Source to taps investigation of natural organic matter in non-disinfected drinking water distribution systems

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10 Abstract

11 Despite being reduced by treatment, natural organic matter (NOM) is ubiquitous in drinking water distribution systems (DWDSs) from sources to consumers taps where it can potentially have 12 13 negative impacts on drinking water quality. While few studies have studied its behavior in 14 disinfected and NOM-rich DWDSs, its dynamics in non-disinfected systems, characterized by low 15 NOM content, have not been explored yet. In this study, we monitored the NOM variations 16 occurring between sources and consumers taps of a non-disinfected DWDS using both absorbance 17 and fluorescence, selected due to their increasing adoption by water utilities. PARAFAC analysis of fluorescence data, combined with absorbance indices, highlighted how NOM characteristics in 18 19 groundwater can vary likely due to the combination of multiple factors, especially in case of 20 shallower aquifers. The treatment processes acted differently on fluorescent components and 21 absorbance likely due to the differences among fluorophores and between fluorescent and 22 chromophoric molecules. Within the distribution network, variations were detected only at selected 23 sampling locations suggesting the importance of the "last meter" factor, especially for sampling locations located within buildings. These findings remark the overall stability of water quality 24 25 within non-disinfected DWDSs, but they stress the importance of localized water quality variations, 26 suggesting several implications for DWDS monitoring and management.

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28 Graphical abstract



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31 Table of content entry

Characteristics of natural organic matter present in drinking water from undisinfected system fed on
 groundwater were investigated by spectroscopic methods highlighting changes due to seasonality,
 treatment and water distribution.

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36 Water impact statement

Understanding natural organic matter (NOM) behavior in drinking water is crucial given its impact on treatment performances and water quality, which reflects on consumers' safety. Hence, this study investigates NOM occurring between drinking water sources and consumers' taps in a nondisinfected systems fed on groundwater, by spectroscopic methods, providing also guidance for future monitoring campaigns and management strategies.

42

43 **1 Introduction**

44 Natural organic matter (NOM) is a complex mixture of compounds which is present in all water matrices ranging from environmental to drinking water.¹ Monitoring and controlling NOM 45 concentration and composition in drinking water distribution systems (DWDSs), including 46 47 treatment and distribution, is fundamental as NOM can potentially be a nuisance for consumers (e.g., contributing to the water organoleptic properties),² or can even be detrimental for the quality 48 of the delivered water. In fact, NOM can interact with residual disinfectant, favoring the production 49 50 of toxic disinfection by-products.³ NOM can also affect contaminants kinetics within the network⁴ and can also interact with the metallic materials of the pipes, eventually aiding their release.⁵ In 51 52 addition, NOM can cause biological instability supporting microbial growth in drinking water distribution networks (DWDNs),⁶ favoring the development of biofilm, possibly resulting in pipe 53 54 biocorrosion and offering a favorable habitat for pathogens.⁷

55 Due to its heterogeneity and complexity, several techniques are required to fully characterize NOM.

56 Commonly, in the field of drinking water monitoring, NOM is measured through the estimation of

57 total or dissolved organic carbon (TOC, DOC). However, such measurement provides only a

quantitative estimate of the NOM concentration, without providing any qualitative information 58 59 regarding its composition.^{8,9} Several advanced analytical methods, such as LC-OCD-OND, NMR and FT-ICR-MS, overcome this limitation assessing different NOM characteristics.^{8,10,11} However, 60 61 recently, absorbance and fluorescence spectroscopy have started to be adopted by several water utilities.^{9,12} These techniques, coupled with advanced post-processing techniques, such as 62 PARAFAC and differential absorbance spectra,^{13,14} allow to probe the chromophoric and fluorescent 63 NOM fractions without the need of complex analytical workflows, allowing also for their real-time 64 monitoring.^{15–18} 65

66 Several studies exist regarding the variation of concentration and composition of NOM within drinking water treatment plants (DWTPs) (e.g., ¹⁹⁻²¹). However, only few studies have focused on 67 68 DWDNs, despite their importance in guaranteeing suitable water quality at the point of use. Such 69 studies report contrasting results on the spatial and temporal NOM variations within DWDNs. For 70 example, in the presence of relatively high NOM content (i.e., $2.5 - 8.9 \text{ mg}_{\text{DOC}}/\text{L}$) and residual disinfectant, both Wang and Wang and collaborators²² and Heibati and collaborators²³ highlighted 71 72 how the NOM concentration and composition did not vary with the water residence time in the DWDN. On the contrary, Kurajica and collaborators²⁴ observed an increase of the intensity of 73 74 protein-like fluorescent component in two groundwater-fed DWDSs with TOC concentrations between 1 and 2.5 mg/L, similarly to the increase of fluorescence registered by Han and 75 collaborators²⁵ at DWDS taps. Such heterogeneity suggests that NOM variability is highly affected 76 77 by the specific DWDS characteristics, including, but not limited to, NOM concentrations and 78 composition, source water, type of treatments and pipe materials.

