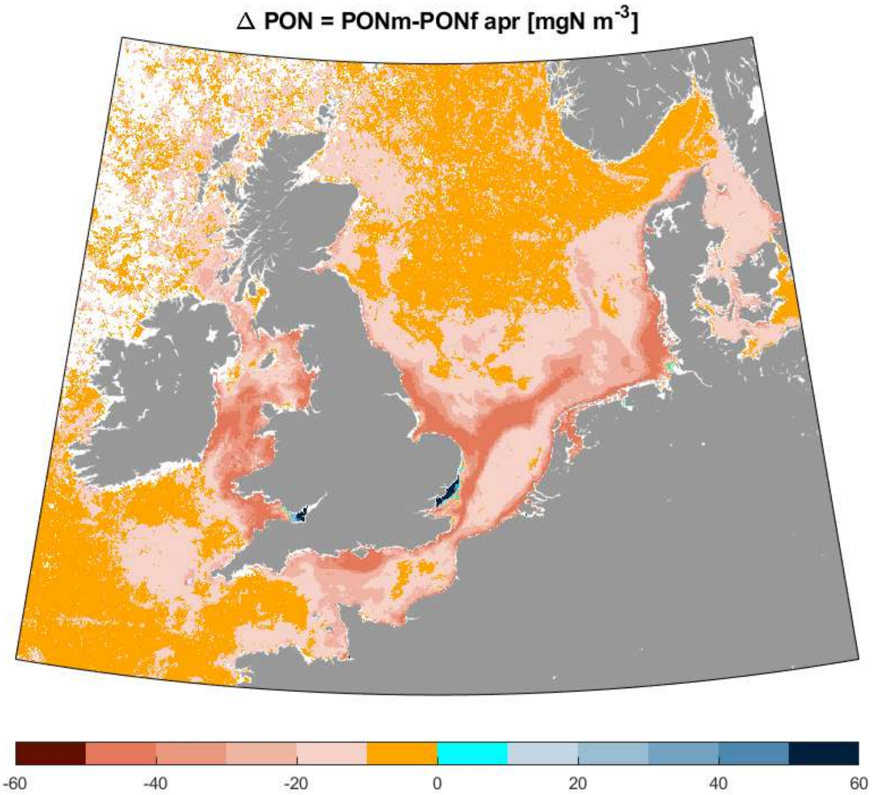
KONINKLIJK BELGISCH INSTITUUT VOOR NATUURWETENSCHAPPEN
OD NATUUR – BEHEERSEENHEID VAN HET MATEMATISCH MODEL

MOnitoring en MOdellering van het cohesieve sedimenttransport en evaluatie van de effecten op het mariene ecosysteem ten gevolge van bagger- en stortoperatie (MOMO)



Activiteitsrapport (1 januari - 30 juni 2022)

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MOMO/10/MF/202210/NL/AR/1

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1. Inleiding

1.1. Voorwerp van deze opdracht

Het MOMO-project (monitoring en modellering van het cohesieve sedimenttransport en de evaluatie van de effecten op het mariene ecosysteem ten gevolge van bagger- en stortoperatie) maakt deel uit van de algemene en permanente verplichtingen van monitoring en evaluatie van de effecten van alle menselijke activiteiten op het mariene ecosysteem waaraan België gebonden is overeenkomstig het verdrag inzake de bescherming van het mariene milieu van de noordoostelijke Atlantische Oceaan (1992, OSPAR-Verdrag). De OSPAR Commissie heeft de objectieven van haar Joint Assessment and Monitoring Programme (JAMP) gedefinieerd tot 2021 met de publicatie van een holistisch “quality status report” van de Noordzee en waarvoor de federale overheid en de gewesten technische en wetenschappelijke bijdragen moeten afleveren ten laste van hun eigen middelen.

De menselijke activiteit die hier in het bijzonder wordt beoogd, is het storten in zee van baggerspecie waarvoor OSPAR een uitzondering heeft gemaakt op de algemene regel “alle stortingen in zee zijn verboden” (zie OSPAR-Verdrag, Bijlage II over de voorkoming en uitschakeling van verontreiniging door storting of verbranding). Het algemene doel van de opdracht is het bestuderen van de cohesieve sedimenten op het Belgisch Continentaal Plat (BCP) en dit met behulp van zowel numerieke modellen als het uitvoeren van metingen. De combinatie van monitoring en modellering zal gegevens kunnen aanleveren over de transportprocessen van deze fijne fractie en is daarom fundamenteel bij het beantwoorden van vragen over de samenstelling, de oorsprong en het verblijf ervan op het BCP, de veranderingen in de karakteristieken van dit sediment ten gevolge van de bagger- en stortoperaties, de effecten van de natuurlijke variabiliteit, de impact op het mariene ecosysteem in het bijzonder door de wijziging van habitats, de schatting van de netto input van gevaarlijke stoffen op het mariene milieu en de mogelijkheden om deze laatste twee te beperken.

Een samenvatting van de resultaten uit de vergunningsperioden 2017-2021 kan gevonden worden in het “Vooruitgangsrapport (juni 2019) over de effecten op het mariene milieu van baggerspeciestortingen” (Lauwaert et al. 2019) en het Syntheserapport over de effecten op het mariene milieu van baggerspeciestortingen” (Lauwaert et al., 2021) die gepubliceerd werden conform art. 10 van het K.B. van 12 maart 2000 ter definiëring van de procedure voor machtiging van het storten in de Noordzee van bepaalde stoffen en materialen.

1.2. Algemene doelstellingen

Het onderzoek uitgevoerd in het MOMO project kadert in de algemene doelstellingen om de baggerwerken op het BCP en in de kusthavens te verminderen, om de effecten van het storten van baggerspecie te kwantificeren en om een gedetailleerd inzicht te verwerven van de fysische processen die plaatsvinden in het mariene kader waarbinnen deze baggerwerken worden uitgevoerd. Dit impliceert enerzijds beleidsondersteunend onderzoek naar de vermindering van de sedimentatie op de baggerplaatsen en het evalueren van alternatieve stortmethoden. Anderzijds is vernieuwend onderzoek noodzakelijk om beter de effecten van het storten van baggerspecie in te schatten. Dit onderzoek is specifiek gericht op het dynamische gedrag van slib in de waterkolom en op de bodem en de interacties tussen fysische en biologische processen en zal uitgevoerd worden met behulp van modellen, in situ metingen en remote sensing data.

