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Identification of disinfection by-product precursors by natural organic matter fractionation: A critical review – invited article

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Content

Abstract

The presence of natural organic matter in water resources induces the formation of potentially harmful disinfection by-products during drinking water disinfection. However, the identification of disinfection by-product precursors from the complex natural organic matter mixture is very challenging. Therefore, many studies focused on the fractionation of natural organic matter with membranes or resins to better understand how and which organic matter fractions react during chlorination. The outcomes of these studies are rather variable, therefore, a meta-analysis was performed to compare the reactivity of the different fractions towards (un)regulated disinfection by-products. In this study, we review for the first time the influence of key parameters such as chlorination time and dose, specific ultraviolet absorbance ($SUVA_{254}$ = UV absorbance at 254 nm divided by the organic matter concentration) and the column capacity factor used during resin fractionation by collecting results from almost 400 water samples from more than 80 different publications. The major outcomes were: 1) hydrophobic compounds have 10-20 % higher reactivity to both trihalomethane and haloacetic acid formation compared to hydrophilic compounds in waters with high $SUVA_{254}$ (>2 L/(mg·m)), while hydrophobic and hydrophilic compounds have equal reactivity in waters with low $SUVA_{254}$. On the other hand, hydrophilic compounds are 20-80 % more reactive towards emerging disinfection by-products, regardless of $SUVA_{254}$; 2) chlorination time and dose seem to not change the reactivity ratio between the different fractions; 3) an increase in column capacity factor can shift this ratio from hydrophobic to hydrophilic fractions and 4) dead-end, stirred cell ultrafiltration membrane fractionation might not always produce sharply separated fractions, which is mainly due to fouling. Therefore, no clear correlation could be found between membrane fractions and all investigated disinfection by-product groups.

1 Introduction

Natural organic matter, ubiquitous in sources of drinking water, negatively affects drinking water quality. It can contribute to an undesired taste, odor or color of the drinking water and to the formation of biofilms and (pathogenic) bacterial regrowth by acting as nutrients in the distribution system. Chlorine is the most commonly used disinfectant to inactivate waterborne pathogens and to maintain a disinfectant residual in the distribution network. However, chlorine reacts with natural organic matter to form various disinfection by-products and exposure to these by-products has been associated with health issues such as bladder cancer (Diana et al., 2019). More than 700 disinfection by-products have already been identified, where mainly four trihalomethanes and five haloacetic acids are regulated in different countries (Richardson et al., 2007). The USA has set maximum contaminant limits of trihalomethanes and haloacetic acids in drinking water to 80 and 60 µg/L respectively, while trihalomethane levels in the EU cannot exceed 100 µg/L. Haloacetic acid concentrations were recently limited in the EU to 60 µg/L (Council of the European Union, 2020; EPA, 2010).

Unregulated disinfection by-products such as haloacetonitriles, haloacetamides or haloketones are formed in lower concentrations (typically low µg/L to ng/L) (Richardson et al., 2007). Nevertheless, the toxicity of these compounds is higher than that of the regulated by-products and thus, these compounds may cause greater public health issues. The presence of bromide and/or iodide in the water matrix leads to the formation of brominated and iodinated disinfection by-products (Criquet and Allard, 2021). These compounds are even more genotoxic and cytotoxic than their chlorinated analogues, *e.g.* iodoacetic acid, which is the most genotoxic compound identified to date (Dong et al., 2019; Wagner and Plewa, 2017).

In the past decades, many research focused on identifying natural organic matter compounds responsible for disinfection by-product formation. However, dissolved organic carbon, *i.e.* the fraction that passes through a 0.45 µm filter, is a very complex mixture of aromatic and aliphatic hydrocarbons. The concentration, composition and chemistry are highly variable and depend on the natural organic matter source, the season, temperature, pH and ionic strength of the water (Filella, 2009; Leenheer and Croue, 2003). Therefore, dissolved organic carbon is characterized by bulk parameters such as total organic carbon and specific ultraviolet absorbance at 254 nm ($SUVA_{254}$) or by more in-depth characterization techniques such as nuclear magnetic resonance spectroscopy, Fourier transform infrared spectroscopy and 3D-fluorescence excitation-emission matrices (Filella, 2009; Matilainen et al., 2011).

This characterization is however very difficult due to the simultaneous presence of hundreds of different molecules. Therefore, with fractionation processes, organic matter is split beforehand into several fractions with similar physical or chemical properties. This can be done analytically by the use of chromatographic methods such as high performance-size exclusion chromatography or field flow fractionation, which both split the organic matter by size and shape (Matilainen et al., 2011; Pan et al., 2016). Huber et al. (2011) developed a method that consists of liquid chromatography coupled to both an organic carbon detector and organic nitrogen detector. This technique is capable of identifying five different fractions of organic matter; (a) biopolymers, (b) humic substances, (c) building blocks, (d) low molecular weight acids and (e) low molecular weight neutrals.

With analytical fractionation, the different fractions are lost after analysis, because they are not readily available as separate extracts nor in adequate volumes to conduct further experiments. Therefore, preparative fractionation such as membrane or resin fractionation is performed to split natural organic matter into available fractions or extracts with similar physical (with membranes) or chemical (with resins) properties in sufficient quantities (Matilainen et al., 2011; Ratpukdi et al., 2009). Subsequently, researchers seek to correlate these properties to certain water-related issues, such as disinfection by-product formation, bacterial regrowth or membrane fouling behavior which might be overly expressed with a certain fraction. Finally, precise solution strategies can be developed targeting this specific fraction (Krzeminski et al., 2019; Pi et al., 2021; Sambo et al., 2020; Yin et al., 2019).

Membrane and resin fractionation are widely used in an attempt to identify disinfection by-product precursors. In this respect, fractionation parameters such as membrane and resin type, or chlorination parameters such as chlorination dose, reaction time, pH and temperature are key factors for the outcome and the interpretation of the results. Although research already looked into the influence of chlorination parameters on bulk samples (Hua and Reckhow, 2008; Iriarte et al., 2003), no assessments are done so far on how individual fractions react on certain changes in chlorination parameters.

Therefore, this review will focus for the first time on (i) all the different membrane and resin fractionation approaches used in the identification of disinfection by-product precursors and assess their advantages and drawbacks and, (ii) critically evaluate if certain fractionation and chlorination parameters can influence the formation of both regulated and unregulated disinfection by-products in these fractions and identify their precursors.

2 Factors controlling fractionation and disinfection by-product formation

Many research has been executed in the past to identify the most important precursors for disinfection by-product formation. However, several approaches were used in these attempts. It is therefore important to identify the parameters that are varied among the different papers, because this can possibly affect the results and outcome. In this review, papers will be separated based on their method and the influence of different parameters will be assessed to make a clear, statistical comparison regarding disinfection by-product formation.

For membrane fractionation, both the membrane material and the pressure can influence the filtration. Overall, regenerated cellulose is used and the pressure varies between 0.2 and 3.5 bar, which is believed not to change the fractionation significantly (section 3.1). Furthermore, it appeared that for resin fractionation, not the resin type, but the column capacity factor (k') is the only parameter that differs largely between papers, having a value of 50 or 100 (Leenheer, 1981; Malcolm and Maccarthy, 1992). Kitis et al. (2002) showed a gradual increase in trihalomethane and haloacetic acid formation in a particular fraction when changing the column capacity factor from around 30 to 105 (section 4.1 for further discussion).

Chlorine is the principal disinfectant used in drinking water, an extensively studied reactant for disinfection by-product formation potential and therefore, the only disinfectant reviewed here. Temperature, pH, reaction time and chlorine dose are the 4 main parameters controlling disinfection by-product formation kinetics (Hua and Reckhow, 2008). Ambient temperature and neutral pH are reported in all papers collected and will therefore be assumed constant (sections 3 and 4). On the other hand, the reaction time and chlorine dose is very variable among papers. Short reaction times are mostly accompanied with low free chlorine residual (~1 mg Cl_2/L), while during long exposure, chlorine is added in excess to seek reaction completion (~3 - 5 mg Cl_2/L chlorine residual), as followed by different APHA standard methods for the examination of water and wastewater such as 5710B (sections 3 and 4). While the uniform formation condition test with short reaction time and low chlorine dose illustrates distribution system conditions, the formation potential test determines a maximal amount of disinfection by-products that could be formed through the complete reaction of the disinfection by-product precursors with chlorine in a sample (Kanan and Karanfil, 2020).

Finally, specific ultraviolet absorbance ($SUVA_{254}$) is one of the most frequently used parameters to characterize natural organic matter in a water source. $SUVA_{254}$ is defined as the absorbance of UV at 254 nm divided by the organic matter concentration (Ho et al., 2013). This wavelength is especially absorbed by aromatic species (Matilainen et al., 2011). In this review, the threshold between high and low $SUVA_{254}$ waters is set at 2 L/(mg·m). Since resin fractionation is mainly based on hydrophobicity, this parameter might have an important role and will be included together with the chlorination time, dose and column capacity factor when assessing the reactivity of different fractions towards disinfection by-product formation.

3 Membrane fractionation

3.1 Principle of membrane fractionation

Generally, a series of ultrafiltration membranes with decreasing molecular weight cut-offs are used to prepare fractions with different size-ranges (Fig. 1a). Regenerated cellulose membranes in dead-end stirred cell configuration is the most frequently applied method. The molecular weight cut-off of the membranes range from 0.5 kDa up to 100 kDa or even 500 kDa (Chang et al., 2001; Goslan et al., 2004; Hu et al., 2015; Hua and Reckhow, 2007b; Hua et al., 2015; Özdemr, 2014; Wei et al., 2008b; Xu et al., 2007; Zhang et al., 2020b; Zhao et al., 2009).

Generated membrane fractions are defined as a molecular weight range which is based on the molecular weight cut-off of the membranes used, *e.g.* molecules that pass a membrane with a molecular weight cut-off of 100 kDa, but are rejected by a membrane with one of 30 kDa are defined as the 30-100 kDa fraction. This will be further called the theoretical molecular weight range of a fraction. However, Goslan et al. (2004) and Zhao et al. (2009) characterized their generated membrane fractions with size exclusion chromatography coupled to a ultraviolet detector at 254 nm. From this, it was concluded that the chromatograms of all fractions from the respective paper are largely overlapping. Furthermore, Zhao et al. (2009) reported that the apparent mean molecular weight values of the fractions measured from the chromatography were lower than expected from the molecular weight cut-offs.