79 Even though the published studies investigate DWDSs fed on different source waters (i.e., surface 80 and groundwater), all the investigated systems are disinfected, reflecting the widespread application 81 of this practice. However, specific water utilities or even countries (e.g., The Netherlands, 82 Switzerland) distribute disinfectant-free water, achieving limited microbial regrowth by a reduced presence of substrate.²⁶ Extending the results of disinfected DWDSs to these systems might not be 83 accurate, as residual disinfectant is known to interact with NOM.³ Besides the lack of disinfectant, 84 while available studies monitored DWDSs with relatively high DOC concentrations (i.e., > 185 mg/L), non-disinfected systems are also characterized by limited NOM content.²⁶ Moreover, given 86 that half of worldwide groundwaters present DOC concentrations below 1.2 mg/L,²⁷ previous 87 studies on NOM in DWDSs might not be representative of a large fraction of groundwater-fed 88 89 and/or non-disinfected systems.

In this context, this study aims at (i) evaluating the applicability of TOC, fluorescence and
absorbance for NOM monitoring within non-disinfected DWDSs fed by NOM-poor groundwater,
(ii) deepening our understanding of NOM temporal dynamics occurring within such DWDSs and

93 the changes of NOM characteristics from water sources to consumers' taps, and (iii) providing a 94 guidance for future monitoring campaigns of these systems. For this reason, a monitoring campaign 95 was organized over one year collecting samples in 18 locations within a non-disinfected DWDS in 96 northern Italy, for a total of 212 samples. Data were interpreted and compared through PARAFAC 97 model, as for fluorescence, and absorbance indices, as for absorbance.

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99 2 Materials and methods

100 **2.1 Sampling campaign**

101 The investigated non-disinfected DWDS, comprising three DWTPs, serves a 5800-inhabitants city 102 in northern Italy. It is fed by three wells spread across the city which, depending on the wells' depth, 103 adopt different treatment strategies. In DWTP A (well filters depth = 84-133 m), ferrous sulphate is 104 dosed prior to a rapid sand filtration to remove hexavalent chromium; in DWTP B (well filters 105 depth = 48-70 m), the dosage of the reducing agent is followed by a granular activated carbon 106 (GAC) filter. DWTP C (well filters depth = 126-186 m) directly pumps the withdrawn water in the 107 distribution network. In each sampling day between November 2020 and February 2021, July and October 2021 and January and February 2022, water was sampled from all DWTPs, collecting both 108 109 raw and treated water, and from 11 public water fountains or commercial buildings, spread 110 throughout the DWDN. In addition, a specific sampling campaign was dedicated exclusively to 111 each DWTP, sampling both inlet and outlet waters multiple times to assess the daily variability of 112 water quality characteristics. In total 212 samples were collected. Details of all sampling points are presented in Table S1 and Figure S1. At each sampling location, water was allowed to flow for at 113 114 least 5 minutes before collection using 0.5 L glass bottles with teflon-coated caps and 250 mL 115 polyethylene (PE) bottles. After collection, samples were stored in the dark in a refrigerated 116 container during transport to the laboratory. Samples collected in glass bottles were then kept at 4 °C and analyzed within 5 days, while samples contained in PE bottles were frozen and analyzed 117 118 successively, within 1 month. Whenever possible, water temperature was measured directly upon 119 samples collection. In addition, monthly abstraction flowrates data for each DWTP during the 120 monitoring period was provided by the managing water utility.

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122 **2.2** Water quality characterization and analytical methods

Samples in glass bottles were analyzed without a preliminary filtration, given the negligible turbidity highlighted in previous sampling campaigns carried out by the water utility (data not shown). To support this protocol in the case of fluorescence measurements, preliminary tests were performed to assess the effect of sample filtration, using samples taken from the DWDS (see Supporting Information S1). Negligible differences were observed in fluorescence in most of the

128 emission-excitation matrices (EEMs), with the exception of fluorescence at low emission and 129 excitation wavelengths (Ex < 290 nm, Em < 375), for which a slight increase was observed after filtration, likely due to the extra handling step. Samples were first warmed to room temperature 130 using a water bath. Such water samples were then used to measure: pH and conductivity using a 131 132 multi meter (HQ40D, Hach, USA) after daily pH calibration, and UV-Vis absorbance (range: 190 -800 nm) using both a 1 cm and 4 cm cuvettes in a UV-VIS DR6000 spectrophotometer (Hach 133 Lange, Germany). Fluorescence EEMs were collected every 5 nm between 230 and 450 nm 134 excitation and 270 and 600 nm emission using a Varian Cary Eclipse spectrofluorometer (Agilent, 135 136 USA) in two analytical replicates, using a PMT voltage of 720 V, slit width of 10 nm, averaging time of 0.125 s and default correction factors. Both the spectrophotometer blanks and daily Raman 137 scatter profiles²⁸ were obtained using MilliQ water. 138