De specifieke acties die binnen dit onderzoek uitgevoerd worden om de algemene doelstellingen in te vullen zijn:

1. Streven naar een efficiënter stortbeleid door een optimalisatie van de stortlocaties.

2. Continue monitoring van het fysisch en biogeochemisch milieu waarbinnen de baggerwerken worden uitgevoerd (Taak 1) en aanpassing van de monitoring aan de nog op te stellen targets voor het bereiken van de goede milieutoestand (GES), zoals gedefinieerd zal worden binnen MSFD;

3. Uitbouw en optimalisatie van het numerieke modelinstrumentarium, ter ondersteuning van het onderzoek (Taak 2.1).

1.3. Algemeen Onderzoek 2012-2026

Het onderzoek heeft als doel om de effecten van baggerspeciestortingen op het mariene ecosysteem (fysische en biogeochemische aspecten) te onderzoeken. Hiervoor worden in situ metingen verzameld, gebruik gemaakt van remote sensing data en worden numerieke modellen ingezet. Voor de vergunningsperiode 2022-2026 worden volgende taken voorzien:

1) In situ en remote sensing metingen en data-analyse

De monitoring van effecten van baggerspeciestortingen gebeurd met behulp van een vast meetstation in de nabijheid van MOW1, en met meetcampagnes met de RV Belgica (een 10-tal meetcampagnes voor het verzamelen van traject informatie, profielen en de calibratie van sensoren; en een 10-tal campagnes voor het onderhoud van het meetstation te MOW1). De geplande monitoring is gericht op het begrijpen van processen, zodoende dat de waargenomen variabiliteit en de effecten van baggerspeciestortingen in een correct kader geplaatst kunnen worden. Een belangrijk deel is daarom gericht op zowel het uitvoeren van de in situ metingen, het garanderen van kwalitatief hoogwaardige data en het archiveren, rapporteren en interpreteren ervan. Remote sensing data afkomstig van onder andere satellieten worden gebruikt om een ruimtelijk beeld te bekomen.

2) Uitbouw en optimalisatie van het modelinstrumentarium

Het tijdens de voorbije jaren verbeterde en aangepaste slibtransportmodel zal verder worden ontwikkeld. Dit zal parallel gebeuren met de nieuwe inzichten die voorvloeien uit de metingen en de procesgerichte interpretatie van de metingen.

3) Ondersteunend wetenschappelijke onderzoek

Monitoring gebaseerd op wetenschappelijke kennis is essentieel om de effecten van menselijke activiteiten (hier het storten van baggerspecie) te kunnen inschatten en beheren. Om te kunnen voldoen aan de door OSPAR opgelegde verplichtingen van monitoring en evaluatie van de effecten van menselijke activiteiten is het ontwikkelen van nieuwe monitorings- en modelleractiviteiten nodig. Dit houdt in dat onderzoek dat de actuele stand van de wetenschappelijke kennis weerspiegelt wordt uitgevoerd en dat de hieruit voortvloeiende nieuwe ontwikkelingen geïntegreerd zullen worden in zowel de verbetering van het modelinstrumentarium als voor het beter begrijpen van het kustnabije ecosysteem.

1.4. Onderzoek Januari 2022 – December 2024

Voor de periode 2019-2021 werd rekening gehouden werd met de aanbevelingen voor de minister ter ondersteuning van de ontwikkeling van een versterkt milieubeleid zoals geformuleerd in het “Syntheserapport over de effecten op het mariene milieu van baggerspeciestortingen (2021)” dat uitgevoerd werd conform art. 10 van het K.B. van 12 maart 2000 ter definiëring van de procedure voor machtiging van het storten in de Noordzee van bepaalde stoffen en materialen.

Taak 1: In situ en remote sensing metingen en data-analyse

Taak 1.1 Langdurige metingen te MOW1 en W05

Sinds eind 2009 worden er continue metingen uitgevoerd te MOW1 met behulp van een meetframe (tripode). Met dit frame worden stromingen, slibconcentratie, korrelgrootte-verdeling van het suspensiemateriaal, saliniteit, temperatuur, waterdiepte en zeebodem altimetrie gemeten. Om een continue tijdreeks te hebben, wordt gebruik gemaakt van 2 tripodes. Na ongeveer 1 maand wordt de verankerde tripode voor onderhoud aan wal gebracht en wordt de tweede op de meetlocatie verankerd. Op de meetdata wordt een kwaliteitsanalyse uitgevoerd, zodat de goede data onderscheiden kunnen worden van slechte of niet betrouwbare data.

Veranderingen in kustnabije ecosystemen zijn dikwijls gecorreleerd met veranderingen van de helderheid van het water of de concentratie aan particulair suspensiemateriaal (SPM) en dus ook met het gehalte aan particulair organisch materiaal. De zone waar de invloed van het minerale en kustnabij suspensiemateriaal overgaat in een zone met dominantie van organisch suspensiemateriaal van mariene origine is van bijzonder belang. De monitoring wordt uitgebreid met de verankering van een meetboei in locatie W05 (51°N 24.96’, 2°E 48.7’). W05 is één van de drie monitoringspunten waar waterstalen en sensormetingen maandelijks worden uitgevoerd.

Taak 1.2 Calibratie van sensoren tijdens in situ metingen

Tijdens meetcampagnes met de R/V Belgica zullen een voldoende aantal 13-uursmetingen uitgevoerd worden met als hoofddoel het kalibreren van optische of akoestische sensoren en het verzamelen van verticale profielen. De metingen zullen plaatsvinden in het kustgebied van het BCP (MOW1, W05). De optische metingen (Optical Backscatter Sensor) zullen gekalibreerd worden met de opgemeten hoeveelheid materie in suspensie (gravimetrische bepalingen na filtratie) om te komen tot massa concentraties

Taak 1.2 Bio-geo-chemische monitoring van het SPM (BGCMonit)

SPM bestaat uit minerale deeltjes van fysicochemische (b.v. kleimineralen, kwarts, veldspaat) en biogene oorsprong (b.v. calciet, aragoniet, opaal), levend (bacteriën, fyto- en zoöplankton) en niet-levend organisch materiaal (b.v. fecale pellets, detritus, exopolymeren), en partikels van menselijke oorsprong (microplastiek). Het SPM kan door hydrofobe organische polluenten of metalen gecontamineerd zijn. De samenstelling en concentratie van het SPM inclusief de hydrofobe polluenten verandert in functie van de tijd en de locatie. Deze variaties worden beïnvloed door de interacties tussen de fysische processen (getij, meteo, klimaat), biologische cycli (algenbloei), chemische processen (koolstofcyclus) en menselijke activiteiten (aanvoer van nutriënten, bagger- en stortactiviteiten, offshore constructies). De samenstelling van het particulair en opgelost suspensiemateriaal zal bepaald worden tijdens meetcampagnes met de RV Belgica tijdens een 10-tal campagnes per jaar. Naast de totale hoeveelheid aan SPM worden ook de concentraties aan verschillende organische bestanddelen (POC, PON, TEP, chlorofyl en phaeofytine) bepaald. De opgeloste stoffen zijn inorganische nutriënten, DOC, DIC en alkaliniteit. Stalen van suspensiemateriaal zullen genomen worden met de centrifuge om de samenstelling ervan te bepalen.

