transition in a chromophore, shifting the absorption maximum to a longer

631 wavelength (Fedenko et al. 2017). The spectral modification observed in the absorption spectra
632 upon metal complexation is very difficult to explain in term of binding sites. This is why it is
633 possible to have more detailed structural information by using absorption spectroscopy coupled
634 with quantum chemistry methods to determine the preferential binding site on a multisite ligand
635 that constitutes a model molecule of humic substances (Cornard and Lapouge, 2004). The
636 difference in the metals' effect on spectral properties of NOM is due to the individual preference
637 of metals for certain binding sites and pH (Langford and Khan, 1975; Cabaniss, 1992).

638 However, the spectral changes observed in the UV-visible absorption spectra remain limited
639 and difficult to interpret. Those observed in fluorescence emission are much more important
640 and especially allows to highlight finer phenomena and further analysis of the data. The
641 presence of metals can serve as quenchers or enhancers of fluorescence intensities due to the
642 high affinity between metals and aromatic moieties though metals can sometimes be associated
643 with oxygenated aliphatic carbons (Cabaniss, 2011). During complexation with metals, the
644 properties of the fluorophores are modified making it possible to compare the free and the
645 complexed ligands.

646 Fluorescence quenching, on the one hand, occurs by the fluorophore donating electrons to the
647 quencher. Generally, quenching can occur without any permanent alteration of the molecule or
648 photochemical reaction (Lakowicz, 2006). The complexation of Cu^{2+} and Ni^{2+} for instance,
649 result in fluorescence quenching while that of Al^{3+} enhances the fluorescence of phenolic
650 compounds at pH 5.0 and quenches at pH 7.5 (Cabaniss, 2011). A change in pH affects both
651 the shape and magnitude of the quenching spectrum of Cu^{2+} ; at pH < 6, Cu^{2+} is more bonded to
652 the carboxylic functional groups while at pH > 8, it is more bonded to the phenolic groups of
653 fulvic acid. Likewise, Fe^{3+} quenches fluorescence very weakly when complexed with poly-acid
654 ligands at pH 7.5 due to the formation of iron oxyhydroxides which sequester much of the Fe^{3+}
655 though a much stronger quenching is observed at pH 5.0 (Cabaniss, 1992). On the other hand,

656 fluorescence enhancement, occurs by a modification in the NOM complex through; (a) the
657 movement of fluorophores into solvent regions (b) an increase in the rigidity of the molecular
658 structure which consequently increases the fluorescence quantum yield (Lakowicz and Masters,
659 2008). Due to the indirect nature of optical measurements, quenching or increase of
660 fluorescence may not necessarily be due metal binding but also the presence of marginal
661 aromatic ligands surrounded by abundant aliphatic ligands in the environment (Cabaniss, 2011).

662 Fluorescence excitation-emission matrix (EEM) coupled with parallel factor analysis
663 (PARAFAC) allows categorizing NOM samples into combination of several groups of
664 fluorophores with similar optical properties. This method is widely used to characterize the
665 metal binding with DOM (Stedmon and Bro, 2008; Xu et al., 2013). The fit of fluorescence
666 quenching by models, (for example, the Ryan-Weber model) enables the characterization of the
667 fluorophore affinity for a given metal cation and the estimation of a complexation constant
668 (McIntyre and Guéguen, 2013; Yuan et al., 2015). Recently, two dimensional
669 fluorescence/Fourier transform infrared correlation spectroscopy allowed the localization of
670 functional groups in different fractions of humic substances and thus to observe the ability of
671 these groups to complex metal cations (Tang et al., 2019). Because molecular spectroscopy
672 methods alone can be limiting in information about the coordination, and the structure of the
673 metal ion binding site as well as conformational changes that occurs on the ligand sites, they
674 may require other supporting techniques (Cornard and Merlin, 2002). One of such techniques
675 that can accompany spectroscopic techniques to provide additional information on the different
676 fractions of NOM with respect to their molecular weight is the high performance size exclusion
677 chromatography (HP-SEC) (Her et al., 2002). The advent of ultrahigh resolution Fourier
678 transform ion cyclotron resonance mass spectrometry (FT-ICR-MS) has equally helped to
679 advance knowledge on NOM characterization. FT-ICR-MS is capable of resolving
680 simultaneously thousands of individual molecules from complex organic mixtures like NOM

681 and subsequently provides the molecular formulas for most of the resolved ions (Koch et al.,
682 2008). One major challenge however with this technique is the difficulty in separating noise
683 from analyte peaks (Riedel and Dittmar, 2014).