Analyses of TOC and metals (Cr, Fe, Mg, Zn) were performed in the water utility laboratory on samples collected in PE bottles, using a QbD1200 TOC analyzer (Hach, USA) and a ICP-MS Agilent 7700 (Agilent, USA), in accordance with Italian and ISO standard procedure.^{29,30} Such metals were selected being the most variable across the DWDN based on the water utility data and presenting evidence of interactions with NOM.^{31,32} Duplicated aliquots of 10 samples were frozen and measured at different dates to test the accuracy of the TOC analyses.

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146 **2.3 Source water determination of DWDN samples**

147 The origin of the water at the various sampling points within the DWDN was estimated using conductivity measured in samples collected at both the DWTPs outlet and the locations within the 148 DWDN, considered as a passive tracer.^{33,34} A confidence interval of conductivity variability was 149 150 estimated thanks to the repeated conductivity measurements conducted at the DWTPs outlet and it 151 was applied around the conductivity measured at the DWTPs outlet in each sampling day. In case the conductivity of a DWDN sample was within the confidence bounds of a DWTP, the sample was 152 153 entirely attributed to it. In case the conductivity laid between the confidence bounds of different DWTPs (i.e., not belonging to the confidence bounds of any DWTP) the sample was considered as 154 155 mixed between the two sources, and the relative contribution of each one was estimated.

Coincidentally, the relative contribution of each source was predicted using a calibrated dynamic
DWDN hydraulic model provided by the water utility, considering only the hours of the day during
which sampling was performed (i.e., approximately 7:00 – 14:00).

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160 **2.4 Natural organic matter characterization**

161 The EEM were analyzed using the drEEM v6.4 toolbox³⁵ in Matlab 2020 (MathWorks, USA). Inner

162 filter effect was corrected using the absorbance spectra collected using the 1 cm cuvette,³⁶ after

which EEMs were normalized using the Raman scatter intensity collected in the same day.²⁸ First 163 and second order Rayleigh and Raman scatter were excised from the affected EEM regions.³⁵ 164 Finally, samples' fluorescence was normalized using the 3/2th root of the standard deviation of each 165 EEM³⁷ due to the high variability of fluorescence intensities. After samples pre-processing, 166 167 PARAFAC modelling was carried out imposing a non-negative constrain on all modes. The fitting 168 of preliminary PARAFAC models allowed to identify, manually inspect and eventually remove 12 outliers out of 212 samples and excise EEM scans with high leverage and fitting errors.³⁵ The final 169 170 PARAFAC model was validated using a split-half analysis, maintaining replicates of the same samples in the same split to preserve their independence.³⁵ Validated components were then 171 compared to previously published fluorescence spectra present within the OpenFluor database.³⁸ 172 173 Finally, the intensity of the fluorescent components obtained by PARAFAC in the duplicated 174 measurements of each sample were averaged sample-wise in order to limit the effect of 175 measurement noise.

Absorbance spectra collected with 4 cm cuvette were first corrected subtracting the average absorbance between 750 nm and 800 nm and then used to estimate the absorption coefficient at 254 nm (UV254) as indicated by Helms and collaborators.³⁹ To characterize the variability in average molecular weight of chromophoric NOM, the same data was used to estimate the absorbance index S₂₇₅₋₂₉₅ fitting a linear regression on the log-transformed spectra between 275 nm and 295 nm.³⁹

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182 **2.5 Data elaborations and statistical analyses**

Removal percentages in the DWTPs were estimated for each sampling date as $1 - V_{in}/V_{out}$, with V representing the value of interest (i.e., PARAFAC component intensity, absorption coefficient value). The effect of the distribution network on organic matter was isolated by subtracting the mean value of the variable of interest at the DWTP outlet to the values measured in the samples attributed to such DWTP. Samples considered as composed of mixed sources were not included in this analysis.