Taak 1.4: Archivering en verwerking van de data

De meetdata worden gearchiveerd en er wordt een kwaliteitsanalyse uitgevoerd, zodat de goede data onderscheiden kunnen worden van slechte of niet betrouwbare data. Slechte data kunnen bv optreden doordat het instrument slecht heeft gewerkt en verkeerd werd ingesteld. Niet betrouwbare data zijn typisch geassicieerd met bv biofouling. De data en metadata worden gearchiveerd. De metingen worden verwerkt en geïnterpreteerd. En zullen dienen als basis voor het verder gebruik bij wetenschappelijke vraagstellingen.

Taak 2: Uitbouw en optimalisatie van het modelinstrumentarium

Taak 2.1: Opstellen van een slibtransportmodel voor het BCP met Coherens V2

Een slibtransportmodel zal worden geïmplementeerd met de software Coherens V2. De software laat toe om rekening te houden met gemengde sedimenten en dus met de interactie tussen zand en slib en laat morfologische berekeningen toe door een verbeterde implementatie van het schema voor het massabehoud en gebruik van lagen met gemengde sedimenten. Verdere aanpassingen en verbeteringen aan het model zullen worden uitgevoerd, meer bepaald:

- Kritische bodemschuifspanning voor erosie van gemengde sedimenten,
- Formulering voor de bodemschuifspanning,
- Koppeling van het model met het TILES voxel model voor een betere voorstelling van de bodemkarakteristieken.

Taak 2.2: Validatie van het slibtransportmodel voor het jaar 2013 (stortproef)

Een eerste toepassing van het model kan het jaar 2013 zijn, waarin de terreinproef voor alternatieve stortplaats alsook een intensieve monitoring plaatsvond. Deze laatste zal gebruikt worden voor de validatie van het model. Verder zal het model vergeleken worden met andere modellen van het BCP.

Taak 2.3: Optimalisatie baggerwerken

Een operationeel stortmodel zal worden opgezet in overleg met aMT. Dit model zal geïntegreerd worden in de binnen BMM-OD Natuur beschikbare operationele modellen. Het model zal gebruikt worden om in functie van de voorspelde fysische (wind, stroming, golven, sedimenttransport, recirculatie), economische (afstand, grootte baggerschip) en ecologische aspecten op korte termijn een keuze te kunnen maken tussen de beschikbare stortlocaties. Een eerste test hiervoor werd uitgevoerd in Van den Eynde en Fettweis (2011) waarin werd aangetoond dat door een optimale positie te kiezen voor het storten van baggerspecie in functie van de meteorologische omstandigheden, een vermindering van de aanslibbing van de vaargeulen en haven van Zeebrugge kan worden verwacht.

Het model zal worden gebruikt voor de optimalisatie van de baggerwerken. Verschillende simulaties kunnen worden uitgeoefend waarbij de invloed van de verschillende mogelijke stortplaatsen kunnen worden geëvalueerd.

Taak 2.4: Flocculatiemodel

De inzichten die voortvloeien uit de in situ data (Taken 1.4, 3.1 en 3.2) zullen worden geïntegreerd in een numeriek model dat het verband tussen SPM, TEP en flocculatie langsheen temporele (getij, seizoenen) en geografische (waterkolom, onshore-offshore) schalen combineert. Het model zal worden opgezet als 1D verticaal en zal gekoppeld worden met het 2 klassen populatie model van Lee et al. (2011). Hierdoor zal de verticale verdeling van de minerale en de organische fractie van het SPM en hun interactie kunnen worden voorspeld.

Taak 3: Ondersteunend wetenschappelijk onderzoek

Monitoring gebaseerd op wetenschappelijke kennis is essentieel om de effecten van menselijke activiteiten (hier het storten van baggerspecie) te kunnen inschatten en beheren. Om te kunnen voldoen aan de door OSPAR opgelegde verplichtingen van monitoring en evaluatie van de effecten van menselijke activiteiten is een verdere implementatie van huidige en het ontwikkelen van nieuwe monitoringsactiviteiten nodig. Meer specifiek gericht op de activiteit ‘storten van baggerspecie’ worden hier – wat het fysische milieu betreft - turbiditeit, samenstelling van de zeebodem, bathymetrie en hydrografische condities beoogt. Deze taak speelt hierop in door de ontwikkeling en de implementatie van nieuwe tools die de actuele stand van de wetenschappelijke kennis weerspiegelen teneinde de mathematische modellen te optimaliseren en verfijnen.

Taak 3.1: SPM samenstelling - minerale fractie

Door de aanwezigheid van gemengde sedimenten in de zeebodem (zand en slib) zal tijdens sterke stroming en of hoge golven ook een gemengde minerale fractie in suspensie komen. Dit heeft twee consequenties voor monitoring. Ten eerste reageren akoestische en optische sensoren verschillend op zand en slib, zodat de verzamelde tijdreeksen een grotere onnauwkeurigheid hebben tijdens zo'n momenten (Fugate & Friedrichs, 2002; Baschek et al., 2017; Schwarz et al, 2017; Fettweis et al., 2019). Ten tweede bevatten zandkorrels geen mineraal-gebonden organisch materiaal en stalen genomen tijdens dit soort momenten kunnen dus de onzekerheid van het SPM-POM model vergroten. Indien er geen rekening gehouden wordt hiermee zal de SPM concentratie onder- of overschat worden alsook de afgeleid organische fracties. Doel is om de zand en slibfractie te identificeren door gebruik te maken van innovatieve meettechnieken (Pearsons et al., 2021) die optische en akoestische sensoren combineren. Het ultieme doel is om te komen tot tijdreeksen van zand- en slibconcentratie te MOW1.

Uit visuele inspecties van de bodemsamenstelling te MOW1 tijdens de laatste jaren blijkt dat het sediment zandiger is geworden. De hypothese is, dat dit verband houdt met erosie van de vooroever na de strandopspuitingen die de voorbije jaren werden uitgevoerd. Aan de hand van de boven aangehaalde methode zal nagegaan worden of er een trend naar zandaanrijking kan vastgesteld worden in de omgeving van MOW1.

Taak 3.2: SPM samenstelling - organische fractie

Het semi-empirisch POM-SPM model (Fettweis et al., 2022) zal verfijnd worden met de nieuwe data verzameld in taak 1.3. Hierdoor zal de inschatting van de minerale en de vers en mineraal-gebonden organische fractie nauwkeuriger kunnen worden gedaan.

Op basis van dit POM-SPM model kan de samenstelling van het suspensiemateriaal (minerale fractie, vers en mineraal gebonden POC, PON en TEP) worden berekend voor de tijdreeksen te MOW (vanaf 2005) en voor de satellietdata (vanaf 1997). Dit zal toelaten om de geografische en temporele variabiliteit van de transitiezone tussen het kustgebonden turbiditeitsmaximum en de offshore wateren te kwantificeren. De dynamica van het suspensiemateriaal in beide gebieden is verschillend, wat consequenties heeft naar de modellering ervan. Verder kan uit de lange tijdsreeksen gekeken worden of het gebruik van de stortplaatsen, meer bepaald S1, geleid heeft tot een zeewaartse uitbreiding van het turbiditeitsmaximum.