684 **4. Impact of cations–NOM interaction on water treatment efficiencies**

685 The main goal of the drinking water industry in characterizing NOM is to predict its behaviour
686 in the different treatment processes. This section looks at the impact of the presence of NOM-
687 cation complexes on treatment efficiencies of most common techniques used in drinking water
688 treatment plants.

689 **4.1. Coagulation and flocculation**

690 Coagulants can be either inorganic salts, organic polyelectrolytes or inorganic-organic
691 composites. Although baseline coagulation targets to remove turbidity, advanced coagulation
692 also targets the removal of NOM as the dose and pH conditions are optimized. Several other
693 factors such as coagulant type, mixing conditions, temperature, properties of NOM, as well as
694 the presence of cations, influences the efficiency of coagulants to remove NOM (Matilainen et
695 al., 2010). When the dominant fraction of NOM has a high molecular weight, the removal
696 mechanism is mainly by charge neutralization and the required coagulant dose is low, while
697 when the dominant fraction has a low molecular weight, the required dose is higher as the
698 removal mechanism is mainly by adsorption onto metal hydroxide surfaces (Matilainen et al.,
699 2010). The most common salts used in coagulation are aluminium sulfate (alum), ferric chloride
700 and ferric sulfate. These coagulants are added to water with the aim of forming coagulant-NOM
701 complexes to remove mainly NOM by two main mechanisms; adsorption and charge
702 neutralization (Davis and Edwards, 2017). The main NOM removal mechanism for ferric salt
703 is by the adsorption of NOM onto ferric hydroxide flocs (Davis and Edwards, 2014). At a low
704 Ferric/NOM ratio however, NOM has the capacity to interfere with the hydrolysis of a low dose
705 of Fe-based coagulant by forming Fe-NOM complexes, which subsequently influences the size,

706 reduce zeta potential, morphology and identity of the Fe precipitates, thereby limiting the
707 coagulation efficiency of the iron salt. The presence of other cations such as Ca^{2+} can neutralize
708 NOM and restore the coagulation efficiency of the low dose of iron-based coagulant, thereby
709 making enough Fe ions to be available for effective coagulation. When the Ferric/NOM ratio
710 is high, irrespective of the presence or absence of Ca^{2+} , the coagulation efficiency is not reduced
711 as there is sufficient Fe for coagulation (Davis and Edwards, 2017). Generally, ferric-based
712 coagulants are seen to be more efficient in removing NOM than aluminium-based coagulants
713 (Budd et al., 2004; Golob et al., 2005; Chow et al., 2009; Matilainen et al., 2010). Though the
714 overall removal efficiency of both salts are very close (70 and 67 % respectively for ferric and
715 aluminium based coagulants), ferric salts have an advantage of being able to remove more
716 (25%) intermediate molar masses (1000 – 4000 Da) than aluminium salts. Aluminium salts
717 however have a higher turbidity removal efficiency (Matilainen et al., 2005).

718 For alum, even at low concentrations of 0.5 mg and 1.0 mg Al L^{-1} , there is the formation of
719 small $\text{Al}(\text{OH})_3$ -humic substance colloids, and the size of the precipitate colloid formed grows
720 with an increase in the alum concentration (Wang et al., 2014). The presence of Ca^{2+} improves
721 the coagulation of alum and equally increases the pH range for effective removal of even the
722 low molecular weight acids especially at pH 7 and 8 (Duan et al., 2012; Davis and Edwards,
723 2017). The zeta potential of DOM in the presence of Al^{3+} was observed to increase with
724 increasing addition of Mg^{2+} indicating that unlike Ca^{2+} , the presence of Mg^{2+} may suppress the
725 binding between coagulant Al^{3+} and DOM (Zhou et al., 2017). In using the aluminium coagulant
726 at low dosages, residual aluminium concentrations after treatment can be relatively high
727 because less humic substances are removed (and vice versa). High aluminium residual has been
728 attributed to the presence of dissolved Al-NOM complexes formed when a high proportion of
729 aluminium monomers is present in the aluminium-based coagulant (Yan et al., 2008; Kimura
730 et al., 2013). Dissolved residual aluminium is complexed with almost all MW ranges (500 Da