This observation was also confirmed by other analytical techniques such as flow-field flow fractionation (Assemi et al., 2004). Here, the minimum, maximum and mean molecular weight value from each membrane fraction was determined. Fig. 2 shows the difference between the theoretical molecular weight range (crossed pattern bars) and the real molecular weight range of a fraction measured with flow-field flow fractionation (solid bars). Apart from the prominent overlap between the fractions, it can be seen that the 10-30 kDa and > 30 kDa fraction only contain molecules which are much smaller than 10 kDa, meaning that molecules bigger than 10 kDa were not present in the raw water. However, it is contra-intuitive that molecules smaller than 10 kDa were retained by the 30 kDa membrane. For ultrafiltration membrane fractionation, most authors use a dead-end stirred cell configuration. Here, the water flow is perpendicular to the membrane resulting in accumulation of the retained compounds and thereby inducing fouling onto the membrane. This fouling layer will act as an extra barrier, possibly retaining molecules smaller than the molecular weight cut-off of the membrane. Furthermore, the pore sizes of membranes are known not to be uniform, but to have a pore size distribution (Mulder, 1991). Therefore, molecular weight cut-off is defined as the molecular weight of compounds that are retained by the membrane for only 90 %, which might explain the partial overlap between the fractions (Chow et al., 2005; Zhao et al., 2009).

An alternative approach to perform a membrane fractionation was recently developed by Yin et al. (2019) (Fig. 1b). With the use of both a nanofiltration and ultrafiltration membrane in spiral wound modules, three distinct fractions from seawater were successfully obtained and characterized by liquid chromatography, namely (i) a fraction containing 95 % biopolymers, (ii) a fraction with 93% humic substances and their building blocks and (iii) a 87 % low molecular weight compound fraction (Yin et al., 2019). After pretreating a raw water sample with a 0.2 µm filter to remove the particulate matter, nanofiltration was performed to collect the low molecular weight molecules in the permeate stream. Humic substances and biopolymers are rejected by the nanofiltration membrane and are fed to a subsequent ultrafiltration membrane in which humic substances and biopolymers are separated on respectively the permeate and the retentate side. Diafiltration is performed in each step to ensure a higher purity of the fractions (Yin et al., 2019).

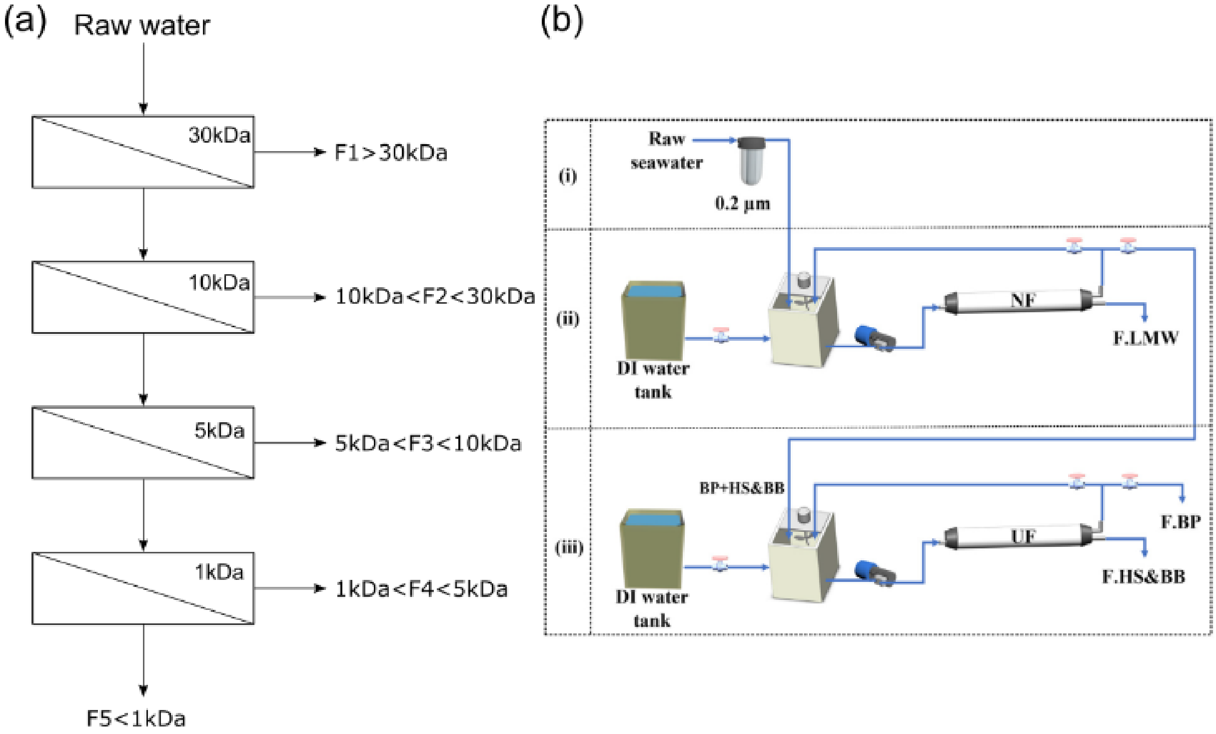

Fig. 1 (a) Dead-end ultrafiltration membrane fractionation of natural organic matter into five fractions (F1-5). Their molecular weight range is based on the molecular weight cut-off of the membrane (presented in the upper right corner of the rectangle) **(b)** Crossflow membrane fractionation by Yin et al. (2019) using consecutive nano- (NF) and ultrafiltration (UF) processes to split organic matter present in seawater into biopolymers (F.BP), humic substances & building blocks (F.HS&BB) and low molecular weight molecules (F.LMW). Demineralized (DI) water is added during the process to increase the purity of the fractions. Reprinted from [Water Research, 159, Wenqiang Yin, Xin Li, Stanislaus Raditya Suwarno, Emile R. Cornelissen, Tzyy Haur Chong, Fouling behavior of isolated dissolved organic fractions from seawater in reverse osmosis (RO) desalination process,385-396, copyright (2019)] with permission from Elsevier

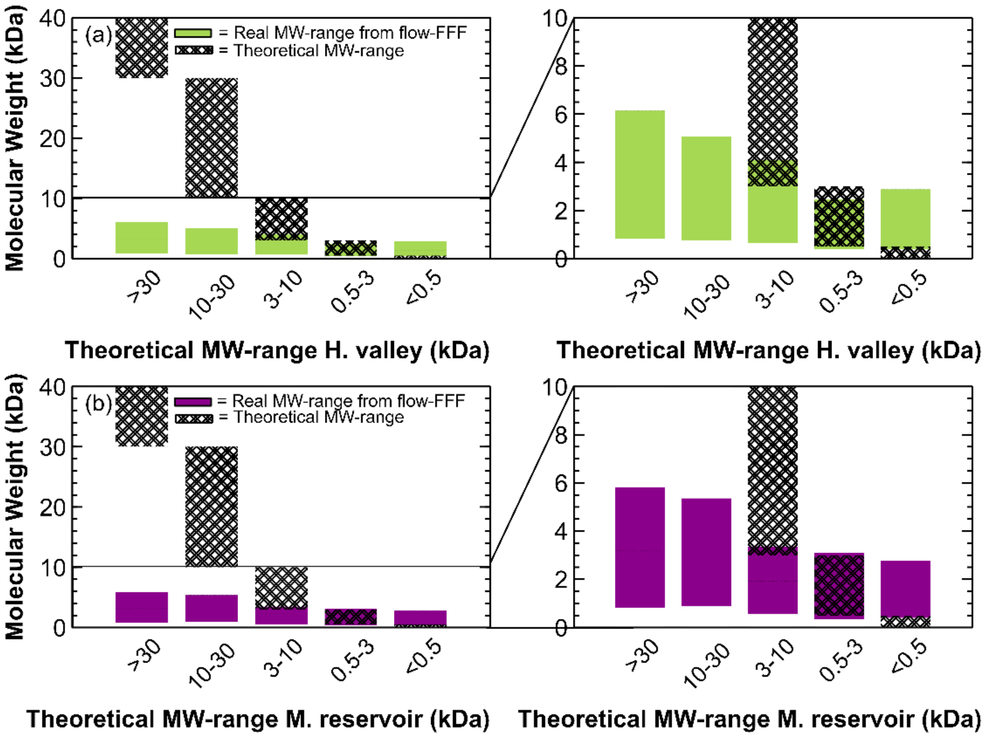

Fig. 2 Visualization of the results from Assemi et al. (2004) where organic matter in water samples from **(a)** Hope valley and **(b)** Myponga reservoir was fractionated into 5 fractions by dead-end ultrafiltration membrane fractionation and subsequently analyzed by flow-field flow fractionation (Flow-FFF). Each fraction is plotted on the x-axis and their theoretical molecular weight (MW)-range is determined by the molecular weight cut-off of each membrane. This range is visualized by cross pattern bars plotted on the y-axis. Flow-field flow fractionation (Flow-FFF) was used to determine the real molecular weight-range of each fraction, which is shown by solid bars plotted on the y-axis. A magnification of (a) and (b) between 0 and 10 kDa is given on the right side of these graphs. It is clear that the real molecular weight range of a fraction can differ substantially from its theoretical range. Furthermore, the real molecular weight range of the fractions are largely overlapping, meaning that the separation of organic matter based on size was unsuccessful.

Although membrane fractionation is a relatively fast and cheap method through the use of commercially available membranes, it seems to lack the ability to produce sharply separated fractions. The two main causes could be (i) the molecular weight cut-off of a membrane is not strict and (ii) dead-end cell operation causing fouling can influence the retention of all compounds. Therefore, care should be taken when interpreting the results of different studies using ultrafiltration fractionation, since it is not guaranteed that the fractions really contain the molecular weight range as defined by the molecular weight cut-offs of the ultrafiltration membranes. A crossflow filtration seems more reliable, since it reduces fouling and has the ability to pass the feedwater several times over the membrane, allowing the gradual removal of the desired compounds with diafiltration. This will however dilute the final concentrations in the membrane fractions. The relationship between membrane fractions and disinfection by-product formation is extensively studied and will be discussed in the next section.

3.2 Identification of membrane fractions involved in disinfection by-product formation

Fig. 3 represents the specific trihalomethane formation potential after different chlorination times and different specific ultraviolet absorbance ($SUVA_{254}$) values in several membrane fractions (section 6 for Methods). $SUVA_{254}$ is defined as the absorbance of ultraviolet light at 254 nm divided by the organic matter concentration (Ho et al., 2013). From this, it appears that the reactivity for trihalomethane formation increases when the molecular weight of organic material decreases, although the correlation remains weak. After 48 h with low chlorine dose or after 7 days with high chlorine dose, there is a clear difference between the highest and lowest membrane fractions. Here, the < 1 kDa fraction has significantly higher specific formation potential compared to the > 10 kDa fraction. On the other hand, only a small, non-significative discrepancy is seen between the highest (> 10 kDa) and lowest (< 1 kDa) membrane fractions after 24 h (low chlorine dose) or 72 h (high chlorine dose). It seems that $SUVA_{254}$ has no influence on the results, since fractionated waters with either high or low $SUVA_{254}$ give a same trend in specific trihalomethane formation potential (Fig. 3a,c).