Taak 3.3: Trends in SPM concentratie

Om significante statistische trends te kunnen documenteren in SPM concentratie over de laatste decades, zijn metingen nodig die een lange tijdspanne omvatten en een groot gebied omvatten. Deze data zijn helaas niet beschikbaar. Wat er wel beschikbaar is zijn de tripode metingen te MOW1 (vanaf 2005) en op andere locaties, de puntmetingen verzameld met onderzoeksschepen in het Belgisch Deel van de Noordzee sinds ongeveer 1970 (cf. Belspo 4DEMON project) en satellietbeelden (vanaf 1997). De tripode data geven de temporele variabiliteit weer, maar zijn heel beperkt wat ruimtelijke spreiding betreft. De 4DEMON en satellietbeelden zijn beschikbaar over een lange periode en over een groot gebied, maar kunnen de temporele schaal niet oplossen. Om deze heterogene datasets samen te kunnen gebruiken, zal gekeken worden naar de statistische verschillen tussen de datasets en naar een manier om deze te combineren. Doel is om mogelijke trends in de SPM concentratie te identificeren en deze te linken aan natuurlijke veranderingen of aan menselijke activiteiten.

De trendanalyse van de historische data zal de basis vormen om de verandering van de SPM concentratie in de nabijheid van de nieuwe stortplaats ZBW te kwantificeren.

Taak 4: Rapportage en outreach

Om de zes maanden zal er een activiteitenrapport worden opgesteld dat de onderzoeksresultaten beschrijft. Jaarlijks wordt er een 'factual data' rapport opgesteld van de verzamelde meetgegevens. De resultaten uit het onderzoek zullen tevens worden voorgesteld op workshops, conferenties en in de wetenschappelijke literatuur.

1.5. Gerapporteerde en uitgevoerde taken

Periode Januari 2022– Juni 2022

Taak 1.1: De meetreeks te MOW1 werd verdergezet.

Taak 1.2: Calibratie van OBS sensoren werd uitgevoerd tijdens RV Begica campagnes 2022/01, 2022/03, 2022/06, 2022/09 en 2022/14.

Taak 3.1: De akoestische en optische sensoren werden gebruikt om veranderingen in sedimentsamenstelling te zien te MOW1. Eerste resultaten worden getoond in hoofdstuk 2.

Taak 3.2: Intensieve bio-geochemische monitoring werd uitgevoerd te MOW1, W05 en W08 tijdens RV Belgica campagnes 2022/01, 2022/03, 2022/07, 2022/11, 2022/14). Eerste resultaten worden besproken in hoofdstuk 3.

1.6. Publicaties (Januari 2022 – December 2026)

Hieronder wordt een overzicht gegeven van publicaties met directe betrokkenheid van het KBIN waar resultaten en data uit het MOMO project in werden gebruikt.

Activiteits-, Meet- en Syntheserapporten

Fettweis M, Baeye M, Desmit X. 2022 MOMO activiteitsrapport (1 januari – 30 juni 2022). BMM-rapport MOMO/10/MF/202210/NL/AR/1, 21pp + app.

Conferenties/Workshops

Baeye M, Delhaye L, Fettweis M. 2022. Acoustic and optical turbidity response to altering particle size distribution during extreme events. EuroSea/OceanPredict workshop, 29 June – 1 July, Exeter (UK)

Fettweis M, Desmit X, Terseleer N, Parmentier K, Van der Zande D, Schartau M, Lee BJ, Riethmüller R. 2022. The characteristics of the organic matter in biomineral flocs. Ocean Science Meeting, 24 February – 4 March, Honolulu (USA).

Peer reviewed artikels

Fettweis M, Schartau M, Desmit X, Lee BJ, Terseleer N, Van der Zande D, Parmentier K, Riethmüller R. 2022. Organic matter composition of biomineral flocs and its influence on suspended particulate matter dynamics along a nearshore to offshore transect. Journal of Geophysical Research Biogeosciences, 126, e2021JG006332. doi:10.1029/2021JG006332

Ho QN, Fettweis M, Spencer KL, Lee BJ. 2022. Flocculation with heterogeneous composition in water environments: A review. Water Research. 118147. doi:10.1016/j.watres.2022.118147

2. Samenstelling van het suspensiemateriaal: Minerale fractie

The interplay between optical and acoustic backscatter may reveal subtle changes in SPM characteristics because of ebb-flood dynamics, spring tide-neap tide dynamics, and even seasonality. And each type of sensor has its own sensitivities towards particles in the water.

The focus was on measurements at MOW1 i.e., an area dominated by flocs. The optical backscatter sensor (Campbell Sc.) measurements collected at 2.35 mab on the benthic tripod, measurements in counts were converted towards FNU and ultimately towards suspended particulate matter concentration(SPMC, g/L). Conversion factors were obtained through lab calibrations with standard turbidity solutions (Fettweis et al. 2019); the FNU to g/L was realized by in-situ calibrations. Concerning the acoustic sensor, the backscatter from the SonTek 3MHz ADP bin number 1 (3-beams average) is located at 2.25 mab, of which BIN nr 1 is located 1.9 mab. The raw backscatter was corrected for spherical spreading loss of sound, sound absorption due to the water molecules and due to the presence of particles in the water, resulting in a backscatter intensity (BI).

Sound loss due to particles depends on the acoustic ADP frequency and particle size (Holdaway et al. 1999, Richards et al. 2003). Here, for MOW1 this is negligible as the absorption for flocculi considered as being the building parts (between 10 and 15 µm) of the flocs is very low (0.044 dB m^2 kg^-1). E.g., SPMC of 0.5 g/L corresponds to only 0.01 dB sound loss. The sound loss due to seawater is 0.12 dB (Mullison 2017). The MOW1 data used in this study were from the period between 2012 and 2014.

The goal is to investigate the conditions when optical-acoustic relationships differ significantly (here without focusing on extreme events), and then ultimately to be able to use ADP data in the absence of OBS measurements (e.g., due to biofouling). Considering the logarithmic unit of BI, dB, the optical SPMC needed to be converted to its logarithmic form. In this way BI plotted against 10*log10(SPMC) with SPMC in g/l results in a linear relationship (Figure 2.1).