731 - 100 kDa) (Kimura et al., 2013). The use of aluminium-based coagulants is currently of concern
732 because aside the presence of residual aluminium in treated waters affecting the aesthetic
733 properties, it may also cause health risk as it is linked to adverse neurological effects such as
734 Alzheimer's disease (Flaten, 2001). Although an adjustment of the pH can minimize the
735 aluminium residue from aluminium coagulants, this is often not done as another post pH
736 correction is needed to prevent corrosion in distribution channels.

737 **4.2. Precipitation**

738 **4.2.1. Lime softening**

739 The main targets of softening are calcium ions, even though this method may also remove a
740 limited portion of the hydrophobic NOM fraction (Semmens and Staples, 1986). Caustic soda
741 (NaOH) and calcium hydroxide (lime) are added to increase the pH of the solution (> 9.5) and
742 cause the formation of insoluble CaCO_3 and $\text{Mg}(\text{OH})_2$ which would precipitate out of solution
743 (USEPA, 2011). Unlike CaCO_3 which has an overall negative charge on its surface (Stumm,
744 1992), $\text{Mg}(\text{OH})_2$ precipitates as positively charged particles with high surface area and
745 amorphous structure which aids the sorption by NOM onto its surface (Thompson et al., 1997).
746 Russell et al. (2009), however observed that at very high pH above 11.5, both CaCO_3 and
747 $\text{Mg}(\text{OH})_2$ have positive charges with a great affinity for NOM adsorption. In addition, a limited
748 NOM fraction is removed through precipitation, co-precipitation or both (Thompson et al.,
749 1997). At high concentrations, (no specific values given in literature) NOM can complex with
750 the Ca^{2+} cations and cause them to precipitate in a different phase (organo-calcium salt) from
751 the CaCO_3 if the aqueous solubility of the complex is exceeded, thus inhibiting the formation
752 of CaCO_3 and making the lime softening method inefficient (Liao and Randtke, 1986; Russell
753 et al., 2009). In a jar test experiment of a modified lime-soda softening process to enhance NOM
754 removal by the addition of MgCl_2 , lime-soda ash removed about 43% of DOC in the presence
755 of the magnesium salt (7.5 mg/l) compared to 13% when no magnesium was added (Bob and

756 Walker, 2006). Polyaluminium chloride is also proposed to increase the formation of $Mg(OH)_2$
757 precipitates thereby increasing the removal efficiency of NOM at relatively low pH <10 (Yan
758 et al., 2008).

759 **4.2.2. Chemical precipitation**

760 Chemical precipitation is one of the principal technologies used to remove dissolved metal
761 pollutants from wastewater streams. This process, which is dependent on the metal
762 concentration and solution pH, is achieved by modifying the solution chemistry through the
763 addition of precipitating agents like $Ca(OH)_2$, $Mg(OH)_2$, NaOH and Na_2CO_3 . The agents are
764 added to raise the solution pH and form insoluble complexes with target metals (Wang et al.,
765 2005). Unlike the lime-soda softening technology that mainly focuses on the major cations,
766 chemical precipitation can target a wide range of trace metals. The presence of simple but strong
767 complexing ligands like EDTA in wastewater, however, reduces the efficiency of this process.
768 The formed metal-EDTA complexes are highly soluble, poorly biodegradable and extremely
769 stable over a broad pH range (Wu et al., 2013). In quantifying the speciation of EDTA in
770 influents and effluents of sewage treatment plants, it is estimated that Fe(III)EDTA represents
771 the dominant EDTA species comprising 20-90% of the total EDTA in the effluents. While no
772 significant EDTA is removed by biological or chemical processes during sewage treatment,
773 nitrilotriacetic acid is degraded to a large extent (> 90%) (Kari and Giger, 1996). At higher pH
774 (> 7), Fe(III)EDTA is not stable and so other metals present like Zn can compete for binding
775 sites (Nowack, 2002).