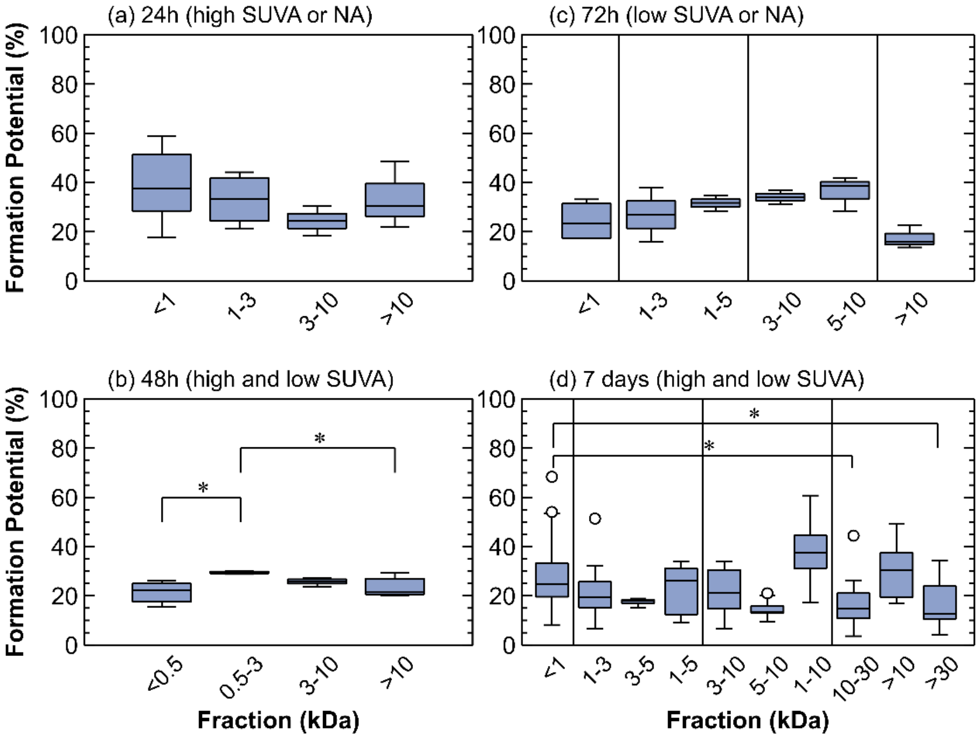

Fig. 3 Specific trihalomethane formation potential (%) in different membrane fractions after **(a)** 24h, high or not available (NA) specific ultraviolet absorbance at 254 nm ($SUVA_{254}$), low chlorine dose (5 water samples) **(b)** 48h, high and low $SUVA_{254}$, low chlorine dose (6 water samples) **(c)** 72h, low $SUVA_{254}$ or not available, high chlorine dose (5 water samples) and **(d)** 7 days, $SUVA_{254}$ is high, low or not available, high chlorine dose (29 water samples). * = statistical difference, ° = outlier. The specific trihalomethane formation potential slightly increases towards smaller molecular weight fractions. $SUVA_{254}$ or chlorine dose seem not to have an influence on this trend.

Moreover, di-halogenated acetic acid formation follows the same relationship as trihalomethanes between molecular weight and formation potential, since the < 1 kDa fraction has significantly higher formation potential compared to 3-10 kDa and > 10 kDa fraction (Fig. 4a). This trend is not visible at all for tri-halogenated acetic acid formation, where all 4 fractions have the same formation potential behavior (Fig. 4b). When overall specific haloacetic acid formation potential is measured, a small increase in reaction potential is seen after 7 days of reaction for lower molecular weight fractions, although it was not significant (Fig. 4d). However, after 72 h, an opposite trend is noticeable with a maximum formation potential in the 5-10 kDa fraction (Fig. 4c). No assessment of the effect of $SUVA_{254}$ could be made due to a lack of data. Table S1 provides the data collected for emerging disinfection by-products, but this dataset is too limited to draw any conclusion (Ge et al., 2020; Hua et al., 2015; Hua et al., 2020; Lin et al., 2014; Zhang et al., 2021; Zhang et al., 2020b).

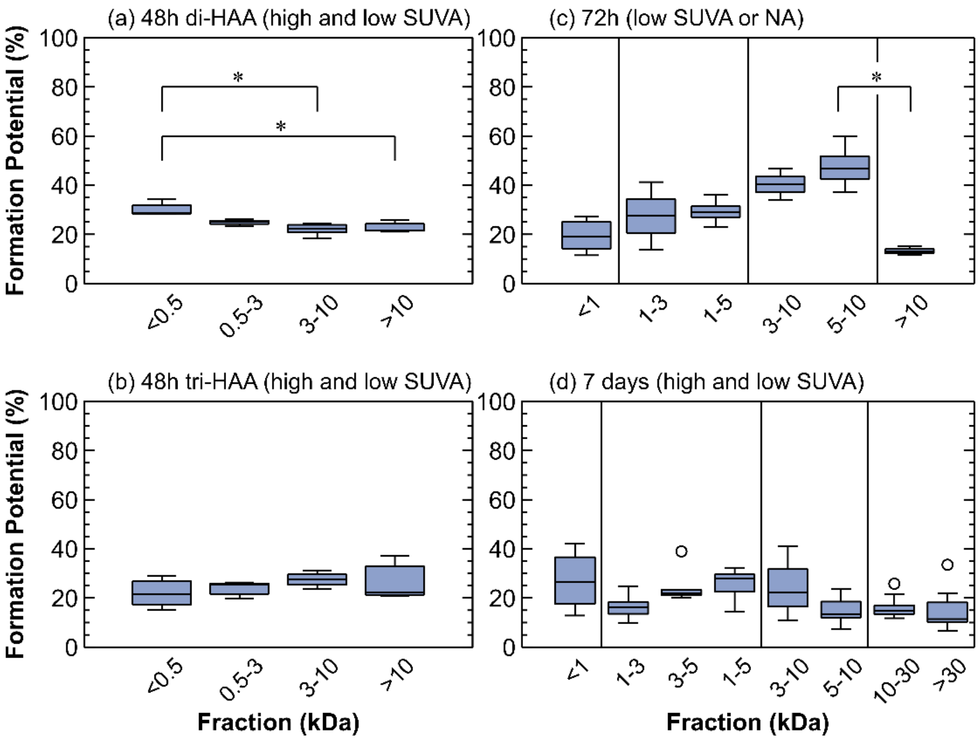

Fig. 4 Specific haloacetic acid formation potential (%) in different membrane fractions after **(a)** 48h, di-halogenated acetic acids (di-HAA), high and low specific ultraviolet absorbance at 254 nm ($SUVA_{254}$), low chlorine dose (6 water samples) **(b)** 48h, tri-halogenated acetic acids (tri-HAA), high and low $SUVA_{254}$, low chlorine dose (6 water samples) **(c)** 72h, low $SUVA_{254}$ or not available (NA), high chlorine dose (6 water samples) and **(d)** 7 days, $SUVA_{254}$ is high, low or not available, high chlorine dose (14 water samples). * = statistical difference, ° = outlier. Specific di-halogenated acetic acid formation is higher towards lower molecular weight fractions, while all fractions have the same formation potential for tri-halogenated acetic acids. No correlation was established when all haloacetic acids are included.

Also in literature, conflicting trends between specific trihalomethane formation potential and molecular weight range are stated. For example, the specific formation potential is reported to increase when the molecular weight of the fractions decreases, while on the other hand authors have reported a peak in specific formation potential in medium molecular weight fractions. In contradiction to the above findings, increasing formation potential with increasing molecular weight have also been reported and some studies show no correlation at all between the formation potential and molecular weight. Conflicting conclusions exist as well for both specific di-halogenated and tri-halogenated acetic acid formation potentials and emerging disinfection by-products (An et al., 2017; Avsar et al., 2015; Chang et al., 2001; Chiang et al., 2002; Gang et al., 2003; Ge et al., 2020; Goslan et al., 2004; Hu et al., 2015; Hua and Reckhow, 2007b; Hua et al., 2015; Hua et al., 2020; Karapinar et al., 2014; Kitis et al., 2002; Lin et al., 2014; Liu et al., 2011; Özdemr, 2014; Pi et al., 2021; Pramanik et al., 2015; Wei et al., 2008a; Wei et al., 2008b; Xu et al., 2007; Xu et al., 2011; Zhang et al., 2021; Zhang et al., 2020b; Zhang et al., 2010; Zhang et al., 2018; Zhao et al., 2006; Zhao et al., 2009).

In addition, Hua et al. (2020) analyzed waters with both high and low $SUVA_{254}$ values, including commercial humic acid as high $SUVA_{254}$ source and a surface water as low $SUVA_{254}$ source. Here, high molecular weight compounds (> 30 kDa) contributed the most to specific regulated and unregulated disinfection by-product formation potential. Precursors from high $SUVA_{254}$ waters showed a clear humic-acid like signal with high molecular weight, while precursors from low $SUVA_{254}$ waters showed a high molecular weight protein-like signal. On the other hand, both high and low molecular weight fractions have been indicated as having high regulated and unregulated disinfection formation potential consisting of humic acid-like and/or soluble microbial by-product-like compounds (Hua et al., 2007; Zhang et al., 2020b). The latter ones cover a wide range of molecular weight (0.5-50 kDa) (Barker and Stuckey, 1999). Furthermore, Zhang et al. (2016) showed with commercial humic acids that the formation of iodinated trihalomethanes increases with molecular weight.

The aforementioned $SUVA_{254}$ or molecular weight correlations were however not visible when data from all papers were taken together. Regarding the previous discussion on overlapping fractions in membrane fractionation (section 3.1), this could be an important drawback in the studies which intended to discriminate disinfection by-product formation on molecular weight. It would be beneficial to optimize the membrane fractionation approach. A possible starting point for this could be the fractionation protocol developed by Yin et al. (2019) (section 3.1). Analyzing trihalomethanes and haloacetic acid formation potentials on well-defined fractions might clarify the most important natural organic matter precursors.

Another observation made in literature is that the lowest molecular weight fractions produce relatively more brominated disinfection by-products and therefore, it has been stated that low molecular weight compounds are more reactive towards bromine (Hu et al., 2015; Xu et al., 2007). Nonetheless, the bromide-to-total organic carbon ratio in the different fractions will change depending on the retention of both organics and bromide during membrane filtration. When the concentration of bromide is adjusted to the initial concentration for all fractions, either the previous statement is confirmed or no specific trend is seen in bromide incorporation for the different fractions (Hua and Reckhow, 2007b; Kitis et al., 2002).

