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Suspended matter filtration causes a counterintuitive increase in UV-absorption

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ABSTRACT

In water treatment, filtration is often a first step to avoid interference of chemical or UV-disinfection with suspended matter (SPM). Surprisingly, in testing a ballast water filter with 25 and 40 μm mesh screens, UV-absorption (A, 254 nm) of filtered water increased with the largest increase in the finest screen. The hypothesis that filtration partly removes large particles and partly replaces them with small unfiltered ones, leading to an overall increase in absorption, was tested by measuring particle counts, particle-size distributions (PSD) and by modeling the Mass Normalized Beam Attenuation Coefficient (A/SPM) before and after filtration. An independent model verification was made by measuring and modeling A/SPM of three differently sized Arizona test dust suspensions. It is concluded that filtration is a good pretreatment for chemical disinfection systems because it removes the suspended matter mass, but that the production of smaller particles increases UV-absorption and hence may reduce disinfection performance.

1. Introduction

To prevent the global spread of harmful aquatic organisms and pathogens (HAOPs), the International Maritime Organisation (IMO) adopted the Ballast Water Management Convention (IMO, 2004). Untreated ballast water may contain HAOPs, and the convention aims to prevent their spread by prescribing standards and procedures for the management of ships' ballast water. In water disinfection such as ships' ballast water treatment, filtration is often a pretreatment before the actual disinfection step (Jang et al., 2020). The primary aim of filtration is to remove potentially invasive organisms. In addition, the removal of suspended solids such as clays do no longer interfere with disinfection that is mainly performed by chlorination or by UV-radiation (Stehouwer et al., 2015). In an oxidation process such as chlorination, the removal of the mass of suspended solids is important to reduce the reductive power of organic particles so that sufficient oxidative potential is available to kill the living organisms that were not removed by filtration. The UV-dose needed to inactivate living organisms is correlated with the UV-intensity of the lamps, the UV-absorbance of the water and the radiation time. During water treatment, the UV-intensity and the radiation time can be decreased, while maintaining the required UV-dose, if the UV-absorbance of the water decreases. The UV-absorbing properties of the water include absorption by dissolved chemicals as well as by solids in suspension. For that reason, the UV-absorbance of the water to be treated is often measured directly by a UV-sensor or approximated by measuring its turbidity (Christensen and Linden, 2003). The pretreatment of water by filtration is expected to reduce suspended matter and to decrease UV-absorbance. As a result, UV-intensity and radiation time can be decreased resulting in a more cost-effective water treatment.

One of the procedures for the IMO approval of ballast water treatment systems (BWTSs) is land-based testing of these systems using water with minimum concentrations of chemical and biological constituents (IMO, 2018). Approval testing is performed with complete systems, most of them containing a filter. BWTS makers usually obtain a filter from a filter manufacturer, and these may opt for specific filter performance tests. During such performance tests at the Control Union Ballast Water Test Facility in The Netherlands, a ballast water filter system with differing mesh-sized screens was challenged with increasing concentrations of Suspended Particulate Matter (SPM, mg/L). Such filter systems operate at high rates (up to 250 m^3/h and 0.3 m s^{-1}) and high turbulence (Reynolds number, $Re > 4 \times 10^5$). As expected, SPM in the filtered water decreased with 10 to 20 % depending on the filter screen

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mesh size. Measuring SPM before and after filtration is a routine analysis in Control Union filter performance testing. Out of curiosity UV-absorbance was also measured in a selected number of samples before and after filtration. Interestingly, and counter-intuitively, despite the removal of SPM, the absorbance of UV in filtered water increased. In addition, a larger increase in UV-absorbance was measured in 25 μm-filtered water compared to 40 μm-filtered water.