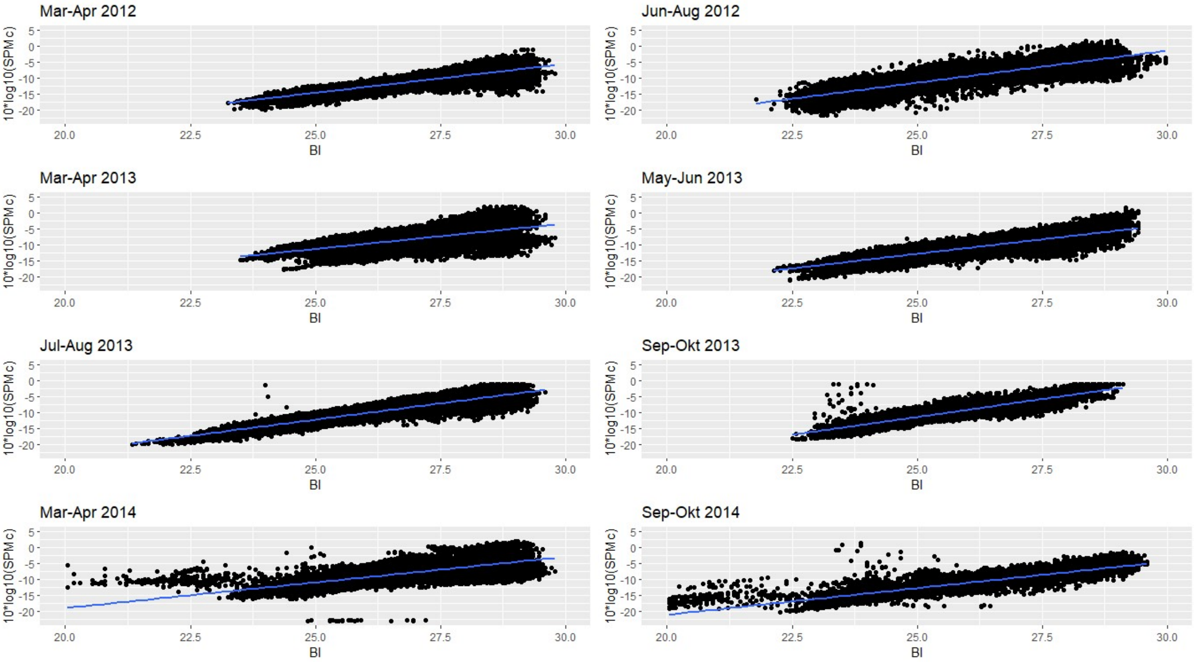

*Figure 2.1: Correlation plots between 10*log10(SPMC) and the BI with the linear regression (least squares) fitting line in blue.*

Pearson et al. (2021) introduced the sediment composition index (SCI) that is basically 10*log10(SPMC) minus BI, examining the relative optical-acoustic backscatter response in their study area (sandy Waddenzee environment) in the Netherlands. It is thinkable that it should be able to directly apply this technique to understand the relative dynamics of sandy vs fine sediment fractions. The exact values of SCI will not be directly comparable with theirs as SCI is dependent on the specific instruments and sediment characteristics, but it can still provide a useful metric, especially to examine variations in sediment properties within the time series. They found that the SCI becomes more negative when sand particles are in suspension, and less negative when there is only mud suspension.

Concerning instrument dependency, Figure 2.2 clearly illustrates the alternating use of two of our own ADPs (in green the ADP M947 and in black the ADP M284).

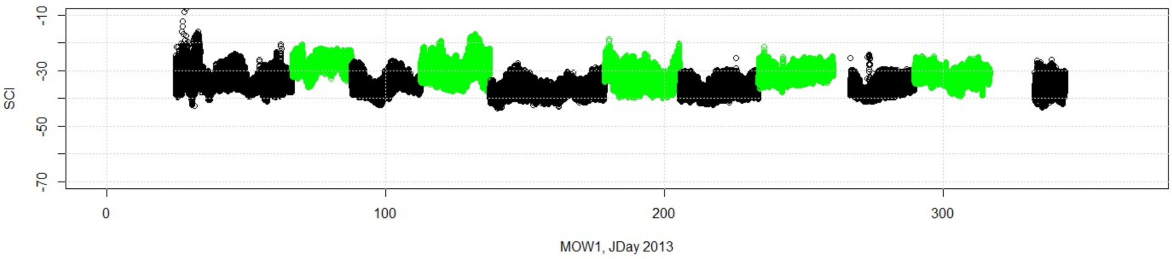

Figure 2.2: Two ADPs used on the benthic tripod (MOW1): ADP sn 947 (black) and ADP sn 284 (green). Offset of about 5 dB.

The Blankenberge site where the benthic tripod was deployed three times in 2008 shows SCI that is overall (subtly) more negative (Figure 2.3). The Gootebank short-duration measurement is significantly more negative (Figure 2.4). All green colored measurements refer to the ADP with the same serial number (M947). These differences may hint towards slightly different SPM grain size.

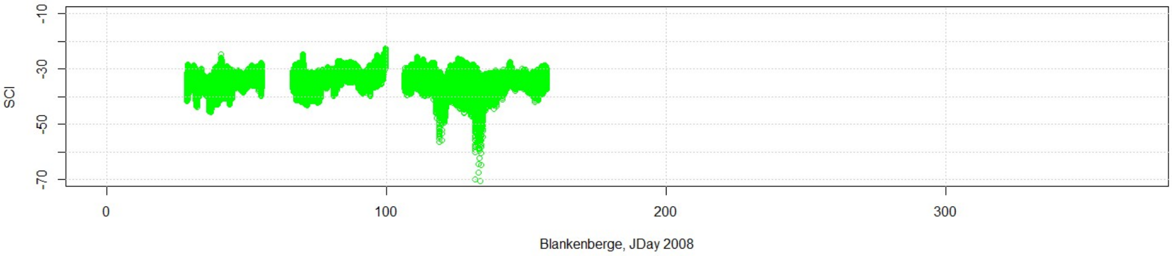

Figure 2.3: The overall slightly lower SCI values at Blankenberge site compared to MOW1.

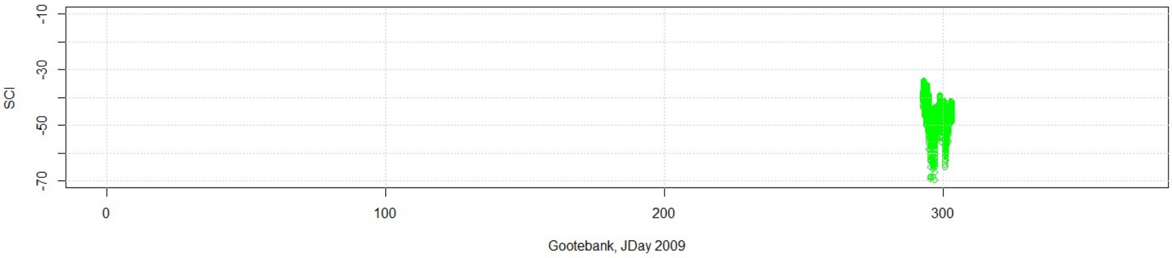

Figure 2.4: The offshore, sandy location of Gootebank with lower SCI values compared to the near-shore locations MOW1 and Blankenberge.

When we now focus on the SCI from one deployment (Figure 2.5) at MOW1 (Sep-Okt 2013), we find that the SCI is more negative during the lower SPM concentration range and less negative during increased turbidity. Sediment dynamics are in the area controlled by tide and thus the current. Current and turbidity are positively correlated. The tidal ellipse with colored points based on SCI values (Figure 2.6), shows indeed higher SCI during reduced current speeds (slack tides), and lower SCI during increased currents (maximal ebb and flood current speeds). These findings are the opposite from what Pearson et al. 2021 presented.