In summary, the relationship between molecular weight and disinfection by-product formation appeared to be very weak. Alternatively, natural organic matter is split based on hydrophobicity instead of size by the usage of resins. These different techniques will be elaborated in the next section.

4 Resin fractionation

4.1 Principle of resin fractionation

In resin fractionation, a liquid sample is fed to a polymeric resin adsorbing organic matter which is subsequently eluted using a solvent of suitable polarity (Minor et al., 2014). Aiken et al. (1979) introduced this technique for the first time using commercially available non-polar XAD–resins. The resins can be composed of styrene-divinylbenzene or methyl-methacrylate polymers (Daignault et al., 1988; Kim and Yu, 2005). Several modifications have been made over the years to optimize this method (Matilainen et al., 2011). XAD-8 and XAD-4 are the main resins used in the different fractionation methods. Since XAD-8 is no longer commercially available, XAD-7HP, DAX-8 or C18 silica resins have been used as alternatives. XAD-8 and DAX-8 show very comparable physical and chemical properties and their comparability for aquatic use has been proven (Chow, 2006). XAD-7HP has the same chemical structure as XAD-8 (polymethyl-methacrylate), but XAD-7HP has a larger surface area and is more porous (Pan et al., 2016). XAD-4 is composed of non-ionic styrene divinylbenzene polymer and C18 resins are composed of hydrocarbons bonded to a silica matrix and have generally higher recoveries than XAD-resins (Minor et al., 2014).

The simplest resin fractionation method generates a hydrophobic and hydrophilic fraction using a single XAD-8 resin at pH 2 (Fig. 5a). Adsorption onto XAD-resins occurs through aromatic π- electron and hydrophobic interactions (Bond et al., 2009). Therefore, compounds that are not retained are defined as hydrophilic compounds. The less hydrophilic compounds are adsorbed on the XAD-8 resin and defined as the hydrophobic fraction (Aiken et al., 1979; Jung and Son, 2008; Kim and Yu, 2005; Kim et al., 2006b; Kitis et al., 2002; Liang and Singer, 2003; Thurman and Malcolm, 1981). They are eluted with sodiumhydroxide at pH 11. Increasing the pH will ionize carboxyl and phenolic hydroxyl groups and desorb the hydrophobic compounds (Aiken et al., 1979).

An additional step has been added to this method by passing the hydrophilic fraction over a XAD-4 resin at pH 2 (Fig. 5b). The fraction that is not retained, is the hydrophilic (non-acid) fraction. The fraction that is retained by XAD-4 and eluted at pH 13 with sodiumhydroxide or acetonitrile is called the transphilic or hydrophilic acid fraction (Aiken et al., 1992; Croué, 2004; Golea et al., 2017; Hu et al., 2015; Hua and Reckhow, 2007b; Hua et al., 2015; Leenheer et al., 1999; Li et al., 2014; Malcolm and Maccarthy, 1992; Rho et al., 2019; Song et al., 2009; Tubić et al., 2013; Xu et al., 2007). The hydrophobic fraction is retained in a similar way as in the previous method with XAD-8, only the pH used to desorb the fraction is different (pH 11 vs. 13). A 100% effective elution at pH 13 is obtained due to the (complete) ionization of carboxyl and phenolic hydroxyl groups and a near 100% carbon recovery is obtained by co-current elution of a 75/25 acetonitrile/water mixture (Aiken et al., 1979; Croué, 2004).

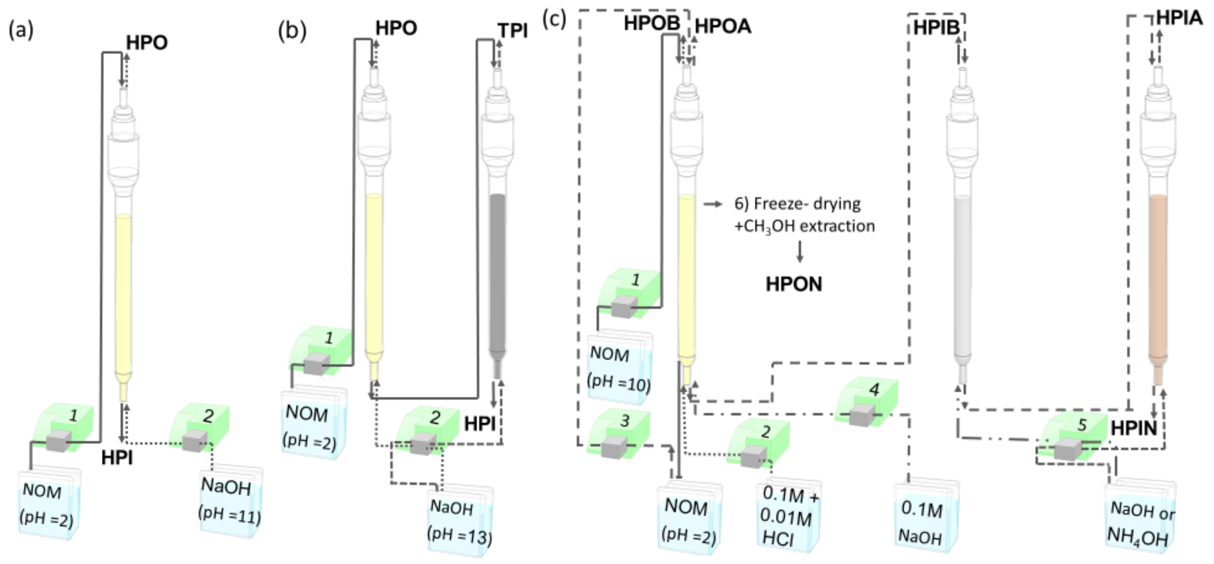

Fig. 5 Resin fractionation schemes to split natural organic matter (NOM) based on hydrophobicity. The numbers on the pumps represent the sequence of adsorption-desorption. HPO = hydrophobic, HPI = hydrophilic, TPI = transphilic. A = acid, B = base, N = neutral. Yellow = XAD-8, XAD-7HP or DAX-8 resin; black = XAD-4 resin; orange = Duolite A7, IRA 93 or WA10 resin; grey = AG-MP-50, Dowex MSC resin (a) HPO-HPI fractionation, (b) HPO-TPI-HPI fractionation. Acetonitrile can also be used as desorbent instead of sodiumhydroxide, (c) HPO(A+B+N)-HPI(A+B+N) fractionation. The water solution is acidified to pH =2 after the first run

A very elaborate resin fractionation splits natural organic matter into six fractions: hydrophobic acids, bases, neutrals and hydrophilic acids, bases and neutrals (Fig. 5c). More detailed information on organic species present in the water is obtained with this fractionation, which can facilitate subsequent analysis in different research fields, such as disinfection by-product formation. The most common method is to pass the sample through the XAD-8 resin twice. After the first run at pH 10 or without pH adjustment, hydrophobic bases are recovered by desorption with hydrochloric acid, which protonates the basic compounds. The second run is performed at pH 2, after which hydrophobic acids are eluted with sodiumhydroxide. This is the same approach as in the previous methods to obtain the overall hydrophobic fraction. The hydrophobic neutral fraction is obtained by (freeze-) drying the XAD-8 resin and extracting the compounds from the resin with methanol. DAX-8 and Bond Elute ENV cartridges (styrene-divinyl benzene) are also used for this purpose.

Subsequently, the hydrophilic compounds are split into acids, bases and neutrals by the use of ion exchange resins. The water sample at pH 2 is introduced to a cation exchange resin (AG-MP-50/Dowex MSC/Strata X-C) which retains the hydrophilic base compounds (Chang et al., 2000; Chang et al., 2001; Chen et al., 2008; Goss and Gorczyca, 2013; Kanokkantapong et al., 2006b; Lamsal et al., 2012; Leenheer, 1981; Marhaba et al., 2003; Ratpukdi et al., 2009; Zhang et al., 2009; Zhang et al., 2008). These are all strong acid, sulfonated resins with different backbone structures. AG-MP-50 consists of a polystyrene backbone, while Dowex MSC has a styrene-divinylbenzene structure (Leenheer, 1981; Meyer et al., 2020; Ratpukdi et al., 2009). A weak anion exchange resin (WA10/Duolite A7/IRA 93/Strata X-AW) retains the hydrophilic acid fraction at pH 2, while the hydrophilic neutral compounds are not retained. The anion exchange resins all consist of amine functionality (primary, secondary or tertiary) with different backbones, going from polystyrene, to acrylic polymers and even phenol-formaldehyde condensation matrices. Duolite A7 suffers from severe resin bleeding (Kananpanah et al., 2009; Leenheer, 1981; Marhaba et al., 2003; Miyazaki and Nakai, 2011; Ratpukdi et al., 2009). Ammoniumhydroxide or sodiumhydroxide are used to desorb both fractions. Ammoniumhydroxide returns the resins in their hydrogen (cation exchange resin) or free-base form (anion exchange resin) (Chang et al., 2000; Chang et al., 2001; Chen et al., 2008; Goss and Gorczyca, 2013; Kanokkantapong et al., 2006b; Lamsal et al., 2012; Leenheer, 1981; Marhaba et al., 2003; Ratpukdi et al., 2009; Zhang et al., 2009; Zhang et al., 2008).

Resin fractionation is a very common, relatively cheap and widely applied technique with the use of commercially available resins. The method can be either fast (into hydrophobic-hydrophilic) or time-consuming (into their respective acids, bases and neutrals). It simultaneously concentrates and fractionates organic matter, but there have been some doubts about possible changes in the chemical and/or physical nature of the water matrix due to the extreme pH-alterations (Matilainen et al., 2011; Swietlik et al., 2004). Furthermore, different column capacity factors are used among different authors. This factor is defined as

$$k' = \frac{mass\ of\ solute\ sorbed\ on\ the\ resin}{mass\ of\ solute\ dissolved\ in\ water}$$

and is directly proportional to the volume of water applied on a certain resin volume (Leenheer, 1981). The higher the value, the lower the percentage of hydrophobic compounds that is retained on a XAD-8 column for one water sample which can influence further assessments (Song et al., 2009). Also, flow rate and bed height of the column influence the adsorption equilibrium as both parameters change the contact time between adsorbate and adsorbent (Patel, 2019). These parameters are, however, very often lacking in the method sections.

In general, studies investigating disinfection by-product precursors with resin fractionation use one of the abovementioned resins and fractionation techniques. The only parameter that varies substantially is the column capacity factor which will therefore be considered in the next section when comparing the results of these studies.