Clearly, the filtration caused a change in the absorption properties of the suspended material. Because the absorption of filtered water is an important variable in ballast water treatment, it was decided to further investigate this phenomenon. The most likely reason for this change is the fact that the surface to volume ratio is larger for smaller particles. This implies that in the filtration process, at high turbulence, large particles disintegrate in a larger number of smaller particles. Suppose we have a spherical particle with mean diameter D (μm) and a volume of ($\pi D^3/6$). When the laws of geometric optics can be applied the attenuation of light will be proportional to the surface (πD^2). Thus, when one particle breaks up in N equally sized spherical particles, we expect that the light attenuation will increase by a factor $N^{1/3}$. This implies that if $N = 10$, the 10 smaller particles together will attenuate more light than the one large particle by a factor of $10^{1/3} = 2.2$. For an ensemble of particles with a large range in diameters we build upon the approach by Hill et al. (2011), who studied the relation between beam attenuation and Particle Size Distribution (PSD). According to this Hill model, a shift in PSD towards smaller particles, despite a relatively small or even zero change in absolute mass reduction, can lead to a large change in A/SPM.

Here we test the hypothesis that although filtration removed large particles, a) the concentration of unfiltered smaller particles increased, b) the PSD shifted towards smaller particles, leading to c) an increase in the Mass Normalized Beam Attenuation Coefficient (A/SPM).

First, particle concentrations and PSDs were measured in samples before and after filtration, and A/SPM was calculated from absorbance and SPM concentration.

Second, the applicability of Hill's model (Hill et al., 2011) was tested by comparing measured A/SPM of three suspensions of different Arizona test dusts (coarse, medium and fine) with model outcomes based on PSD measurements, assuming for each particle-size a constant attenuation efficiency and a constant density, expecting $A/SPM_{coarse} < A/SPM_{medium} < A/SPM_{fine}$. Arizona dusts are test dusts according to ISO 12103-1, with median PSDs of 5, 13 and 24 μm (Peperzak and Stuut, unpublished data).

Third, the calculated A/SPM values of the filter test were compared with values that resulted from applying Hill's model to the PSD filter data, which resulted in confirmation of the hypothesis that the increase in small particles by filtration caused the increase in absorbance of the filtered water.

2. Material and methods

The ballast water filter (manufacturer confidential), with either a 25 μm or a 40 μm mesh size metal screen, was tested at the Control Union Test Facility in The Netherlands in accordance with a specific procedure according to which the filter performance was monitored during a stepwise increase of SPM up to and beyond 1000 mg/L by adding a suspension of bentonite in seawater (Haliburton, Houston, USA; for PSD see Results and discussion). Each test started with filtering ambient water at a flow rate of 200 m^3/h. The bentonite was added stepwise by increasing the suspension flow rate into the main ballast line where, due to the high turbulence, it was thoroughly mixed with the ambient water before entering the filter system. During each SPM-step, samples were taken before and after the filter for UV-absorbance and SPM concentration and were analyzed according to Control Union's Standard Operating Procedures. A selected number of samples were analyzed for flow cytometer particle counts and PSD.

Flow cytometer counts of three samples before and after 25 μm filtration were made with a Canto™ (Becton-Dickinson, Franklin Lakes, USA) with particle-size calibration as described previously (Peperzak et al., 2020). The flow cytometer particle counts were divided into five intervals: 1–2.5 μm, 2.5–5 μm, 5–10 μm, 10–50 μm and 50–100 μm and because of the different SPM concentrations between samples the counts were converted to particle concentration per mg SPM.

PSDs of three samples before and after 25 μm filtration and of the three Arizona test dusts were measured with a LS13 320 Laser Diffraction Particle-size Analyzer (Beckman Coulter, Indianapolis, USA).

SPM was measured in duplicate by filtering 50 to 1000 mL aliquots, depending on SPM concentration, on 47 mm dried and pre-weighed Whatman™ GF-F filters with a nominal pore size of 0.7 μm (VWR/Avantor, Radnor, USA). Each filter was rinsed with 30 mL deionized water to remove dissolved salts, dried and weighed again. Because the maximum volume was 1 L, both mg/L and g m^{-3} (in modeling) are used.

UV-absorbance (a) was measured in well-mixed triplicate subsamples on a UV-1600PC spectrophotometer (VWR/Avantor, Radnor, USA) in 10 mm quartz cuvettes at 254 nm and converted to UV-absorption (A, m^{-1}) as:

$$A = {}^{e}log(10)^{*}a/0.01 \quad (1)$$

Arizona dusts (ISO 12103-1, Powder Technology Inc., San Fernando, USA): A2-fine (median size = 5.3 μm), A3-middle (median size = 12.7 μm), and A4-coarse (median size = 23.5 μm) were suspended in deionized water. To examine the effect of particle-size on UV-absorbance the Arizona dust suspensions were measured in a range of 0 to 2000 mg SPM/L. PSD measurements were made in suspensions of ca. 1000 mg dust-SPM/L each.