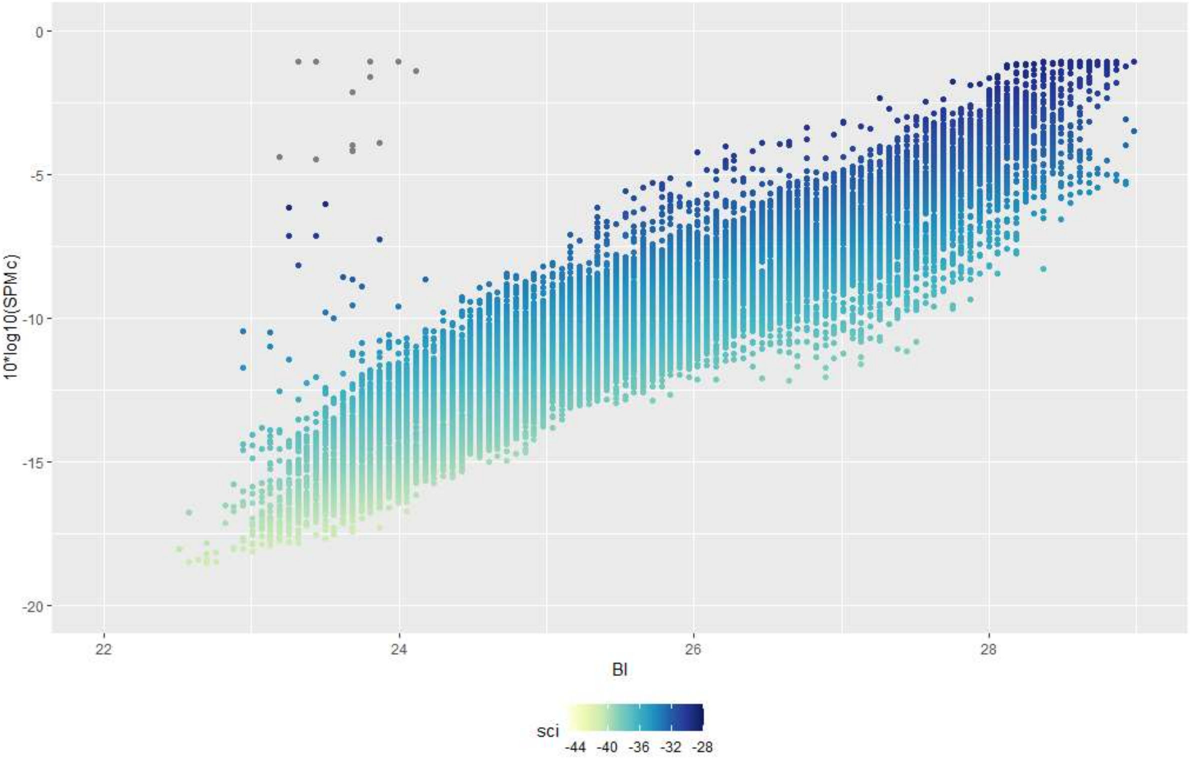

Figure 2.5: Optical-acoustic relationship for deployment September-October 2013 at MOW1. Colored points refer to SCI value.

Neap tide SCI seems to cover a smaller range (towards the more negative values) compared to the spring tide, as illustrated in Figure 2.7. Springtide SCI corresponds to 279-280 and the neaptide SCI to 271-272 (see Figure 2.8 for the full deployment with different hydro-meteorological data). Neaptide is asscoiated here with smaller d50 floc size variability as break-up and aggregation is moderate, when compared against the spring tide case (Figure 2.9). Additonal figures show the the floc size dynamics in response to the along-shore current speed (- speed is to SW, + speed to NE), see Figure 2.10; and illustrate the neaptide and springtide current speeds with associated d50 and SCI values, see Figures 2.11 and 2.12. For springtide, there are two parallel relationship separated by an offset of 1dB. So, the OBS 'sees' the same turbidity although acoustically the response is different, likely controlled by particle size. For bigger flocs, the OBS will 'see' an overall turbidity to a lesser degree, compared to the ADP as this sensor still 'hears' the building parts (flocculi) (Vincent & MacDonald, 2015). For neap tide, this is not the case as floc size is not varying to such a degree.

In summary, and as start for further research, the SCI in the Belgian near-shore area (MOW1) seems to be mainly controlled on the tide-controlled floc size. Increased currents will result in smaller flocs and better agreement between optically and acoustically measured turbidity, whereas decreasing currents (with associated increasing floc size) will likely decrease the OBS performance.

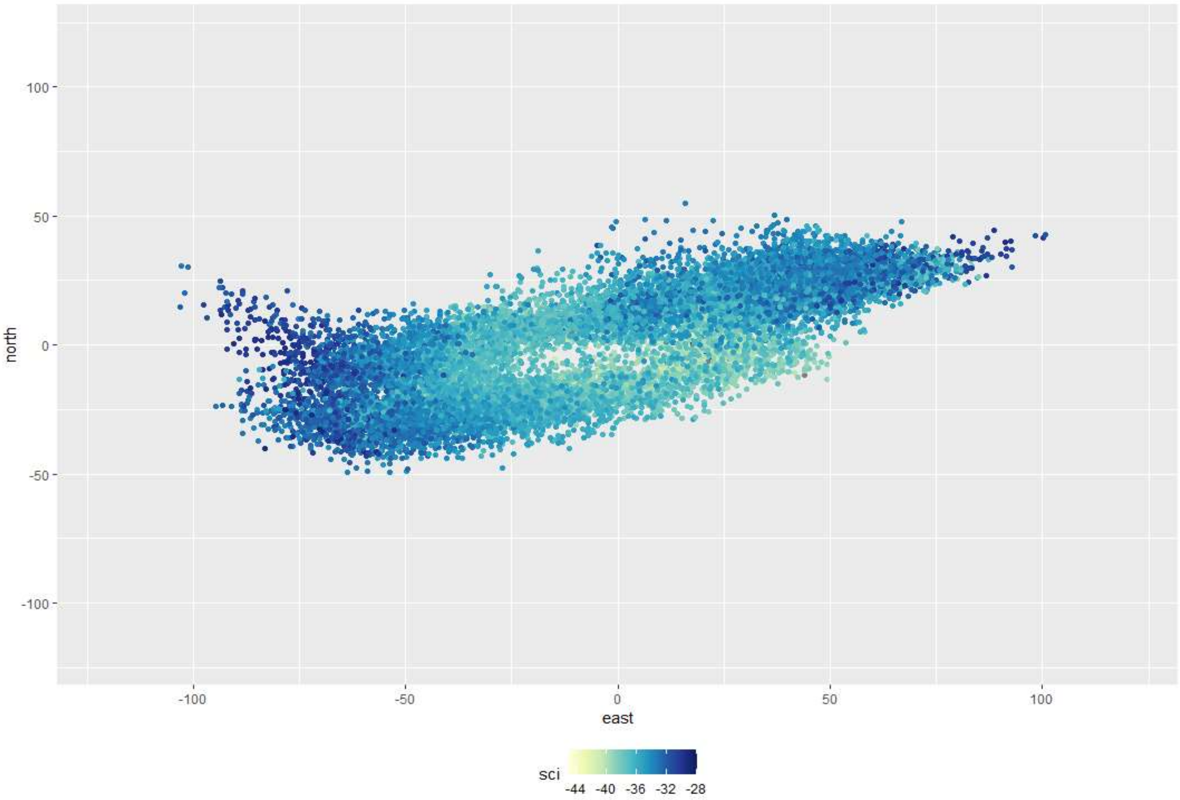

Figure 3.6: September-October 2013 at MOW1: Rather flat tidal ellipse (typically for near shore) with lower SCI values during slack tide, and higher SCI values during ebb and flood maximal currents.