776 **4.3. Membrane separation**

777 During membrane filtration (tight ultrafiltration, nanofiltration, reverse osmosis), NOM is
778 removed principally through size exclusion, charge repulsion and hydrophobic interactions
779 (Metsämuuronen et al., 2014). NOM is also known to be one of the main factors responsible
780 for the fouling of low-pressure membrane in natural waters with the biopolymers' and

781 hydrophobic fractions being the largest contributors. This fouling is primary caused by the
782 adsorption of NOM onto membrane pore walls, which blocks the pore spaces. The adsorbed
783 NOM further interacts with other substances in the solution, making the solution chemistry an
784 important factor for fouling (Tian et al., 2013). The presence of cations in solution would
785 therefore influence fouling. Divalent cations in particular partially neutralize the carboxyl
786 functional groups of NOM and consequently reduce the repulsion effect on NOM. The partially
787 neutralized NOM complex maybe easily adsorbed onto the membrane surface forming a
788 densely packed fouling layer. The presence of Ca^{2+} increases the humic acid (HA) fouling of
789 ultrafiltration (UF) Ca^{2+} probably forms Ca-HA complexes which are larger in sizes and
790 consequently reducing the membrane pore sizes, sometimes reaching the cut off values for acids
791 and humics (Amy, 2001; Galjaard et al., 2004; Comerton et al., 2009). Li and Elimelech (2004),
792 likewise, observed a decrease in the nano-filter membrane permeate flux of 49% and 16% when
793 1mM of Ca^{2+} and Mg^{2+} were present, respectively. On the contrary, monovalent Na^+ has the
794 ability to mitigate HA fouling. The mechanism is probably due to Na^+ ability to form
795 neutralized Na-HA complexes with a size below the pore cut off size (Hong and Elimelech,
796 1997; Tian et al., 2013). Hence, both the nature of the ions as well as the NOM constituent have
797 a considerable effect on the treatment process (Xi et al., 2004). The effect on fouling has also
798 been attributed to high ionic strength, which reduces the electrostatic double layer thicknesses
799 of both membrane surface and NOM resulting in fouling (Ahn et al., 2008). But even at the
800 same ionic strength, Ahn et al. (2008), observed that Na^+ and Mg^{2+} cause less fouling of UF
801 polyethersulfone membrane compared to Ca^{2+} due to the strong interaction of Ca^{2+} with
802 negatively charged carboxyl groups of NOM (Kalinichev et al., 2008; Iskrenova-Tchoukova et
803 al., 2010). However, this statement has been controverted, or cannot be applied to all types of
804 membranes as Tang et al. (2014) observed that monovalent cations caused more fouling of

805 polyvinyl chloride UF membrane by forming a gel layer, which blocked pores compared to
806 divalent cations, which formed a porous caked layer structure on the membrane surface.

807 Aside cations complexing with NOM to increase fouling, they can equally form ionic bridges
808 (stronger for Ca^{2+}) between negatively charged sulfonate functional groups of the membranes
809 and the carboxylic groups of NOM which increases the adhesion between the NOM ligands and
810 the fouled membrane surface forming a very compact fouling layer (Iskrenova-Tchoukova et
811 al., 2010). Ahn et al. (2008), however, suggested that divalent cations (Ca^{2+} and Mg^{2+}), which
812 are strongly associated with the carboxylate groups of NOM, may boost the aggregation of
813 NOM rather than forming ionic bridges between NOM functional groups and a
814 polyethersulfone membrane surface as they are weakly attracted to the membrane sulfonyl
815 groups. This suggests that the aggregation of NOM in the presence of divalent cations could be
816 a higher contributor to membrane fouling as partially neutralized NOM molecules are easily
817 adsorbed on membrane surface. Moreover, large size of the organic colloids complexed with
818 trivalent cations like aluminium ($\text{Al}(\text{OH})_3$) could also easily block membranes pores (Leenheer
819 and Croué 2003; Wang et al., 2014). Whereas divalent cations result in irreversible fouling,
820 monovalent cations are only responsible for reversible fouling. The irreversibility of Ca-HA
821 fouling was however, observed to decrease in the presence of Na^+ , as added Na^+ is able to reduce
822 bond strength of Ca-HA and between HA and the membrane, due to electrostatic shielding. A
823 similar trend was observed when bovine serum albumin (BSA) was used as a surrogate for the
824 protein fraction of NOM, though a mixture of both organic molecules (BSA and HA) resulted
825 in more severe fouling suggesting a synergistic fouling effect (Tian et al., 2013).