Hill's model (Hill et al., 2011), Eq. (2), was tested with the PSDs of the three Arizona dusts and then applied using the PSD's of three samples (size range 1.5 to 120 μm) that were obtained before and after filtration with the 25 μm screen.

$$A = SPM \int_{Dmin}^{Dmax} \frac{Q_c(D)}{\rho_s(D)} \bullet f_m(D) \bullet \frac{6}{4\,D} dD \ \left(m^{-1}\right) \quad (2)$$

With A = UV-absorption (m^{-1}), SPM = Suspended Matter concentration (g m^{-3}), D_{min} and D_{max} = the minimum and maximum particle diameter (μm), $Q_c(D)$ = attenuation efficiency (dimensionless), $f_m(D)$ = particle frequency distribution, $\rho_s(D)$ = particle density (g m^{-3}).

For the filter test data $Q_c(D) = 2$ and $\rho_S = 1.15$ kg m^{-3} and for the Arizona dusts: $Q_c(D) = 2$, $\rho_S = 2.65$ kg m^{-3} (Clavano et al., 2007; Gordon, 2011).

2.1. Statistics

The Mass Normalized Beam Attenuation Coefficients (m^2 g^{-1}), the slopes in linear regressions of A over SPM (A/SPM) and their ±95 % confidence intervals were calculated in SYSTAT® version 10.2 (Chicago, USA).

The 95 % confidence intervals of modelled A/SPM values were calculated as:

$$95\%\text{c.i.} = t_{df} \times sd/n^{0.5} \quad (3)$$

With sd = standard deviation and t_{df} = t-value for a given degree of freedom (df, the number of observations ($n = 3$) minus 1) from a t-table at $P < 0.05$ (two-tail probability). Averages with ±95 % confidence intervals that do not overlap are significantly different.

The mean and standard deviation of the PSDs as calculated by the Laser Diffraction Particle-size Analyzer software were used to calculate ±95 % confidence intervals to compare samples before and after filtration assuming 1.962 degrees of freedom ($n = 1000$).

The mass normalized flow cytometer particle concentrations before and after filtration were analyzed for each of the five size intervals in ANOVA's, also in SYSTAT® version 10.2.

In each statistical analysis the null hypothesis tested was that there is

no difference between particle concentration, PSD, or A/SPM between two samples or variables.

3. Results and discussion

First and as expected the UV-absorption increased linearly with Suspended Matter (SPM) concentrations in all three sample series: one series taken before and two taken after the two filter screens that were tested (25 and 40 μm) (Fig. 1). The slopes (A/SPM) of the three series (Fig. 1) increased from unfiltered to 40 μm and from 40 μm to 25 μm filtered water (Table 1), which means that UV-absorption increased after filtration. In fact, A/SPM in the samples that were filtered by the finest filter, 25 μm, was significantly higher than in the unfiltered water ($P < 0.05$).

To examine if filtration increased the abundance of small particles, the particle concentrations were counted. Indeed, in 25 μm filtered water particle concentrations increased significantly in all size intervals up to 50 μm compared to unfiltered water (Fig. 2).

An increase in the concentration of smaller particles after filtration should be noticeable in the particle-size distributions. This was confirmed: the mean particle-size distribution of the particles in 25 μm filtered water decreased significantly compared to unfiltered water (Fig. 3, Table 2).

Second, the smaller particle-higher absorbance hypothesis was tested by measuring UV-absorbance in suspensions of three differently sized ISO-certified Arizona dusts. As expected, the UV-absorption was relatively higher in the finer test dusts (Fig. 4). In addition, the UV-absorption per mg dust corresponded to $A/SPM_{coarse} < A/SPM_{medium} < A/SPM_{fine}$ (Fig. 4) and were significantly different from each other (Table 3).