4.2 Resin fractions involved in disinfection by-product formation

4.2.1 Trihalomethanes

When looking at the simplest fractionation technique, namely splitting natural organic matter into a hydrophobic and hydrophilic fraction, results are quite consistent (Fig. 6, section 6 for Methods). The hydrophobic fraction produces the highest specific trihalomethane formation potential regardless of chlorination time and $SUVA_{254}$ (k' = 100 or undefined). Specific ultraviolet absorbance ($SUVA_{254}$) is defined as the absorbance of ultra violet light at 254 nm divided by the organic matter concentration (Ho et al., 2013). Up to 72 h and low chlorine dose, hydrophobic moieties have 20 % higher specific formation potential compared to the hydrophilic fraction (Fig. 6a). After 7 days, the difference between the medians even increases to 60 %, although the boxplots themselves show more variability (Fig. 6b). After 7 days reaction time with high chlorine dose, both fast and slow reacting compounds will form trihalomethanes, thereby scattering the data (Chang et al., 2001; Chiang et al., 2002; Chiang et al., 2009; Galapate et al., 2001; Goss et al., 2017; Hyung Kim and Yu, 2005; Imai et al., 2003; Jung and Son, 2008; Kim et al., 2006a; Kim and Yu, 2005; Kitis et al., 2002; Kueseng et al., 2011; Liang and Singer, 2003; Musikavong et al., 2013). The hydrophobic fraction has previously been implicated as the primary source of trihalomethane precursors with some exceptions (Chow et al., 2005). The discrepancies have been allocated to differences in chlorination methods, but no thorough assessment was made.

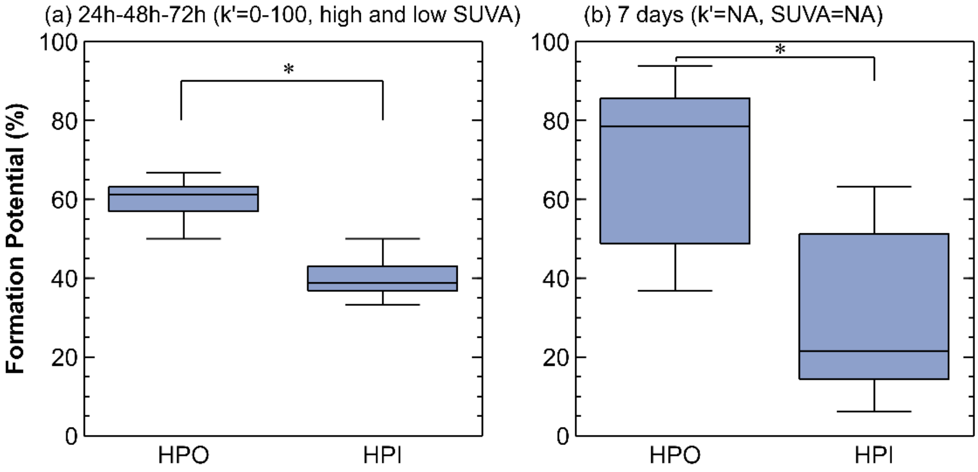

Fig. 6 Specific trihalomethane formation potential (%) in the hydrophobic (HPO) and hydrophilic (HPI) fraction after **(a)** 24h-48h-72h, high and low specific ultraviolet absorbance at 254 nm ($SUVA_{254}$), the column capacity factor (k') is between 0-100, but in most cases 100, low chlorine dose (25 water samples) **(b)** 7 days, $SUVA_{254}$ and k' in general not available (NA), high chlorine dose ($SUVA_{254}$ is 3x high, 1x low and k' is 2x 50 and 1x 100) (16 water samples). * = statistical difference. Hydrophobic compounds clearly have a higher specific trihalomethane formation potential compared to hydrophilic compounds irrespective of $SUVA_{254}$ or k'.

When the hydrophilic fraction is passed over the XAD-4 resin to generate the transphilic (or hydrophilic acid) fraction and the hydrophilic non-acid fraction, the situation becomes more complex, because the $SUVA_{254}$ value of the raw water influences the specific trihalomethane formation potential of the different fractions (Fig. 7). When $SUVA_{254}$ of the raw water is high (> 2 L/(mg·m)), the hydrophobic and transphilic fraction have a similar reaction potential (~30 %) to trihalomethane formation at short reaction times and low chlorine dose, while hydrophobic compounds have significantly higher specific trihalomethane formation potential compared to the transphilic and hydrophilic fraction at long reaction times with high chlorine dosage (Fig. 7a,c). Conversely, when the $SUVA_{254}$ level is below 2 L/(mg·m), hydrophilic organics have equally important trihalomethane formation potential as hydrophobic organics at short reaction times (~40 %), while transphilic organic matter seems slightly more reactive after 7 days of reaction and high chlorine dose (Fig. 7b,d) (Agbaba et al., 2014; Chowdhury et al., 2008; Fang et al., 2021; Goslan et al., 2002; Goslan et al., 2004; Hanigan et al., 2013; Hu et al., 2015; Hua and Reckhow, 2007b; Hua et al., 2015; Li et al., 2014; Lin and Wang, 2011; Lin et al., 2014; Liu et al., 2011; Molnar et al., 2012a; Molnar et al., 2013; Molnar et al., 2012b; Musikavong et al., 2016; Niu et al., 2015; Phetrak et al., 2016; Pi et al., 2021; Roccaro et al., 2014; Smith and Al Qabany, 2009; Tubić et al., 2013; Wang et al., 2013; Wei et al., 2008a; Wei et al., 2008b; Xu et al., 2007; Xue et al., 2010; Zhang et al., 2021; Zhao et al., 2013; Zhi-sheng et al., 2009).

Overall, the hydrophobic fraction is an important contributor to trihalomethane formation at high $SUVA_{254}$, especially at long reaction times with high chlorine dosage, while both hydrophobic and hydrophilic compounds are important at low $SUVA_{254}$. This observation could not be verified in the previous fractionation, since only 5 water samples were found to have low $SUVA_{254}$ values. From these 5 samples, 4 of them were chlorinated with a low dose between 24 and 72 h. Here, the ratio of 60 % trihalomethane formation from the hydrophobic fraction and 40 % from the hydrophilic fraction was valid, except for one sample that had a ratio of 53 % versus 47 %. The only water sample analyzed after 7 days and high chlorine dose showed a ratio of only 37 % trihalomethane formation from hydrophobic compounds and 63 % from hydrophilic compounds (Chiang et al., 2009; Hyung Kim and Yu, 2005; Imai et al., 2003; Kim et al., 2006a; Kim and Yu, 2005).

Disinfection by-product formation investigated with natural organic matter surrogates has shown that activated aromatic moieties in the presence of an electron-donating and ortho-para directing group have high rate constants towards chlorine reactivity, because hypochlorous acid (an electrophile) preferentially reacts with electron-rich functionalities in organic molecules. These moieties will also contribute to high $SUVA_{254}$ values and reside in the hydrophobic fraction (Bond et al., 2012a; Bond et al., 2009). When the $SUVA_{254}$ value is low, other chemical functionalities with lower reactivities, such as amino acids or carbohydrates (hydrophilic compounds), will become important especially after longer reaction time and high chlorine dose (Bond et al., 2012a).

Nonetheless, the behavior of the transphilic fraction for both high and low $SUVA_{254}$ conditions is less clear. This fraction has been characterized as having greater heteroatom and carboxyl content than the hydrophobic fraction, but also as having a number of similar properties with the hydrophobic fraction (Aiken et al., 1992). The C/O, C/H and C/N atomic ratios gradually decrease from hydrophobic to transphilic to hydrophilic (Croué, 2004). Furthermore, fractionation of surrogates with different polarities could not identify molecules having clear transphilic character. Surrogates ending up in the transphilic fraction were evenly distributed in either the hydrophobic or hydrophilic fraction (Bond et al., 2009). This implies that depending on the natural organic matter composition of the water source, the transphilic fraction can have more hydrophobic or hydrophilic character, which will influence its specific trihalomethane formation potential.

Within the hydrophobic fraction in both resin fractionation methods, humic acids are the most important precursors. Humic acids precipitate when acidifying the hydrophobic fraction to pH = 1, while fulvic acids remain dissolved (Agbaba et al., 2014; Goslan et al., 2002; Goslan et al., 2004; Jung and Son, 2008; Molnar et al., 2012a; Molnar et al., 2012b; Tubić et al., 2013; Zhi-sheng et al., 2009).

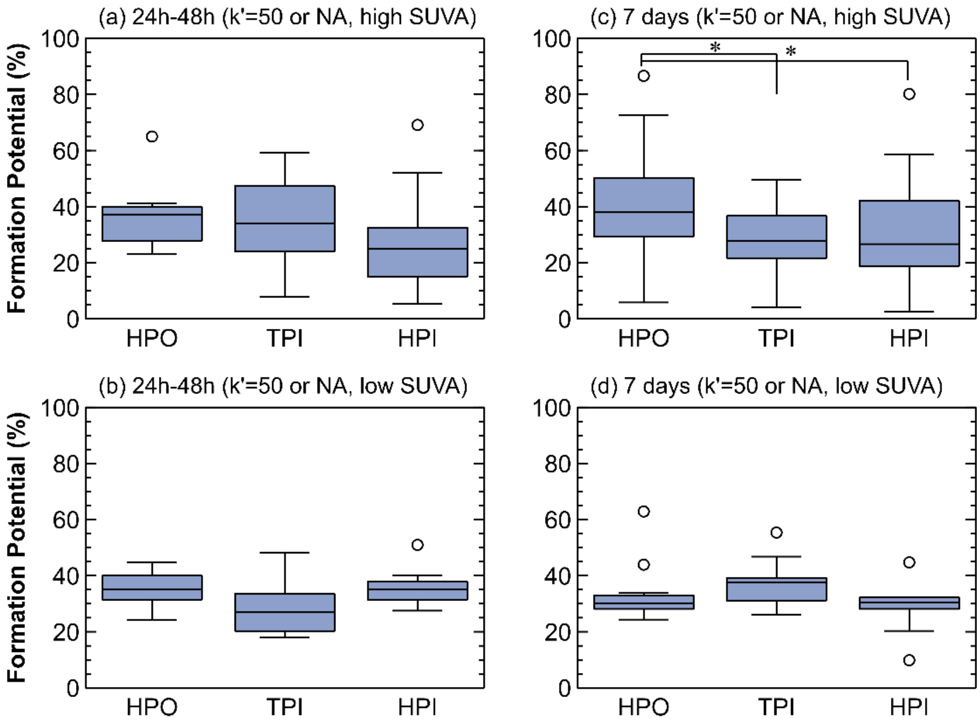

Fig. 7 Specific trihalomethane formation potential (%) in the hydrophobic (HPO), transphilic (TPI) and hydrophilic (HPI) fraction after **(a)** 24h-48h, high specific ultraviolet absorbance at 254 nm (SUVA$_{254}$), the column capacity factor k' is 50 (1x 100) or not available (NA), low chlorine dose (13 water samples) **(b)** 24h-48h, low SUVA$_{254}$, k' is 50 or not available, low chlorine dose (7 water samples) **(c)** 7 days, high SUVA$_{254}$, k' is 50 or not available, high chlorine dose (39 water samples) and **(d)** 7 days, low SUVA$_{254}$, k' is 50 or not available, high chlorine dose (11 water samples). * = statistical difference, ° = outlier. When the SUVA$_{254}$ of the raw water is greater than 2 L/(mg·m), the HPO fraction contributes the most to trihalomethane formation, especially at long chlorination time with high chlorine dose. When the SUVA$_{254}$ is below 2, the hydrophobic and hydrophilic fraction have equal trihalomethane formation potential. The contribution of the transphilic fraction is very variable