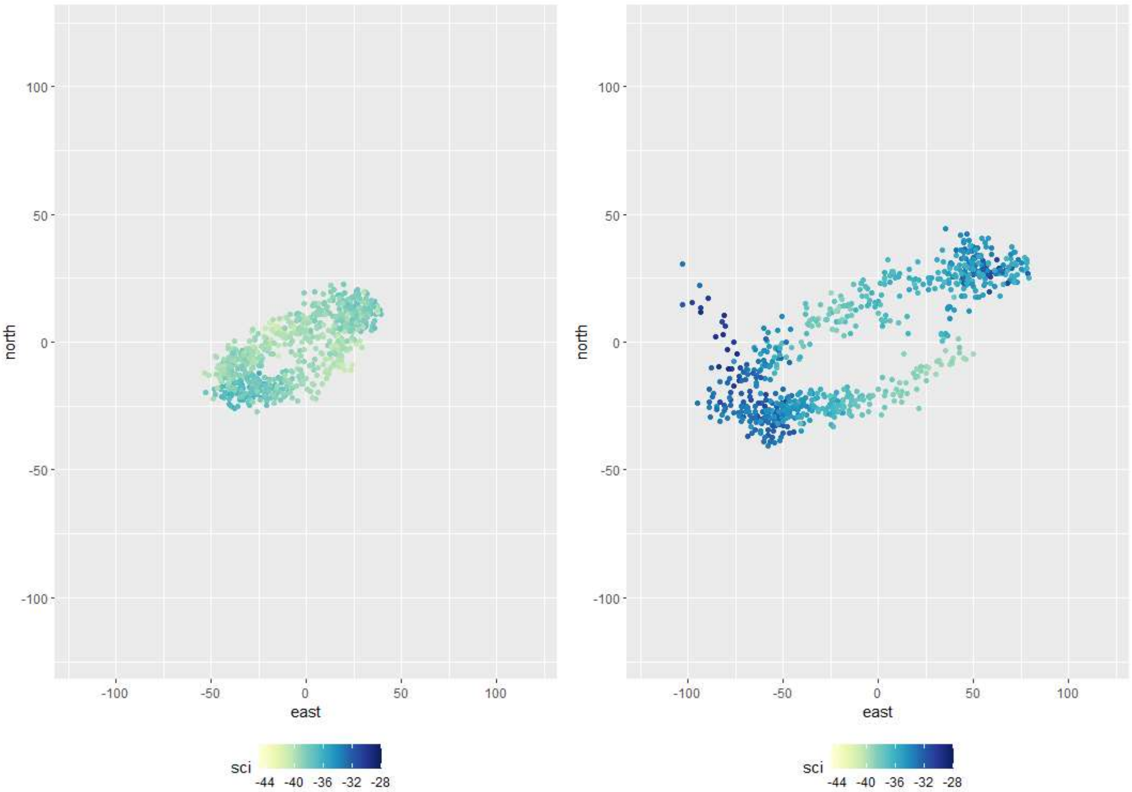

Figure 2.7: Neap tide (LEFT) vs. spring tide (RIGHT) tidal ellipse and corresponding SCI values (dB). North and east axes in cm/s.