In the third and final step the application of Hill's model (Hill et al., 2011) was tested by comparing measured A/SPM values with calculated values by using PSD data of the Arizona dusts (Fig. 5). The maximum difference in measured A/SPM of the Arizona dusts was a factor of three, indicating that the PSD has a large effect on the beam attenuation coefficient. In addition, the test dusts PSD's show several peaks (Fig. 5) which may indicate that they are composed of different substances that have varying attenuation efficiencies ($Q_c(D)$) and particle densities ($\rho_s(D)$). This could have contributed to the difference in modelled and measured A/SPM values because the model was applied with equal and constant attenuation efficiencies and particle densities. However, the modelled Arizona dust A/SPM values, although significantly different from the experimental values, did show a significant decrease with increasing particle-size (Table 3). Furthermore, the modelled A/SPM for unfiltered and 25 μm filtered water were ≤3 % and not significantly different from the measured values (Table 1).

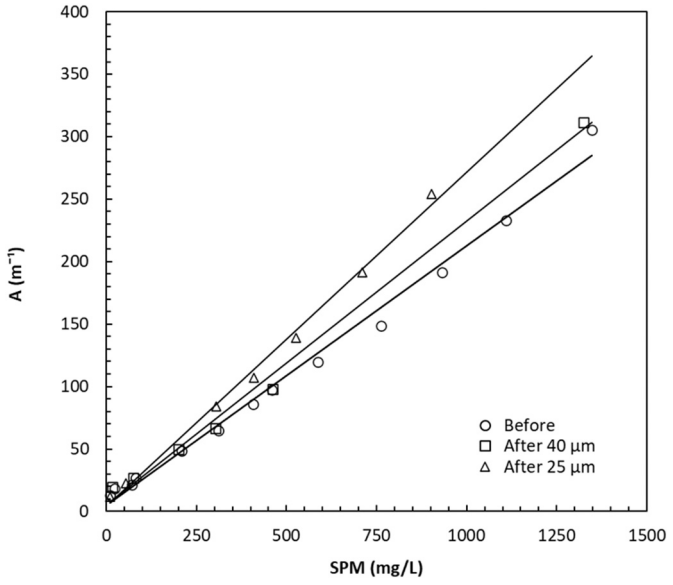

Fig. 1. UV-Absorption at 254 nm as function of Suspended Matter concentration in unfiltered samples (before) and samples filtered (after) by a 40 μm or 25 μm filter.

It may be argued that the removal of organic particles such as zooplankton could have influenced the A/SPM values calculated by Hill's model (Hill et al., 2011) by changing the attenuation efficiencies ($Q_c(D)$) and particle densities ($\rho_s(D)$). However, the test water was natural seawater augmented with bentonite to increase SPM ≥ 1000 mg/L (Fig. 1). This water would indeed contain zooplankton organisms, but it was assumed that their contribution to total SPM and hence the total particle composition is negligible. To test this assumption, the natural (non-augmented) SPM concentrations in NIOZ harbor in the test period were retrieved. Natural SPM ranged from 9 to 22 mg/L and because SPM consists of sand, silt, clay, phyto- and zooplankton, the concentration of zooplankton would be ≪9–22 mg/L, perhaps only 10 % (1–2 mg/L). Compared to SPM concentrations up to 1000 mg/L in the augmented test water, this means that the removal of zooplankton should have had a negligible effect on the composition of the SPM.

It is therefore concluded that the hypothesis that filtration removed large particles but a) increased the concentration of unfiltered smaller particles, b) shifted the PSD towards smaller particles, leading to c) an increase in the Mass Normalized Beam Attenuation Coefficient (A/SPM) was confirmed by both measured data and the application of Hill's model (Hill et al., 2011).

The primary goal of filtration in ballast water treatment is the removal of relatively large zooplankton organisms, i.e. >50 μm in width, that need higher treatment doses than smaller and weaker organisms. When their concentration is ≥10 per m^3 discharged water the ship does not comply with IMO's D-2 limit (IMO, 2004) with the risk of being fined. A second benefit is to remove suspended matter that would otherwise settle and build up in the ballast tanks where it is costly to remove. Thirdly, a reduction of suspended matter would improve chemical treatment efficiency because less oxidant such as chlorine is needed. Fourthly, due to a seemingly lower UV absorbance the required lethal UV dose would be reached at a lower cost or at a faster rate. The dose is the product of UV intensity and irradiation time, and the irradiation time depends on the flow rate of the ballast water through the UV reactor. Therefore, in UV treatment systems an increase in absorbance is unwanted.