826 Backwashing with demineralized water instead of normal permeate can effectively control
827 fouling of UF membrane caused by NOM-Ca complex. This is because UF permeate contains
828 same multivalent cation concentration as feed water, while the absence of cations and NOM in
829 demineralized water reduces the ionic strength and the Ca-bridging effect between NOM and

830 membrane surface. Backwashing with demineralized water, then, substantially reduces the rate
831 of increase in the transmembrane pressure. Another approach may be to raise the pH of the feed
832 water in order to keep the carboxyl functional groups deprotonated, thus preventing their
833 deposit onto negatively charged membrane surface (Hong and Elimelech, 1997).

834 **4.4. Activated carbon**

835 Activated carbon (AC) is mainly used to remove organic substances or micro-pollutants by
836 adsorption. The carbon surface, which is predominantly hydrophobic, contains functional
837 groups, which are formed during the activation process (Kilduff et al., 1996). When the
838 activated surface is further oxidized, electrochemically or chemically (nitric acid and ozone),
839 the number of oxygen containing acidic functional groups, such as carboxylic and phenolic
840 groups, on the surface increases, which, in effect, increases its sorption capacity for cations at
841 near neutral pH. Uptake for cations equally increases with increasing pH due to the dissociation
842 of the weakly acidic oxygen-containing groups (Rangel-Mendez and Streat, 2002). The
843 presence of humic substances can compete with target synthetic organic compounds and reduce
844 the efficiency of the AC (Kilduff and Karanfil, 2002). There can likewise, be competition
845 between cations for adsorption sites confirming that the solution chemistry can also alter the
846 surface charges of the carbon (Sengupta, 2001). For instance, the lower ionic radius of Cu^{2+}
847 (0.70 \AA) makes it a better adsorbate than Pb^{2+} with a higher ionic radius of (1.12 \AA) as higher
848 ionic radius would result in rapid sites' saturation and steric overcrowding (Faur-Brasquet et
849 al., 2002). Moreno-Castilla et al. (2004), observed an increase in the uptake of Cd^{2+} ions on AC
850 pre-adsorbed with organic compounds (tannic acid). The capacity of AC to adsorb gallic acid
851 also slightly increased in the presence of Cr^{3+} . The adsorption of organic molecules on AC
852 increases with increasing ionic strength and divalent ion content (Ca^{2+}). The increase in
853 adsorption may be either due to an adsorption of larger molecules or an effective adsorption of
854 the smaller molecules, as new adsorption sites are created through cationic bridging. Partial

855 neutralization of the surface functional groups reduces intramolecular charge repulsion and
856 molecular expansion. The ionic strength further influences the electrostatic interactions
857 between the adsorbate and adsorbent and/or the solvent (Kilduff et al., 1996). This has been
858 attributed to the neutralization of its functional groups when complexed with the metal ion,
859 making the adsorbate more hydrophobic and increasing the adsorption capacity (Ferro-Garcia
860 et al., 1998). The effect of NOM-metal complex on AC efficiency is thus due to both the
861 properties of the AC (specific surface area, micropore volume, functional groups) and that of
862 the metal ion (ionic radius and electronegativity) (Faur-Brasquet et al., 2002).

863 On the other hand, the presence of a chelating agent alters the adsorption properties of a metal
864 ion as the chelates themselves are adsorbed onto surfaces (Nowack, 2002). This may affect the
865 efficiency of adsorption depending on the targeted compound. Although tri-ammonium
866 functionalized mesoporous silica has proven to remove about 96% of Cu(II)-EDTA chelates
867 from aqueous solution with initial concentration of 0.1mM, the maximum (> 97%) copper
868 adsorption was achieved in acidic condition and low ionic strength (0.01M) (Wu et al., 2013).