Statistical analyses were performed using R v4.2.2.⁴⁰ Homogeneity of variance was tested using the 189 Levene test, as implemented in the package car v3.0-13.⁴¹ Depending on the normality of the data, 190 homoscedasticity and the numerosity of the groups, either parametric (i.e., t-test, ANOVA, Tukey 191 192 HSD) or non-parametric (i.e., Wilcox test, Kruskal-Wallis test, Dunn test with Holm correction) 193 tests were used to assess the differences among groups relaying on either built-in functions or the package dunn.test v1.3.5.42 To perform a multivariate analysis of NOM behavior within the 194 195 investigated DWDN, including both the intensity of the fluorescence components identified through 196 PARAFAC and the absorption at 254 nm, such variables were used to estimate the Euclidean 197 distance among samples. Differences among groups of samples were tested using PERMANOVA,

198 as implemented in vegan v2.6-2.⁴³ A principal component analysis (PCA) was used to extract and 199 plot the two most variable components, being equivalent to an ordination in linear space.⁴⁴

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201 **3 Results and discussion**

202 **3.1 Fluorescent organic matter characteristics**

203 The validated PARAFAC model described the samples fluorescence thanks to the use of three 204 components, namely C1, C2 and C3 (Figure S2). When compared to previously published 205 fluorescent components, C1 was associated with humic-like components indicated as relatively 206 aliphatic and with low molecular weight; C2, despite still being classified as humic-like, was 207 indicated representing high molecular weight compounds with signatures related to highly degraded aromatic organic matter.⁴⁵ Both components corresponded to ones found in other groundwater 208 samples⁴⁶ and drinking water.⁴⁷ On the other hand, C3 was classified as protein-like and potentially 209 210 derived from microbial processes⁴⁸ and detected in the distribution systems of recycled wastewater.⁴⁹ As expected from a non-disinfected groundwater-fed DWDS, the observed 211 212 fluorescence intensities resulted lower than in several disinfected and/or surface water-fed systems,^{20,22,23,50} while resulted comparable to ones measured in a disinfected groundwater-fed 213 system²⁴ and the ones present at the outlet of a DWTP of a non-disinfected DWDN.¹⁹ 214

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216 **3.2 Seasonal variability of water sources**

217 NOM concentration and composition is shown in Figure 1 in terms of fluorescent components, 218 absorbance and TOC concentration in raw and treated water. Both fluorescence intensity and 219 UV254 differ between the three DWTPs inlets (Dunn test, p-values < 0.001), with the highest values in DWTP B and the lowest in C. Comparing the different fluorescent components, the 220 221 majority of the fluorescence belongs to humic-like NOM (i.e., components C1 and C2), rather than 222 protein-like one (C3), in concordance with its lower biodegradability reported by Shi and collaborators.⁹ TOC measurements, on the other hand, present only significant differences between 223 the inlets of DWTP B and C (Tukey HSD, p-value = 0.021). The decrease in NOM content with 224 increasing groundwater depth is concordant with recent results.²⁷ However, while fluorescence and 225 226 absorbance show overall similar patterns in DWTPs inlet (Spearman correlations; $\rho > 0.88$, p-values < 0.001), TOC deviates from the other two measurements, showing only limited, if not non-227 significant (i.e., C3), correlations (Spearman correlations; $\rho < 0.47$, p-values < 0.044). This 228 divergence might partly be due to the presence of organic molecules not detectable using optical 229 methods such as fluorescence and absorbance.⁵¹ However, part of this divergence is also due to the 230 231 precision of the analytical methods. Indeed, the absolute TOC deviations from the mean value 232 ranged from 1 to 53% (median \pm interquartile range = 13 \pm 23%), higher than the repeated fluorescence (C1: $2 \pm 3\%$; C2: $2 \pm 3\%$; C3: $4 \pm 9\%$) and absorbance ($1 \pm 4\%$) measures, indicating the lower precision of the TOC measurement at the concentrations present in the investigated DWDS. This highlights the greater difficulty of measuring fluorescence for protein-like components (C3), as already reported by Moona and collaborators.⁵² Due to their low precision, TOC measurements are not taken into account in further analyses.

238 Focusing on the temporal variations, the fluorescence at the inlets of DWTP A and C remains 239 mostly stable, presenting only limited (i.e., C3 in DWTP C) or no evidence of monotonic correlations with time (Spearman correlation; p-values > 0.062). UV254 values remain also stable 240 241 for DWTP A, while present a positive, even though limited, correlation with time for DWTP C (Spearman correlation; $\rho = 0.51$, p-values = 0.022), possibly suggesting the arrival of a water plume 242 243 with higher organic content. Conversely, the raw water in DWTP B varies throughout the 244 monitoring period both in fluorescence and absorbance, due to the combination of several factors. 245 In fact, DWTP B is characterized by the greatest variation in water extraction throughout the year (ratio between the maximum and minimum monthly values: A = 1.90, B = 2.22, C = 1.59), resulting 246 247 in the greatest variation of the area of influence. Increased pumping rates might have affected the quality of the abstracted water, as reported by Graham⁵³ and Kwon⁵⁴ and respective collaborators. 248 249 Furthermore, other 7 wells (average depth = 18-35 m) are present within 1 km from DWTP B for 250 both irrigation and other uses. Finally, not presenting any clay lens at depths above its well head, DWTP B could also be more influenced by seasonal rainfall recharges.⁵⁵ The combination of all 251 252 these factors could have affected groundwater flowlines, possibly altering the water reaching DWTP B.⁵⁶ Besides changes in the concentration of fluorophores, other factors are known to affect 253 fluorescence measurements, including pH, metals concentrations and others.⁵⁷ However, during the 254 255 monitoring period, the pH measurements highlighted variations below 1 unit and inlet water temperature did not significantly change across seasons (ANOVA; p-value = 0.097), suggesting 256 their limited effect on the measured values.⁵⁸ As for metals, except for the correlation between 257 relative fluorescence (i.e., the fraction of the total fluorescence attributed to a specific component) 258 259 of C1 in DWTP C with Mg (Spearman correlation; $\rho = 0.7$, p-values = 0.023), neither the intensity 260 of fluorescent components (both absolute or relative) nor the absorption coefficient values present significant correlations with the measured metals concentrations at the DWTPs inlets (Spearman 261 correlations; p-values > 0.061). This suggests that the observed values of fluorescence and 262 absorbance are not affected by NOM-metals complexation,³¹ supporting the attribution of the 263 264 observed changes to variations of fluorophores concentrations.