Because filtration may not lead to a decrease but an increase in UV absorbance in ballast water, the necessary increase in UV intensity will raise energy costs. Alternatively, a longer exposure time will slow down ship's operations. Because the primary goal of filtration is to remove large zooplankton organisms to reach IMO compliance and protection of the environment, these disadvantages appear unavoidable. Alternatively, it may be considered to treat ballast water first, and do the filtration afterwards.

By the same break-up of large into smaller particles, filtration will also increase absorbance at higher wavelengths and hence turbidity. In other water treatment applications, when turbidity and not UV absorbance is the input variable for further disinfection (Christensen and Linden, 2003), a trade-off as in ballast water between the required treatment performance and costs should be made.

The results presented in this paper have highlighted the effect of decreasing particle size on the UV absorbance at 254 nm. A more quantitative assessment of the increase in UV absorbance in natural waters due to the filtration process is hard to give. Natural particles can differ in many aspects that are influential on absorbance such as their original PSD, the PSD-fraction above the filter mesh size and their internal cohesion. To our knowledge there is no direct literature on expected changes in PSD after filtration. A review of the typical absorbance by natural silt can be found in Hill et al. (2011). Literature on light transmission in solutions with particles is also limited. Van Eerdenbrugh

Table 1
Mass Normalized Beam Attenuation Coefficient (A/SPM, $m^2\ g^{-1}$) in unfiltered water and after filtration by 40 and 25 μm screens. A/SPM ±95 % confidence limits was also derived by the Hill model using PSD data. N.d. = not determined.

Sample	r^2	P	A/SPM	−95 % c.i.	+95 % c.i.	Modelled	−95 % c.i.	+95 % c.i.
Test before filtration	0.99	<0.0001	0.208	0.194	0.221	0.210	0.187	0.233
Test after 40 μm filtration	0.99	<0.0001	0.227	0.202	0.252	n.d.	n.d.	n.d.
Test after 25 μm filtration	1.00	<0.0001	0.267	0.247	0.288	0.258	0.242	0.274

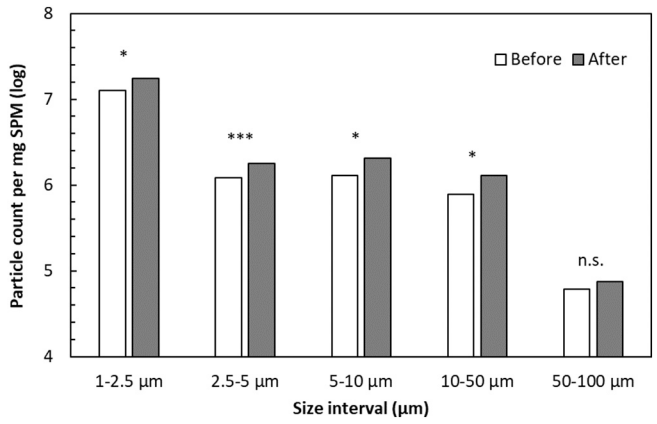

Fig. 2. Number of particles per mg SPM before and after filtration by a 25 μm filter. Significant differences between before and after samples are indicated by * ($P < 0.05$) and *** ($P < 0.001$). n.s. = not significant.

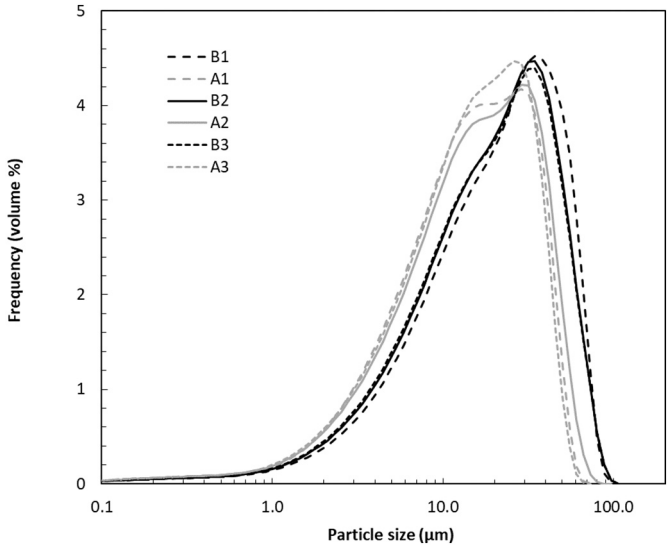

Fig. 3. PSDs before (B1–3) and after (A1–3) filtration by a 25 μm filter. Triplicate samples.