869 **4.5. Oxidation processes**

870 The presence of metal cations in water can influence (positively or negatively) the formation of
871 disinfection by-products by changing the oxidation mechanism of the NOM by chlorination,
872 depending on the cations involved and the NOM composition. For instance the presence of
873 copper oxide reduces the formation of trihalomethanes (THMs) because the metal oxides
874 consume chlorine while the reverse is observed for Cu^{2+} ions (Li et al., 2007; Navalon et al.,
875 2009). The formation of trihalomethanes has been mostly seen to be reduced by the presence
876 of metals from chlorination surrogate compounds as phenol, 2,6-dihydroxybenzoic acid or
877 tannic acid in presence of diverse metals (Ca^{2+} , Mg^{2+} , Mn^{2+} , Fe^{2+} , Cu^{2+} and Al^{3+}) (Blatchley et
878 al., 2003; Navalon et al., 2009; Liu et al., 2012). However, considering the chlorination of
879 humic substances, the reverse is usually found. For instance, the increase of THM formation

880 from humic substances in presence of Mg^{2+} and Ca^{2+} . This has been attributed to the affinity of
881 the metals for carboxylate functional groups of the substrate which consequently increases their
882 reactivity towards chlorination (Navalon et al., 2009; Liu et al., 2012). Also, Cu^{2+} apparently
883 activates certain components of humic substance that are otherwise inefficient precursors and
884 so consequently enhances the formation of chloroform from humic acids during chlorination
885 (Blatchley et al., 2003).

886 On the opposite, the presence of metal ions has been shown to enhance the formation of
887 haloacetic acids (HAAs) from tannic acid through the production of strong oxidative radicals
888 during the chlorination (Liu et al. 2012). Furthermore, complexation of metals to the active sites
889 of organic substrates resulting in a difference in electron densities depending on the type of
890 cation, the change in electron density, affects the reaction activity of electrophilic substitution
891 by chlorine with the corresponding carbon (Liu et al., 2012). The respective inhibitory or
892 enhancement efficiency of the metals is directly proportional to their concentrations (Liu et al.,
893 2012).

894 When the oxidation is by ozonation however, the presence of NOM can affect the stability of
895 ozone by either directly reacting with the ozone or indirectly by scavenging OH radicals. In
896 natural waters, the presence of NOM can act as inhibitors to stop ozone chain reactions by
897 entrapping superoxides after reaction with OH radicals (Buxton et al., 1988). The protonation
898 and complexation of amine functional groups of EDTA, nitrilotriacetic acid, decrease their
899 reactivity towards ozone in water treatment. During complexation especially with transition
900 metals, the rate constants are lower because the metals are able to interact with the nitrogen
901 groups. For instance, the complexation of Fe^{3+} reduces the reactivity of EDTA to ozone by a
902 factor of 500 since EDTA are mono-protonated at nitrogen (Muñoz and von Sonntag, 2000).
903 This explains why EDTA is not removed from natural waters by ozonation. This interaction
904 can however be weakened by a substitution of the ligand with OH^- (Muñoz and von Sonntag,

2000; von Gunten, 2003). To limit the negative effects of NOM complex on treatment process, advance oxidation processes such as UV/H₂O₂ or chlorine, Fenton oxidation, ozonation, TiO₂ photocatalysis and photoelectrocatalytic oxidation, discharge plasma oxidation followed by alkaline precipitation have been proposed as a pre-treatment step to degrade NOM-metal complexes (Wang et al., 2018). These techniques however either do not work for all metal complexes such as Cr(III) complexes or performs averagely. Photo-Fenton process and Fenton derived process combined with precipitation has been shown to exhibit an efficient removal of Cr(III) complexes (Ye et al., 2017, 2018) and Ca-phosphonate complexes (Sun et al., 2019).