Limited data was found for specific trihalomethane formation potential after fractionation of natural organic matter into hydrophobic and hydrophilic acids, bases and neutrals (Fig. S1). At short reaction times, the hydrophobic acid fraction seems equivalent to the hydrophilic base fraction, although the dataset was too small to find statistical differences. The SUVA$_{254}$ was low, so it confirms the statement that both hydrophobic and hydrophilic fractions are important in low SUVA$_{254}$ waters, and possibly, in more detail the hydrophobic acid and hydrophilic base fraction. At long chlorination times, however, it is the hydrophobic and hydrophilic base fraction and to a lesser extent the hydrophobic neutral fraction that have the highest specific trihalomethane formation potential, especially compared to hydrophilic neutrals (Chang et al., 2000; Chen et al., 2008; Fan et al., 2013;

Goss and Gorczyca, 2013; Lamsal et al., 2012; Lin et al., 2010; Marhaba and Van, 2000; Panyapinyopol et al., 2005a; Panyapinyopol et al., 2005b; Rakruam and Wattanachira, 2014; Sharma et al., 2021; Włodyka-Bergier and Bergier, 2011; Yee et al., 2009; Yee et al., 2006). Bases are defined as electron donors, thereby promoting the reaction with the electron poor hypochlorous acid (Bond et al., 2012a). Furthermore, hydrophilic bases have been characterized as amide-like compounds, while the hydrophilic neutral fraction mainly contains lignin and lipids (Wang et al., 2019). From Fig. S1, there is thus an indication that lignin and lipids are recalcitrant to the formation of trihalomethanes, while amide-like compounds might be important precursors. The occurrence of the hydrophobic acid fraction is less straightforward, however, this is only based on 3 water samples.

The column capacity factor k' seems to have no influence on the results. Where the factor k' is 100 in the hydrophobic-hydrophilic fractionation, it is 50 in the hydrophobic-transphilic-hydrophilic fractionation. However, in the latter resin technique, data was found where both values have been used during a 72h chlorination time with high chlorine dose (Fig. S2). Changing k' from 50 to 100 will result in less adsorption of hydrophobic and transphilic compounds on XAD-8 and XAD-4 respectively and this results into a changing trend in specific trihalomethane formation potential from the hydrophobic fraction as most important precursor (Fig. S2a) to the hydrophilic fraction (Fig. S2b) (Liu et al., 2011; Pi et al., 2021; Roccaro et al., 2014; Song et al., 2009; Zhang et al., 2021). So, although the column capacity factor k' value did not affect the comparison between two fractionation techniques, it stays important to be aware of this value at all times.

Finally, the hydrophilic fraction seems more sensitive to the formation of brominated trihalomethanes (Agbaba et al., 2014; Chiang et al., 2009; Goss and Gorczyca, 2013; Hu et al., 2015; Hua and Reckhow, 2007b; Kitis et al., 2002; Li et al., 2014; Liang and Singer, 2003; Molnar et al., 2013; Molnar et al., 2012b; Musikavong et al., 2013; Musikavong et al., 2016; Niu et al., 2015; Panyapinyopol et al., 2005a; Panyapinyopol et al., 2005b; Tubić et al., 2013; Włodyka-Bergier and Bergier, 2011; Xu et al., 2007). In this regard, it is important to keep the same bromide-to-total organic carbon ratio in all fractions. XAD-resins are non-ionic resins thereby not retaining ions (Aiken et al., 1979; Daignault et al., 1988). Most of the bromide ions will therefore elute with the hydrophilic fraction. These bromide ions will compete with organic carbon in the reaction with chlorine (rate constant k (HOCl/Br^{-}) = 1550·1/Ms) to produce bromine, which subsequently reacts with the total organic carbon to produce brominated disinfection by-products (Criquet and Allard, 2021). Bromine reactions towards phenolic moieties, which are important constituents of natural organic matter, are up to three orders of magnitude greater than for chlorine. This higher reactivity explains the tendency of brominated disinfection by-product formation even for a low bromide concentration (Criquet et al., 2015; Heeb et al., 2014). When the bromide-to-total organic carbon ratio is adjusted in all fractions, hydrophilic moieties are still more reactive towards bromine. This implies that bromination occurs with aliphatic precursors while chlorination is more related to aromatic precursors (Hua and Reckhow, 2007b; Kitis et al., 2002; Liang and Singer, 2003).

In summary, hydrophobic compounds produce the highest specific trihalomethane formation potential, regardless of $SUVA_{254}$ or chlorination time, while hydrophilic compounds cannot be ignored when the $SUVA_{254}$ of the raw water is low. Finally, base compounds are identified as one of the most important precursors for trihalomethane formation. Haloacetic acids, as the second regulated disinfection by-product family, have also been the focal point in research with resin fractionation and results from these studies will be discussed in the next section.

4.2.2 Haloacetic acids

Fig. 8 shows the results from the hydrophobic-hydrophilic fractionation. As for the trihalomethanes, the hydrophobic fraction has 60 % contribution to the total specific haloacetic acid formation potential, while this is 40 % for the hydrophilic fraction at shorter reaction times, low chlorine dose and high specific ultraviolet absorbance ($SUVA_{254}$) (Fig. 8a, section 6 for Methods) (Jung and Son, 2008; Kitis et al., 2002; Liang and Singer, 2003). $SUVA_{254}$ is defined as the absorbance of ultraviolet light at 254 nm divided by the organic matter concentration (Ho et al., 2013). Two water samples analyzed after 7 days and high chlorine concentrations also showed around 89% specific formation potential from the hydrophobic fraction compared to only 11% from the hydrophilic fraction (Chang et al., 2001; Chiang et al., 2002). On the contrary, three water samples with low $SUVA_{254}$ showed that hydrophilic compounds have by far the highest reaction potential at short reaction times and low chlorine dose (Fig. 8b) (Hyung Kim and Yu, 2005; Kim et al., 2006a; Kim and Yu, 2005).

Furthermore, in the hydrophobic-transphilic-hydrophilic fractionation, the hydrophobic and hydrophilic fraction are significantly different from the transphilic fraction, but not significantly different with each other at low $SUVA_{254}$, especially after 7 days of chlorination time with high chlorine dose (Fig. 9). Where the hydrophilic fraction has almost 30% higher specific haloacetic acid formation potential compared to the hydrophobic fraction when organic matter is split into hydrophobic-hydrophilic only (Fig. 8b), hydrophobic and hydrophilic compounds contribute both to 30-40% of the total specific haloacetic acid formation potential when the fractionation is done into hydrophobic-transphilic-hydrophilic (Fig. 9b,d) (Fang et al., 2021; Li et al., 2014; Niu et al., 2015). This might be explained by the different column capacity factors k’ used between the 2 fractionation techniques (k’=100 vs. k’=50). Limited data after 72h chlorination time with high chlorine dose shows that the contribution of the hydrophilic fraction becomes higher when this k’-factor changes from 50 to 100 which is in agreement with the higher reaction potential seen for hydrophilic compounds in the hydrophobic-hydrophilic fractionation (Fig. S3) (Liu et al., 2011; Pi et al., 2021; Roccaro et al., 2014; Zhang et al., 2021).

Waters fractionated into hydrophobic-transphilic-hydrophilic moieties with high $SUVA_{254}$ shows that the hydrophobic fraction has a higher formation potential to some degree when comparing the medians, although not significant (Fig. 9a,c). The transphilic fraction is in general the least important fraction to specific haloacetic acid formation potential (Chowdhury et al., 2008; Fang et al., 2021; Hanigan et al., 2013; Karapinar et al., 2014; Li et al., 2014; Molnar et al., 2012a; Qadafi et al., 2021; Roccaro et al., 2014; Tubić et al., 2013; Wang et al., 2013; Zhao et al., 2013).

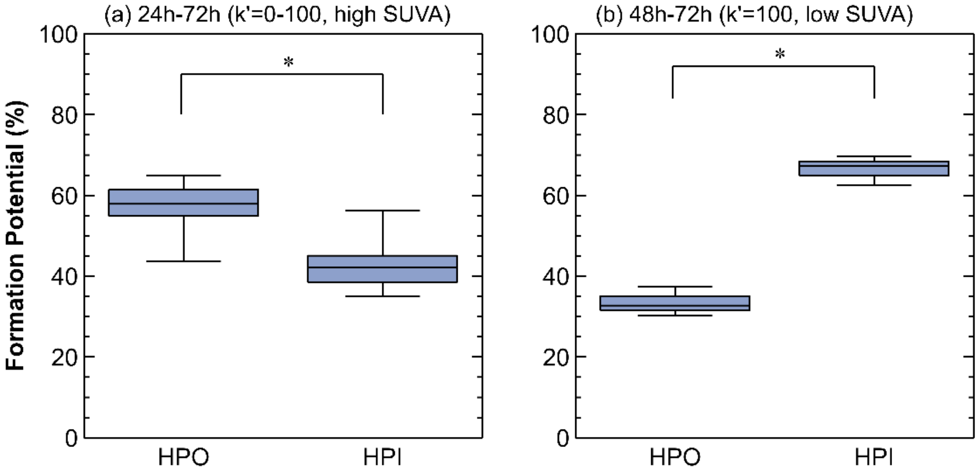

Fig. 8 Specific haloacetic acid formation potential (%) in the hydrophobic (HPO) and hydrophilic (HPI) fraction after **(a)** 24h-72h, high specific ultraviolet absorbance at 254 nm ($SUVA_{254}$), column capacity factor k' is between 0-100, but in most cases 100, low chlorine dose (15 water samples) **(b)** 48h-72h, low $SUVA_{254}$, k' is 100, low chlorine dose (3 water samples). * = statistical difference. The hydrophobic fraction has significantly higher specific haloacetic acid formation potential compared to the hydrophilic fraction when $SUVA_{254}$ is high, while the opposite is seen when $SUVA_{254}$ of the raw water is low

Data for the fractionation of the hydrophobic and hydrophilic fraction into their acids, bases and neutrals is limited to 72 h and 7 days of chlorination, high chlorine dose and 7 water samples (Fig. S4). The bases seem to have a slightly higher influence in specific haloacetic acid formation potential compared to the other fractions which is in agreement with the preference of the electrophilic hypochlorous acid to react with bases (Bond et al., 2012a; Chen et al., 2008; Fan et al., 2013; Kanokkantapong et al., 2006a; Kanokkantapong et al., 2006b; Kanokkantapong et al., 2006c; Lamsal et al., 2012; Marhaba and Van, 2000).