Table 2
Average particle-sizes with ±95 % confidence limits before (B) and after (A) filtration by a 25 μm filter.

Sample	Average	−95 % c.i.	+95 % c.i.
B1	19.4	19.2	19.6
B2	18.0	17.8	18.2
B3	17.7	17.5	17.8
A1	13.6	13.4	13.7
A2	14.4	14.3	14.6
A3	13.4	13.2	13.6

et al. (2011) caution for inaccurate determination of dissolved

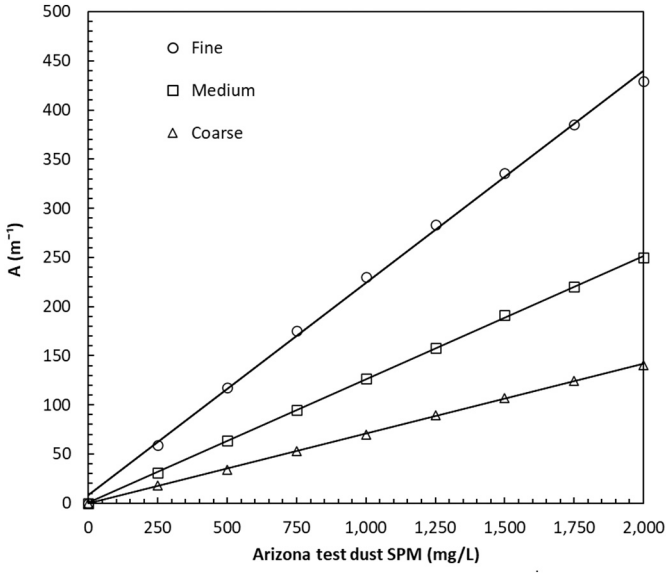

Fig. 4. UV-absorption at 254 nm as function of Arizona test dust total suspended solids concentration.

Table 3
Linear regression data of UV-absorption (A) as function of SPM in Arizona dust suspensions. The linear regression slope (A/SPM) is the Mass Normalized Beam Attenuation Coefficient ($m^2\ g^{-1}$). A/SPM was also derived by the Hill model using PSD data (D_{min} = 1.5 to D_{max} = 300 μm).

Sample	r^2	P	A/SPM	−95 % c.i.	+95 % c.i.	Modelled
Arizona A2-fine dust	1.00	<0.0001	0.216	0.208	0.224	0.187
Arizona A3-middle dust	1.00	<0.0001	0.126	0.124	0.127	0.128
Arizona A4-course dust	1.00	<0.0001	0.071	0.070	0.072	0.101

molecules using UV-VIS photometers if small particles are present, that may either dissolve during sample processing or are generated in supersaturated solutions. Online water quality monitoring systems using UV-VIS photometers to manage the operations of water treatment plants need to correct for the site-specific effect of particles on the absorbance of the dissolved pollutant that is analyzed (Snazelle, 2016). The absorbance effect of particles and their size distribution is, therefore, a problem not limited to ballast water treatment alone.

We proved that forceful filtration through a mesh can significantly increase light attenuation. This effect depends on multiple variables, for example the original fraction of particles with a size above the filter's mesh size as well as cohesive forces in the particles. If a limited concentration of relatively large particles is present or these particles do not break in the filtration process, the beam attenuation will decrease. On the other hand, if each large particle breaks up in 10 equal smaller particles, an increase by a factor 2 is theoretically possible. The overall filtration effect on the treatment efficiency and costs will depend on the filter and disinfection system characteristics and on water quality