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Figure 1. Intensity of fluorescent components (a), absorbance (b) and TOC (c) measured at the inlet and outlet of the monitored DWTPs (A, B, C).

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269 **3.3 Treatment effect on natural organic matter**

While in case of DWTP C abstracted water is directly pumped within the DWDN, DWTPs A and B employ ferrous sulphate dosing and, respectively, a sand and a GAC filter. NOM removal efficiency is reported in Figure 2 for DWTPs A and B, both in terms of fluorescence and absorbance.

The rapid sand filter installed in DWTP A (Figure 2a) shows no significant removal for any fluorescent component (t-test; p-values > 0.3), in agreement with the low removals reported by Yang et al. (2015). Conversely, similarly to Vera et al. (2017), such treatment reduces absorption coefficients values in median by 13% (interquartile range = 9%), indicating the removal of certain chromophoric, but not fluorescent molecules. The increase of absorbance index S₂₇₅₋₂₉₅ across the DWTP A (Figure 2b), suggests that filtration removes prevalently chromophoric molecules characterized by high molecular weight.³⁹

On the other hand, the GAC filter in DWTP B results in fluorescence removals between 60% and 280 281 98% (Figure 2c), with humic-like components C1 and C2 presenting negative trends until mid-282 February 2022, due to their breakthrough before the activated carbon substitution (Spearman 283 correlation; C1: $\rho = -0.75$, p-values = 0.007; C1: $\rho = -0.83$, p-values < 0.001). Interestingly, 284 protein-like component C3 does not show any significant trend before the activated carbon 285 substitution (Spearman correlation; p-value = 0.44) and its removal efficiency is not increased by 286 this operation, indicating that the sorption capacity for fluorescent protein-like compounds was not yet saturated, in contrast with humic-like compounds. In fact, different sorption mechanisms 287 contribute to the removal of humic- and protein-like fluorescent components.⁵² Removals estimated 288 on UV254 values ranges between 76% and 93% (Figure 2d) and similarly to component C3 do not 289 290 show neither a negative trend during the monitoring period, neither a marked increase after the 291 activated carbon substitution. These differences are likely caused by the differences in the pools of 292 molecules probed by the two techniques. In fact, while fluorescent molecules are chromophoric, the opposite is not true.⁵¹ In addition, while different fluorescent components allow to track distinct 293 groups of molecules, UV254 is a bulk parameter, tracking both allochtonous and autochtonous 294 295 NOM.⁵⁹ Besides having a potential detrimental effect in DWDNs, NOM presence affects the sorption of anthropogenic contaminants by occupying sorption sites or forming complexes.^{60,61} The 296 297 breakthrough of such contaminants occurs at different, often higher, bed-volumes than NOM molecules measured by absorbance and fluorescence.^{62,63} Given this fact, combining fluorescent 298 299 components and absorption values for modeling NOM breakthrough could provide useful 300 management information for DWTP managers. Furthermore, even not in this specific case study, a 301 similar technique could be used to assess the DBPs precursors removal, given the high correlations 302 between organic matter measurements and DBPs formation potential.³ Given these tasks, the ability 303 to disentangle the dynamics of different NOM fractions provided by EEM measurements coupled 304 with PARAFAC analysis would likely provide greater benefit than absorption coefficients.



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Figure 2. Removal efficiency of organic matter (a) and the change of absorbance index S₂₇₅₋₂₉₅ (b) in DWTP A (a,b), and
 temporal variations in organic matter removal in DWTP B (c,d) in terms of fluorescence (c) and absorbance (d).