Some research evaluated the formation of di-halogenated and tri-halogenated acetic acids separately (Fig. S5). The formation potential of the hydrophobic fraction for tri-halogenated acetic acids is significantly (~20 %) higher compared to the hydrophilic and transphilic fraction independent from the column capacity value (Fig. S5c,d). On the other hand, di-halogenated acetic acid formation potential is 20% higher in the hydrophobic fraction at high $SUVA_{254}$ and column capacity factor k' of 100, while the hydrophilic fraction has the highest reaction potential at high and low $SUVA_{254}$ and k'-factor of 50 (Fig. S5a,b). It has been stated that dichloroacetic acid and trichloroacetic acid follow a different reaction pathway and that trichloroacetic acid and trihalomethanes are generated by common intermediates. This has been concluded by surrogate analysis, where trichloroacetic acid precursors tend to be more hydrophobic and dichloroacetic acid precursors have more aliphatic structures (Bond et al., 2012a). These statements could not be completely confirmed with the collected data. However, it should be noted that these data were drawn from three different papers only and more research should be done to clarify these assumptions (Hua and Reckhow, 2007b; Hua et al., 2015; Liang and Singer, 2003).

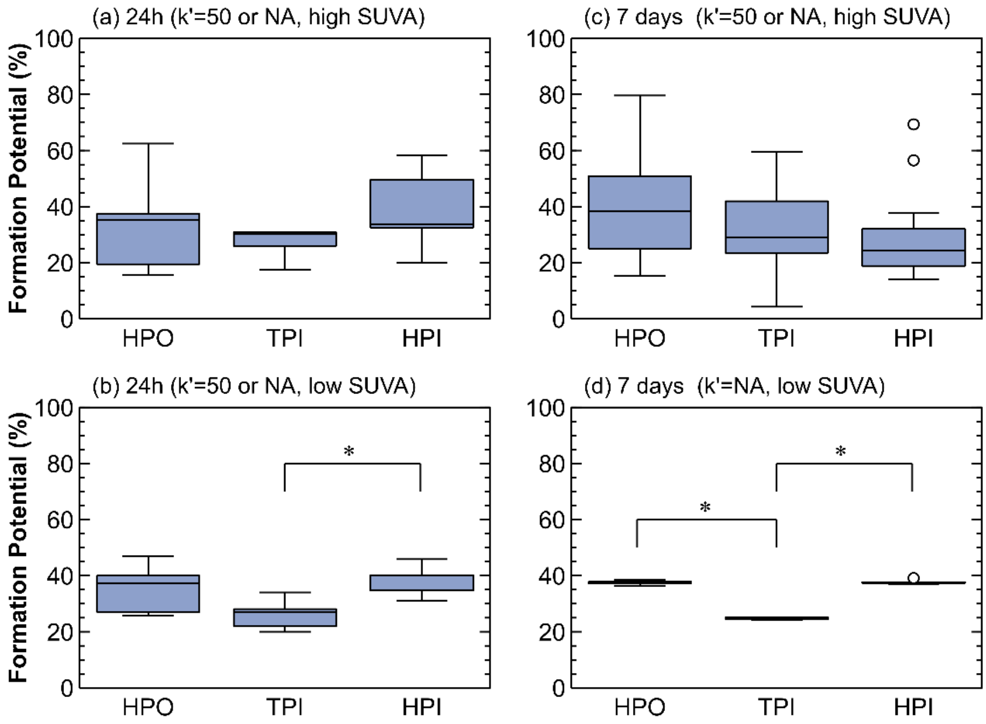

Fig. 9 Specific haloacetic acid formation potential (%) in the hydrophobic (HPO), transphilic (TPI) and hydrophilic (HPI) fraction after **(a)** 24h, high specific ultraviolet absorbance at 254 nm ($SUVA_{254}$), column capacity factor k' is 50 (1x 100) or not available (NA), low chlorine dose (5 water samples) **(b)** 24h, low $SUVA_{254}$, k' is 50 or not available, low chlorine dose (5 water samples) **(c)** 7 days, high $SUVA_{254}$, k' is 50 or not available, high chlorine dose (12 water samples) and **(d)** 7 days, low $SUVA_{254}$, k' is not available, high chlorine dose (5 water samples). * = statistical difference, ° = outlier. Data from (c) suggest that hydrophobic moieties have slightly higher tendency to form haloacetic acids when the $SUVA_{254}$ of the raw water is high (>2 L/(mg·m)). Conversely, at low $SUVA_{254}$ values, both hydrophobic and hydrophilic moieties have equal and consistently higher specific haloacetic acid formation potential compared to the transphilic fraction.

Furthermore, some data on bromide incorporation show a higher reactivity of hydrophilic fractions to produce brominated haloacetic acids (Hua and Reckhow, 2007b; Kitis et al., 2002; Li et al., 2014; Liang and Singer, 2003; Molnar et al., 2012a; Niu et al., 2015; Qadafi et al., 2021; Tubić et al., 2013; Włodyka-Bergier and Bergier, 2011).

To summarize, the precursors of haloacetic acids are found to be very similar to the precursors of trihalomethanes. They have hydrophobic character when $SUVA_{254}$ is high, although less pronounced than for the trihalomethanes, but have both hydrophobic and hydrophilic origin with $SUVA_{254}$ is low. While chlorination time does not affect the outcome, there is an indication that the column capacity factor does change the formation potential behavior in the different fractions. Besides the studies on regulated disinfection by-products, more attention arose in the last years to assess the precursors of emerging disinfection by-products and the results of these studies will be presented in the final section.

4.2.3 Emerging disinfection by-products

Emerging or unregulated disinfection by-products, such as haloacetamides, haloacetonitriles, nitrosamines or haloketones, have received increased attention due to their higher toxicity compared to regulated disinfection by-products (Wagner and Plewa, 2017). However, studies on the formation of these by-products in different membrane or resin fractions with chlorine are nowadays still limited. Most research focused on the formation of emerging disinfection by-products after chloramination. Chloramine can significantly reduce the formation of trihalomethanes and tri-halogenated acetic acids, but will greatly increase the formation of emerging nitrogenous disinfection by-products such as N-nitrosodimethylamine (Chu et al., 2010; Hua and Reckhow, 2007a; Lin et al., 2014; Wang et al., 2013).

A small number of studies focused on the formation of emerging disinfection by-products in resin fractions disinfected with chlorine, *i.e.* haloacetamides, haloacetonitriles, halonitromethanes, halo-aldehydes and haloketones. Insufficient data was collected for the last family to discuss a trend. Studies on emerging disinfection by-products are most often executed with high chlorine dose even at short reaction times, possibly because they are formed in very low concentrations during drinking water disinfection (Richardson et al., 2007).

Despite chlorination time, dose or specific ultra violet absorbance ($SUVA_{254}$), hydrophilic compounds clearly have a higher tendency to form emerging disinfection by-products (section 6 for Methods) (Ho et al., 2013). $SUVA_{254}$ is calculated by dividing the ultraviolet absorbance at 254 nm by the organic matter concentration. Fig. 10 and Figure S6 show a specific formation potential that is 20-80 % higher for the hydrophilic fraction compared to the hydrophobic or transphilic fraction for most families included (Fang et al., 2021; Ge et al., 2020; Hu et al., 2015; Hu et al., 2010; Hua et al., 2015; Lin et al., 2014; Molnar et al., 2013; Molnar et al., 2012b; Roccaro et al., 2014; Tan et al., 2017; Zhang et al., 2020a; Zhang et al., 2021). Halonitromethanes show no significant difference between the formation potentials of all 3 fractions, despite the aspect of the graph (Fig. 10c). This is supported by studies performing disinfection by-product formation tests on surrogates. Proteinaceous material together with amino acids have been identified as haloacetonitrile precursors, while haloacetamides can also be formed through the hydrolysis of haloacetonitriles. However, studies on hydrophilic surrogates showed very low yield for trichloronitromethane, except for glycine (Bond et al., 2012b).

The influence of the column capacity factor k’ stays inconclusive, because either a k’-factor of 50 is used or the value is missing in the studied papers. There is a small indication that the value is less important in the analysis of emerging disinfection by-products, since hydrophilic compounds also had the highest contribution in a water sample with a k’ of 100 for haloacetonitriles and 2 water samples with a k’ of 15 for halonitromethane (Hu et al., 2010; Roccaro et al., 2014). Furthermore, elaborate resin fractionation in acids, bases and neutrals is hardly executed for emerging disinfection by-products. The results for haloacetonitrile, halo-aldehyde and trichloronitromethane are presented in Fig. S7, but no statistical differences or trends could be highlighted (Chu et al., 2010; Fan et al., 2013; Włodyka-Bergier and Bergier, 2011). In synopsis, emerging disinfection by-products clearly have hydrophilic precursors regardless of $SUVA_{254}$, chlorination time or dose.