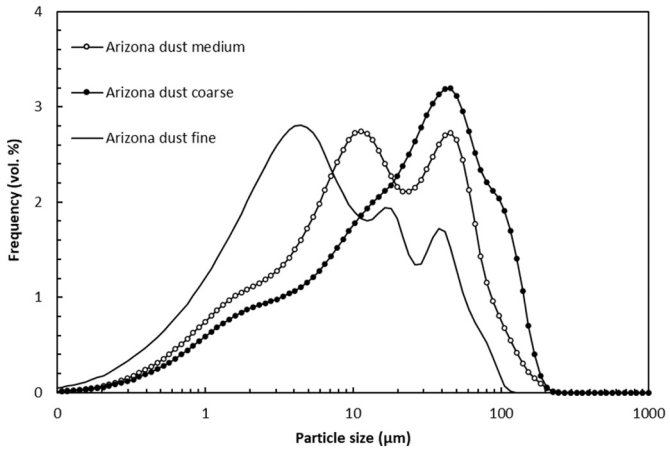

Fig. 5. Particle-size distribution (PSD) of Arizona test dusts suspended in water.

variables as beam attenuation, SPM concentration and SPM composition. As treatment systems can be very different and water quality is highly variable, it would be very difficult to estimate the real-world effect of the counter-intuitive increase in UV absorbance by filtration. It is concluded that filtration is a good pretreatment for chemical disinfection systems because it removes the suspended matter mass, but that the production of smaller particles increases UV-absorption and hence may reduce disinfection performance.

CRediT authorship contribution statement

LP: initial sampling, outline paper
JB: PSD analyses and discussion
HW: Hill model application and discussion

Declaration of competing interest

The authors declare the following financial interests/personal relationships which may be considered as potential competing interests:

Peperzak reports that equipment was provided by an anonymous filter company.

Jan-Berend W Stuut reports financial support and administrative support were provided by NIOZ - Royal Netherlands Institute for Sea Research. Jan-Berend W Stuut reports a relationship with NIOZ - Royal Netherlands Institute for Sea Research that includes: employment.

Data availability

Data will be made available on request.

References

Christensen, J., Linden, K.G., 2003. How particles affect UV light in the UV disinfection of unfiltered drinking water. J.Am.Water Works Assoc. 95, 179–189.
Clavano, W., Boss, E., Karp-Boss, L., 2007. Inherent optical properties of non-spherical marine-like particles from theory to observation. Oceanogr. Mar. Biol.Annu.Rev. 45, 1–38.
Gordon, H.R., 2011. Light scattering and absorption by randomly-oriented cylinders: dependence on aspect ratio for refractive indices applicable for marine particles. Opt. Express 19, 4673–4691.
Hill, P., Boss, E., Newgard, J., Law, B., Milligan, T., 2011. Observations of the sensitivity of beam attenuation to particle size in a coastal bottom boundary layer. J. Geophys. Res. Oceans 116.
IMO, 2004. International Convention for the Control and Management of Ships' Ballast Water And Sediments. BWM/CONF/36. International Maritime Organization, London.
IMO, 2018. Code for approval of ballast water management systems (BWMS Code). In: IMO (Ed.), MEPC.300(72). IMO, London.
Jang, P., Hyun, B., Shin, K., 2020. Ballast water treatment performance evaluation under real changing conditions. J.Mar.Sci.Eng. 8.
Peperzak, L., Zetsche, E.-M., Gollasch, S., Artigas, L.F., Bonato, S., Creach, V., de Vré, P., Dubelaar, G.B.J., Henneghien, J., Hess-Erga, O.-K., Langelaar, R., Larsen, A., Maurer, B.N., Mosselaar, A., Reavie, E.D., Rijkeboer, M., Tobiesen, A., 2020. Comparing flow cytometry and microscopy in the quantification of vital aquatic organisms in ballast water. J.Mar.Eng.Technol. 19, 68–77.
Snazelle, T.T., 2016. The Effect of Suspended Sediment And Color on Ultraviolet Spectrophotometric Nitrate Sensors. US Geological Survey.
Stehouwer, P., Buma, A., Peperzak, L., 2015. A comparison of six different ballast water treatment systems based on UV radiation, electrochlorination and chlorine dioxide. Environ. Technol. 36, 2094–2104.
Van Eerdenbrugh, B., Alonzo, D.E., Taylor, L.S., 2011. Influence of particle size on the ultraviolet spectrum of particulate-containing solutions: implications for in-situ concentration monitoring using UV/Vis fiber-optic probes. Pharm. Res. 28, 1643–1652.