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310 **3.4 Variability within the distribution system**

311 Due to the high level of interconnection of the DWDN, especially in the proximity of DWTP A and 312 B (Figure S1), it was necessary to assess the origin of the water at each DWDN sampling location 313 before analyzing the effect of distribution on the organic matter. Figure 3 shows the comparison 314 between the estimated contribution of DWTP B using either the calibrated hydraulic model 315 provided by the water utility or the conductivity measurements. In most cases both methods agree 316 on the source of the water, but in several cases the hydraulic model predicts a different source than 317 what assessed experimentally. In fact, the model predicts water mixing from DWTP A and B only in three sampling locations (P05, P12, P13), while this was observed in six locations (P01, P02, P03, 318 319 P04, P05, P13). Besides, in P09 water origin alternated between two sources, while only one source was predicted by the model. Noteworthy, these differences were found especially during the first 320 sampling days likely due to the enforcement of a "soft" lockdown^{64,65} which affected water 321 consumption patterns.⁶⁶ These discrepancies highlight how DWDSs behavior is not stable in time, 322 323 but it can vary depending on water consumption. Due to the stochastic behavior of drinking water 324 demands, their uncertainty should be included in DWDSs models. Without its inclusion, calibrated 325 models represent snapshots at a given point in time which might not be representative of other 326 conditions, either due to specific events (i.e., holidays) or fluctuations in consumers behaviors.⁶⁷ 327



Figure 3. Estimated source and influence of DWTP B on each DWDN sample. Markers show the experimental results based on conductivity measurements, while vertical dashed lines and shaded areas indicate the mean and 90% confidence interval of the influence of DWTP B estimated by the dynamic hydraulic model. The presence of confidence intervals on DWTP B influence highlights sampling locations where source mixing is expected, while markers not aligned on the dashed lines indicate samples with discording source attribution.

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Figure 4 shows the projection of the first two PCA components (variance explained = 91.82%), representing the differences of fluorescence and absorbance characteristics among the samples collected at the DWTPs outlet and within the DWDN. Once more the effect of source mixing is evident: samples influenced both by DWTPs A and B are generically placed between the ones served by the two DWTPs. Focusing on the samples with water deriving from DWTP B, it is possible to observe a shift in their position during time due to the effect on the DWDN of the combination of multiple factors, as mentioned above: the variability of source water characteristics, the GAC filter breakthrough and the activated carbon substitution. Comparing the organic carbon characteristics at the DWTPs outlet and within the DWDN, no significant differences are found for the public fountains served by either DWTPs A and B (PERMANOVA; A: $R^2 = 0.13$, p-value = 0.08; B: $R^2 = 0.05$, p-value = 0.07). Conversely, significant differences were found between the sampling locations served by DWTP C (P08) and the DWTP outlet (PERMANOVA; $R^2 = 0.33$, pvalue < 0.001) and between the samples collected from premise plumbings and the outlet of DWTP A (PERMANOVA; $R^2 = 0.33$, p-value < 0.001).

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Figure 4. Principal components plot of the spectroscopic characteristics of the samples collected at the DWTPs outlet and within the DWDN. The labels on the top of each panel indicate the period to which the coloured markers belong to, while grey markers represent the other samples to aid interpretation. Markers inside the dashed circle indicate the samples from DWTP B collected after the activated carbon substitution.

Figure 5 displays the difference of fluorescence and absorbance characteristics between the samples 355 collected within the DWDN and the daily mean value at the DWTPs outlet. By removing the effect 356 of source water and DWTPs removal variability, this analysis highlights the effect of water 357 358 distribution on NOM characteristics, pointing out fluctuations which reach values comparable to the intensities present at DWTPs outlet (Figure 1). Comparing the different fluorescent components, the 359 360 protein-like component C3 tends to have larger fluctuations than the humic-like ones (C1 and C2) (Levene test; A: p-value = 0.067; B: p-value < 0.001; C: p-value = 0.058), possibly linked both to 361 the lower measurement precision ⁵² or to variations in the microbiological quality within the 362 DWDN^{15,68}. The extent of fluorescence and absorbance variability shows differences between the 363 364 DWTPs outlet and the different DWDN sampling locations. This is observable for the samples