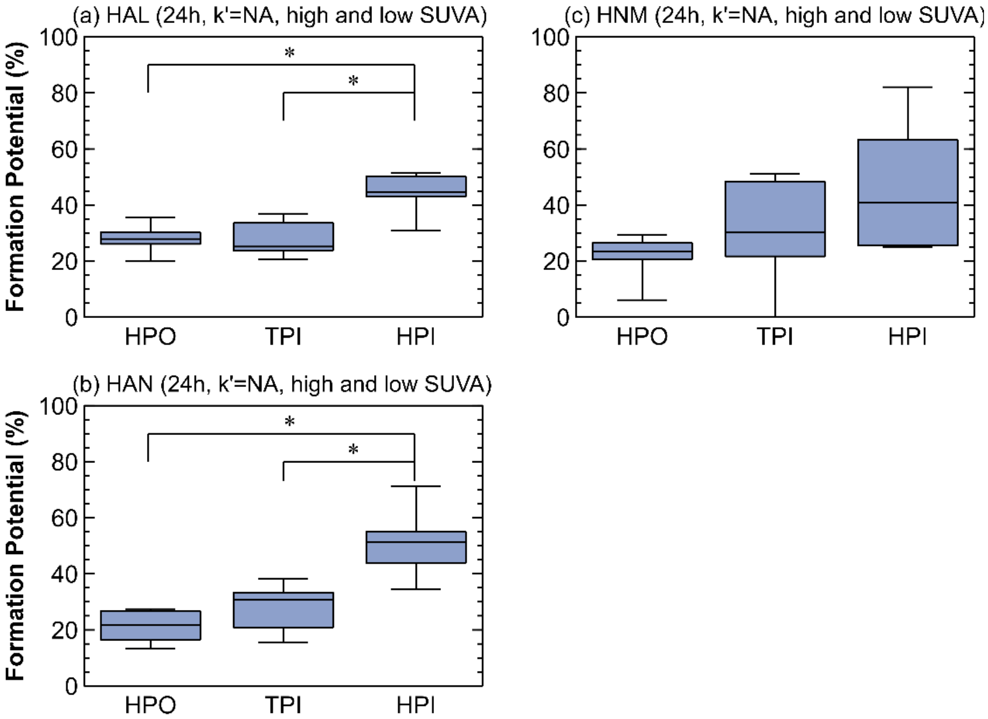

Fig. 10 Specific disinfection by-product formation potential (%) in the hydrophobic (HPO), transphilic (TPI) and hydrophilic (HPI) fraction after 24h and both high and low specific ultraviolet absorbance at 254 nm ($SUVA_{254}$) values of **(a)** halo-aldehydes (HAL), column capacity factor k’ is not available (NA), low chlorine dose (5 water samples) **(b)** haloacetonitriles (HAN), k’ is not available (1x 100), low chlorine dose (6 water samples) and **(c)** halonitromethanes (HNM), k’ is not available (2x 15), low chlorine dose (7 water samples). * = statistical difference. From the data, it is clear that all families are preferentially formed in the hydrophilic fraction, although this was not statistically significant for the halonitromethanes

This meta-analysis determined the parameters affecting the identification of disinfection by-product precursors, because no assessments were done so far in the past. This review identified hydrophobic compounds as having high trihalomethane and haloacetic acid formation potential especially for high $SUVA_{254}$ and low k’- factor values. Hydrophilic moieties are overall the most important precursors for the formation of emerging disinfection by-products, but can also not be neglected as trihalomethane and haloacetic acid precursor when $SUVA_{254}$ of the raw water is low and high column capacity factors are used. Furthermore, this study could not identify the disinfection by-product precursors based on molecular weight, which might be explained by an unsharp separation of natural organic matter during membrane fractionation. A graphical summary of all results can be found in Fig. 11.

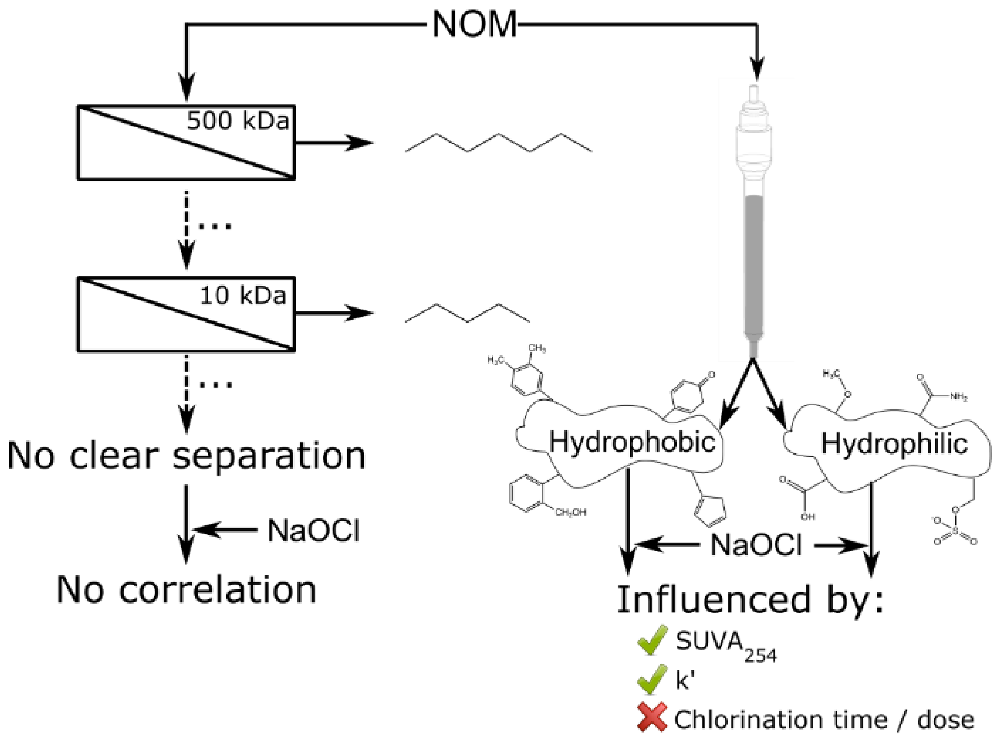

Fig. 11 Overview scheme of the conclusions drawn in this meta-analysis. NOM = natural organic matter. There is an indication that ultrafiltration membrane fractionation cannot produce sharply separated fractions. Therefore, no correlation was found between disinfection by-product formation and molecular weight. During resin fractionation, chlorination time and dose do not affect the ratio of disinfection by-product formation between the different fractions, while the specific ultraviolet absorbance at 254 nm ($SUVA_{254}$) and the column capacity factor k’ do have an effect on this ratio.

5 Conclusions and Outlook

This review critically evaluated different natural organic matter fractionation techniques with regard to disinfection by-product formation. The formation of trihalomethanes, haloacetic acids and emerging disinfection by-products from the different fractions obtained by both membrane and resin fractionation after chlorination was assessed. The general conclusions are:

- Dead-end, ultrafiltration, membrane fractionation allows the production of fractions in large volumes, but there is an indication that it lacks the ability to perform a sharp separation of the different fractions. Therefore, no relationship was found between molecular weight and disinfection by-product formation potentials.
- Resin fractionation splits natural organic matter based on polarity. Despite being a generally accepted method of fractionation, the potential of changing the organic matter composition due to the pH changes is often underestimated. The most important observations of this study are:
    - Chlorination time and dose do not influence the proportion of specific disinfection by-product formation potential between different fractions.
    - Hydrophobic compounds are the most important contributors with 10-20 % higher reactivity to both trihalomethane and haloacetic acid formation in waters with high specific ultraviolet absorbance ($SUVA_{254}$), while hydrophobic and hydrophilic compounds are equally important in water with low $SUVA_{254}$. However, hydrophilic compounds have 20-80 % higher reactivity towards emerging disinfection by-products, regardless of $SUVA_{254}$.
    - Increasing the column capacity factor k' *i.e.* the amount of hydrophobic compounds retained on XAD-resins can shift the highest specific formation potential from hydrophobic to hydrophilic fractions.

Future research should focus on the development of an alternative membrane fractionation method to have sharply, defined and separated size-based fractions. This allows to clearly mark the effect of a certain physical property to disinfection by-product formation. Furthermore, it is important to report the k' value used in resin fractionation, because it can influence the disinfection by-product formation in the different fractions. In addition, fraction analysis for disinfection by-product formation with chlorine is currently limited to regulated disinfection by-product, with only minor research done in this field for emerging disinfection by-product. These groups of disinfection by-product are formed in lower concentrations, but could exhibit a higher toxicity, and therefore, may cause greater public health problems. Therefore, further research should focus on the formation of a broader group of disinfection by-product in different membrane and resin fractions to increase knowledge on natural organic matter precursors and therefore provide safer drinking water now and in the future.

6 Methods

6.1 Data collection

The Scopus library was used to collect papers from the last 2 decades as a continuation of the review paper of Chow et al. (2005) which was at that time only focused on trihalomethanes. The criteria for selecting a paper were water source (*i.e.* fresh water), disinfectant (*i.e.* chlorine) and the use of preparative fractionation. Natural waters were selected from all over the world, since it is believed that this natural organic matter pool is universal due to the natural processes of synthesis and degradation (Zark and Dittmar, 2018). Since treatment processes can influence the organic matter composition, *e.g.* leakage of soluble microbial products from biological activated carbon, only raw water sources were included (Hong et al., 2018). With all these criteria, 83 papers were selected, resulting in data collection from 396 water samples from all over the world with a high number of publications in the United States and Asia (Fig. S8).

6.2 Data processing

The data was uniformized to be able to compare all papers with each other. First, the specific disinfection by-product formation potential from each fraction was collected or calculated, if not readily available. This is a normalization parameter defined as the amount of a certain by-product compound or family formed per unit dissolved organic carbon (generally expressed as µg/mgC). In some cases, especially for membrane fractionation, the specific formation potential of different fractions were merged to one single value to obtain a better comparison, *e.g.* < 0.5 kDa and 0.5-1 kDa fraction were merged to < 1 kDa. This was done using the following formula (Kitis et al., 2002):

$$sDBPFP_{new} = \sum_{i=1}^{n}\left[\frac{m_i}{\sum_{i=1}^{n} m_i} * sDBPFP_i\right]$$

With n the number of fractions to merge in one water sample, m_i the mass of fraction i and sDBPFP the specific disinfection by-product formation potential.

These values were converted into percentages for each fraction in the following way:

$$\%_i = \frac{sDBPFP_i}{\sum_{i=1}^{n} sDBPFP_i}$$

With n the number of fractions collected from a certain water sample and sDBPFP the specific disinfection by-product formation potential.

With this conversion, the relative difference in the specific reaction potential of different fractions towards disinfection by-product formation can be visualized. Therefore, these data were plotted into boxplots to examine the overall relative difference between distinct fractions to a certain disinfection by-product formation deduced from all studied papers. The box itself is ranged within the 1st and 3rd quartile (25th and 75th percentile) with a horizontal line for the 2nd quartile (median). This is also called the interquartile range. The whiskers represent the data that lie within 1.5 times the interquartile range above and below the box. Data exceeding this range were identified as outliers and are represented as dots. The outliers were not removed from the dataset before the statistical analysis.

A two-tailed t-test (2 datasets) or a one-way ANOVA (> 2 datasets) were executed when the assumptions for normality and equal variances were valid. The Shapiro-Wilk test was used to see if the data was normally distributed. The F-test (2 datasets) or the Bartlett-test (> 2 datasets) were used to check if all datasets had equal variances. Not-normally distributed data was first transformed in an attempt to make them normally distributed. If these transformations were not successful, non-parametric tests such as the Mann-Whitney U test (2 datasets) or the Kruskall-Wallis test (> 2 datasets) were executed. For all tests included, the null hypothesis was rejected when the p-value was smaller than 0.05.

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