4.6. Ion exchange

Ion exchange is used in water treatment to remove dissolved ions from waters and more recently to target NOM removal (anionic resins) (Li et al., 2014). The resin surface loaded with loosely bound ions exchanges the ions with similar charged ions in the solution (Bauman and Eichhorn, 1947). The presence of NOM or chelating agents can affect the efficiency of this method, as the formed NOM-metal complex is not in the ionic state to be exchanged. For anionic exchange resins, the presence of higher affinity chelating agents like EDTA can compete with target weakly acidic functional groups for exchange sites. Aside neutralizing cations, organic compounds and other solids present in water can foul exchange resins with anion-exchange resins being more susceptible than cation exchange resins. Fouling which occurs when very strong ions are held onto resins' surface or when the inner surface of resins are occupied by hydrophobic substance can be reversible or irreversible depending on the affinity of the ions involved (Dorfner, 2011). Fouling increases the frequency and volume of backwash requirement, increases the sensitivity to flow rate and temperature, increase conductivity of solution and reduces the overall efficiency by increasing volume of desorption concentrate (Abrams, 1982). Liu et al. (2017) recently improved the capacity of polymeric anion exchanger towards the removal of Cu(II)EDTA with nanoscale zero-valent iron deposition.

930 **4.7. Research challenges for water treatment**

931 The variation in the quantity and quality of NOM in the environment is likely to continue due
932 to the effects of climate change. The variations in DOC trends and its complexation with trace
933 elements may not only significantly impact water treatment process selection, design and
934 operation but may also increase the risk of many treatment facilities violating water quality
935 regulations on NOM, trace metals or DBPs. The description of the phenomena in real matrices
936 remains challenging. The coupling of size exclusion chromatography with elemental detector
937 ICP-MS looks promising but lacks for the moment of quantitative measurement validation
938 (Piatina and Hering, 2000; Rathgeb et al., 2016). Other methods based for example on
939 electrochemistry (Moutcine and Chtaini, 2018) are useful in elucidating complexation in real
940 matrices but applications in the field of water treatment are missing. Progress in many different
941 areas, from high-resolution mass spectrometry to quantum chemistry modelling, could each
942 bring their own valuable information to the field. Also, fluorescence detector are more and more
943 used on-line to also study the diel variability of NOM (Trubetskoj et al., 2018; Ignatev and
944 Tuhkanen, 2019)). This fast measurement will give valuable data on NOM sources, origins and
945 dynamic in the environment and are useful for characterizing water sources. As the trace metals
946 and major elements could modify the response of probes, researchers should attend to take into
947 account those aspects. NOM-metal complexes impact on ozonation is an important aspect to
948 cover in the next years especially considering the increasing use of ozonation for the treatment
949 of wastewaters. The high trace metal concentrations coupled with high level of organic matter
950 make those effluents particularly exposed to such interaction.

951 **5. Conclusion**

952 The complex NOM structure, which contains several functional groups, controls the
953 bioavailability and biogeochemical cycling of trace elements in water. The two main
954 functional groups, *i.e.* carboxylic and phenolic groups show their contribution varying with

955 their deprotonation with pH, inducing a higher contribution of carboxylic acids at lower pH
956 due to their lower pKa values compared to phenolic moieties. The type of bonding that occurs
957 between NOM and cations is mainly coordinate covalent bonding as electrons are donated
958 only by the ligand(s) involved. This coordination modifies the physico-chemical properties
959 like morphology and spectral characteristics of the newly formed product.

960 The NOM-metal formed complex impacts water treatment efficiencies. In coagulation, the
961 complexation between the coagulant salts and NOM helps to remove NOM from solution.
962 This process is further enhanced when Ca^{2+} is added. The impacts however are not always
963 positive as for example the presence of high NOM concentration complexing with free
964 calcium causes it to precipitate in a different form thereby reducing the efficiency of lime
965 softening method. NOM-metal complexes are equally responsible for membrane fouling as
966 cations partially neutralize NOM making the complexes easily adsorbed onto membrane
967 surface. In addition, the presence of metals influences the formation of disinfection by
968 products by modifying the mechanism in which chlorine reacts with NOM either by
969 increasing or decreasing DBP formation or changing the species formed. The modification of
970 rate constants during ozonation process has also been observed limited to model compounds
971 (*e.g.* EDTA and Tannic acid) which are not representative of NOM behavior.

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