365 coming from DWTP A for components C1 and C3, and UV254 (Levene test; p-values < 0.048), 366 while for the samples derived from DWTP B this occurs only for component C3 (Levene test; pvalue = 0.051). Both fluorescent components and UV254 show greater variability at P08 than at 367 DWTP C outlet (Levene test; p-values < 0.003). Besides the different extent of the variability across 368 369 DWDN locations, some sampling locations present values systematically different from the DWTPs outlet. For the samples originating from DWTP A this occurs, in agreement with the PERMANOVA 370 371 analysis, at the premise plumbing locations (P12 and P13) for all fluorescent components (Dunn test, Holm correction; p-values < 0.034) and at P09 and P12 for absorbance (Dunn test, Holm 372 373 correction; p-values < 0.055). Among the sampling locations served by DWTP B, only the 374 component C1 at sampling point P10 presents values different from the DWTP outlet (Dunn test, 375 Holm correction; p-values = 0.035). As already highlighted by the PERMANOVA analysis, both all 376 fluorescent components (Wilcox test; p-values < 0.033) and absorbance (Wilcox test; p-value <377 0.001) differ between DWTP C outlet and P08. Looking at the effect of distribution on NOM apparent molecular weight (Figure 5c), it is possible to observe how the S275-295 index of several 378 samples deviates in many sampling locations from the corresponding DWTPs outlet values, 379 380 resulting in statistically lower values in P04, P08 and P12 (Dunn test, Holm correction; p-values < 381 0.044). This difference suggests the presence of higher molecular weight compounds at such locations compared to the DWTPs outlet.³⁹ 382

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Sample type • DWTP outlet × Premise plumbing • Public fountain

Figure 5. Relative change of NOM characteristics between DWTPs outlet and DWDN in terms of fluorescence (a) and
 UV254 (b) and S₂₇₅₋₂₉₅ (c).

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Previous research on NOM variations in disinfected DWDNs has highlighted both localized^{22,23,69} 387 and systematic^{24,25} variations within DWDSs, stressing the importance of site-specific conditions in 388 389 determining NOM behavior. Both the multivariate and the univariate analyses highlight an overall 390 stability of the NOM characteristics within the investigated non-disinfected DWDN, as most 391 sampling points showed no differences with DWTPs outlet. Coincidentally these results remark the 392 importance of the "last meter" before consumption, as pointed out by the differences found at 393 certain water fountains (P04, P08, P10) and premise plumbing locations (P12, P13), similarly to what found by Heibati and collaborators²³ in a disinfected system. In fact, even though the variation 394 395 of component C1 in P10 might be explained by its greater distance from DWTP B compared to 396 most sampling locations (Table S1), such difference is not observed in the nearby location P09: this 397 suggests that the variation origins between the water main and the public fountain tap. Previous research has highlighted the variety of plastic materials used in premise plumbing and pipe fittings⁷⁰ 398 and their potential leaching of organic molecules.⁷¹ Organics leaching from pipes favors biofilm 399 development,⁷ which can, as well, store, cycle and affect the presence on organic matter in 400 bulkwater.⁷² Similarly to what indicated by the S₂₇₅₋₂₉₅ values at some locations, the first layers of 401 biological activated filters have been shown to increase NOM molecular weight.⁷³ suggesting the 402 403 occurrence of biological NOM transformations within the DWDN. Even though already present in 404 certain water fountains, these effects are exacerbated in buildings where a greater premise plumbing 405 system is in place, which offers greater surface-to-volume ratios and greater opportunities for biofilm development.⁷⁰ The detection of these variations highlights the role of the materials in 406 contact with drinking water and stress the importance of their characterization, as recently 407 408 emphasized by the recent European Directive regarding water for human consumption.⁷⁴

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410 **3.5 Implications for DWDS monitoring and management**

Monitoring the quality of drinking water up to the point of use is a key task in water safety plans⁷⁵ 411 recently introduced in the European drinking water legislation.⁷⁴ In order to be effective, a 412 413 monitoring program should be tailored for each individual DWDS, taking into account its specific 414 characteristics. Noteworthy, in case multiple sources are present within the same DWDS, 415 distinguishing the water origin within the DWDN is a necessary step to avoid a misinterpretation of 416 the results. While this task can be achieved through DWDS simulations, experimental confirmation 417 using a water quality parameter not significantly affected by distribution (e.g., conductivity) is 418 highly recommended. Such verification is needed because, as highlighted in Figure 3, the water source at single DWDN locations might fluctuate between different DWTPs due to the 419 instantaneous water demands which might deviate from the ones collected for model calibration,67 420 limiting the usefulness of traditional DWDS models in supporting day to day management. Digital 421 Twins⁷⁶ and data assimilation techniques⁷⁷ could solve this limitation, employing immediately the 422 DWDS sensor data for model refinement. Furthermore, as environmental causes and human 423 interventions can affect groundwater quality,^{78,79} sampling frequencies should be adapted to track 424 water quality changes either based on previous knowledge or automated algorithms (e.g., ⁸⁰). 425 426 Observed values should be compared with the degree of short-term (daily) variability, possibly with 427 confirmatory sampling performed rapidly (24 h) after unusual results, as possibly required in statelevel US regulations.⁸¹ Finally, sampling locations should be evaluated for their representativeness. 428 429 The results of this study indicate that premise plumbing systems affect NOM characteristics, 430 leading to distinct results compared to water fountains. On one hand, the ability of fluorescence to

431 detect the changes of organic molecules within premise plumbings due to organic leaching and 432 microbial transformations could be used to localize and quantify this phenomenon, and to focus 433 further analyses. On the other hand, the presence of this difference highlights the non-434 representativeness of the water samples collected within buildings to assess NOM quality within 435 DWDN mains. This fact should be taken into account in the design of sampling campaigns.

Besides a correct choice of sampling locations, attribution of water sources and monitoring 436 437 frequency, the analytical method chosen for monitoring affects what variations can be observed. 438 TOC measurement provides only a bulk information of NOM content, without providing any information on its quality.^{8,9} In addition, TOC data reliability is questionable in case of NOM-poor 439 440 groundwater. On the other hand, fluorescence and absorbance allow to obtain qualitative 441 information regarding NOM characteristics and better understand the fate of fluorescent and chromophoric NOM.¹⁰ While fluorescence measurements present higher sensitivity compared to 442 absorbance,^{9,82} only a limited fraction of organic molecules can be detected by fluorescence, 443 limiting the extension of the results to the whole NOM pool.^{10,83} On the other hand, chromophoric 444 molecules make up a larger fraction of the entire NOM pool,⁵¹ but environmental samples present 445 mostly featureless spectra, providing often limited qualitative information compared to 446 447 fluorescence.¹⁴ In fact, while the application of PARAFAC to fluorescence data allows to 448 distinguish between fluorophores with different characteristics and compare them to other spectra to 449 identify matches,³⁸ most absorbance analysis methods involve the estimation of ratios and/or slope coefficients which have been previously correlated to changes in NOM properties.¹⁴ While more 450 451 advanced analyses of absorption data have been developed, such as the Gaussian fitting of 452 differential absorbance spectra, little guidance exists regarding their use with most applications limited to laboratory settings.^{84–86} Given the mentioned pros and cons, fluorescence measurements 453 454 in DWDSs would be more suitable to track specific NOM fraction and characterize their different abundance within DWDSs, while absorbance would be better suited to describe NOM bulk 455 456 characteristics and abundance. In any case, both approaches could be used to screen for sampling locations with peculiar NOM characteristics which could then be inspected by more advanced 457 targeted or un-targeted methods.^{11,87} Regardless of the aim of the sampling campaign, the analytical 458 method chosen should guarantee sufficient accuracy to allow for the detection of the expected 459 460 changes. For example, due to the low precision of TOC measurements at the concentrations present 461 in the investigated case study, such technique would not be able to identify small NOM changes occurring along the network. Similarly, Heibati and collaborators²³ suggested humic-like 462 463 fluorescence over protein-like fluorescence as indicator of external contamination due to its higher 464 stability within the investigated DWDN and higher measurement precision.

465

466 4 Conclusions

467 In this study, fluorescence and absorbance measurements were used to track NOM characteristics 468 within a non-disinfected DWDS from different groundwater sources up to the consumers taps throughout a year. While two of the three monitored groundwater sources were characterized by 469 470 mostly stable NOM characteristics, a significant variability was found in one of the sources likely 471 due to the combination of changes in DWTPs operations and other groundwater abstractions and 472 recharges. Water treatment affected NOM presence differently between chromophoric and humic-473 like and protein-like fractions. One DWTP, equipped with a rapid sand filter, provided only a 474 limited reduction of high molecular weight compounds, without affecting fluorescent compounds. On the contrary, a second DWTP, characterized by the presence of a GAC filter, showed substantial 475 476 NOM removals, even though highlighting different behaviors between humic-like, protein-like and 477 chromophoric compounds. Within the DWDN, both multivariate and univariate analyses 478 highlighted a general stability of the NOM, while, coincidentally, highlighting localized "last 479 meter" variations at specific water fountains and at premise plumbing locations, which showed 480 distinct NOM characteristics from the rest of the DWDN. This effect, likely due to the leaching of organic molecules from plastic materials or organic carbon cycling within biofilms, was more 481 482 noticeable using fluorescence measurements, highlighting the applicability of this technique to track specific NOM fractions compared to the bulk characteristics provided by absorbance. Besides the 483 NOM variations, the performed sampling campaign identified discrepancies between the actual 484 485 DWDS behavior and the one expected by a calibrated hydraulic model, stressing the need to assess 486 experimentally the water origin when sampling within the DWDN. In light of this, monitoring campaigns should be designed not only to take into account the possible variabilities in water 487 488 sources characteristics, but also both the dynamicity of DWDS conditions and the effect of premise 489 plumbing on NOM characteristics which might lead to non-representative results.

490

491 Acknowledgements

The authors would like to thank CAP Holding S.p.A. (CAP) for funding the Ph.D. scholarship of
M.G., Maria Giovanna Guido and Fabio Ferrari for laboratory support and Gloria Salinetti, Cristina
Floris and Ambra Lombardo for their helpful cooperation.

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