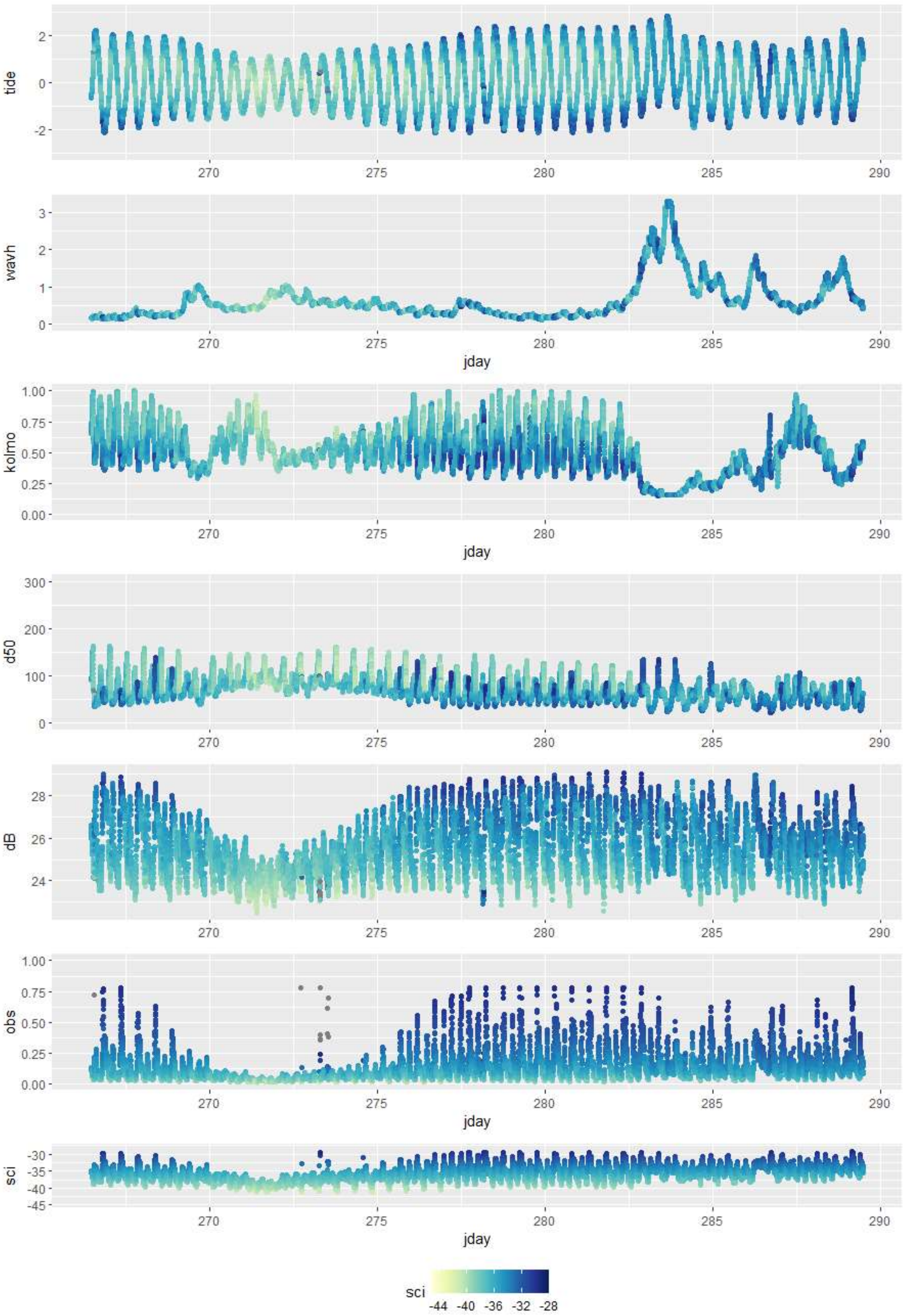

Figure 2.8: September-October 2013 at MOW1 overview plots of different parameters. From top to bottom: tide in m, wave height in m, Kolmogorov scale in m, particle diameter d50 (µm), the backscatter intensity (dB), SPM concentration (g/l) and SCI (dB). Colors in each graph refer to SCI.

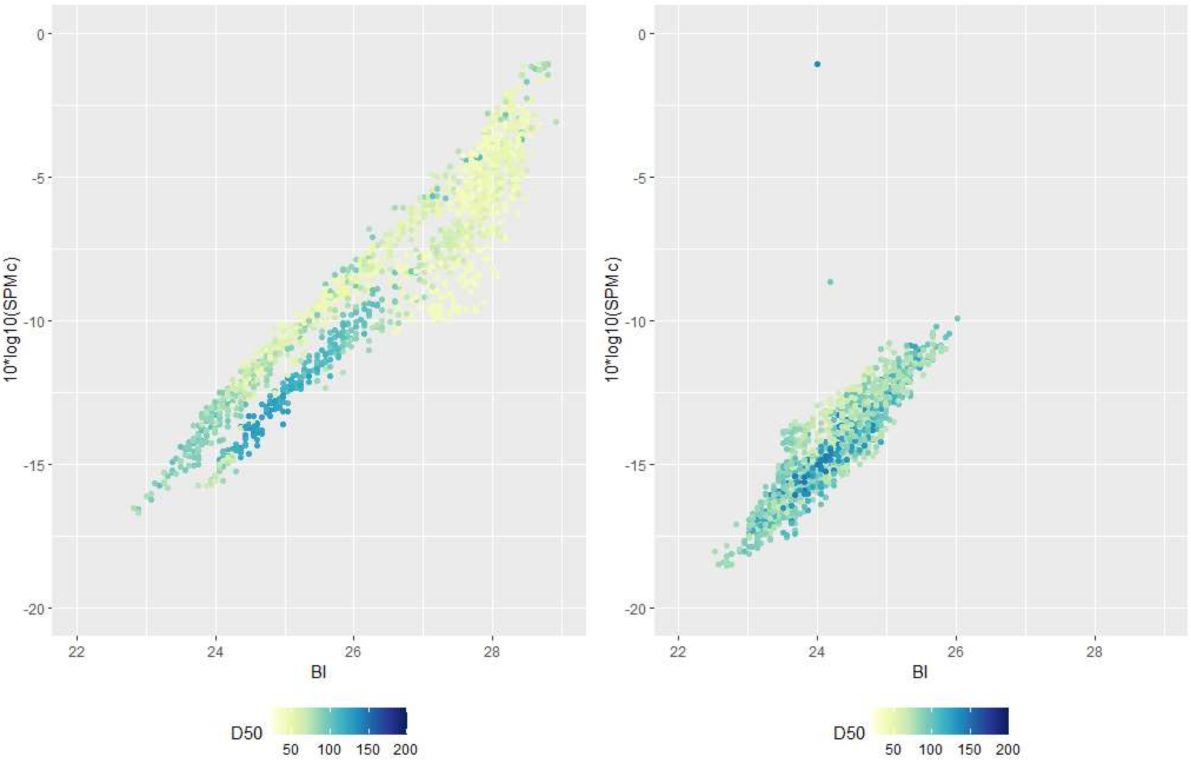

Figure 2.9: Relationship optical-acoustic backscatter response to turbidity during spring tide (LEFT) and during neap tide (RIGHT). Colors refer to D50 (µm).

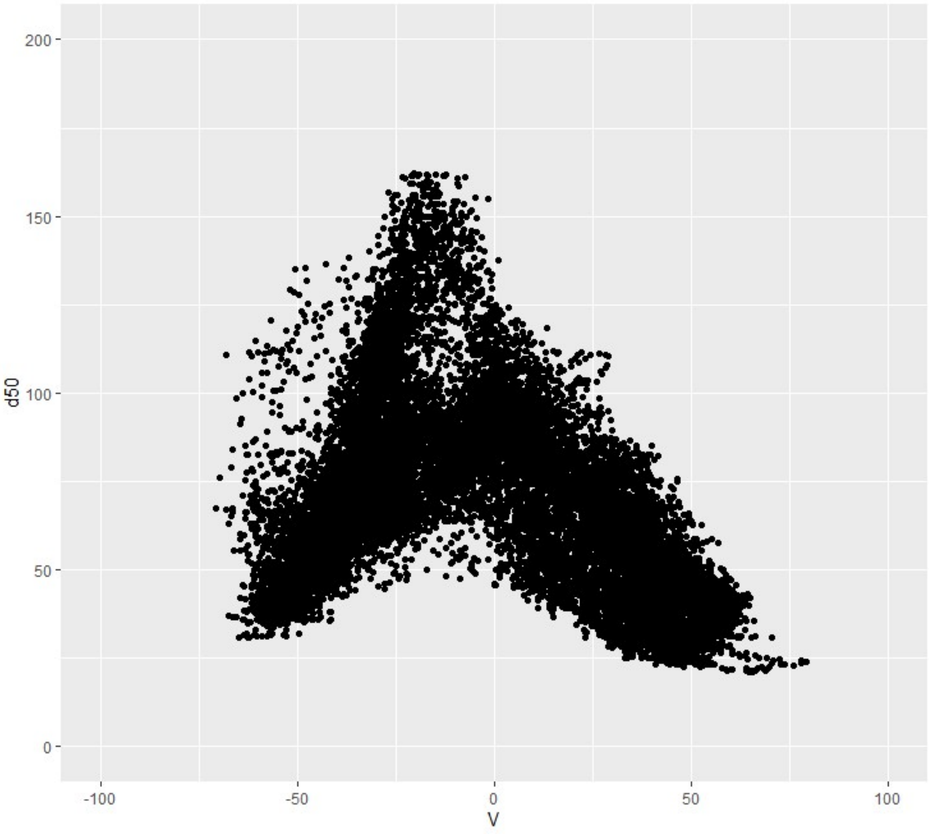

Figure 2.10: Floc dynamics at MOW1 illustrating break-up of flocs during accelerating currents (alongshore current, V in cm/s) and flocculation during decreasing current speeds.

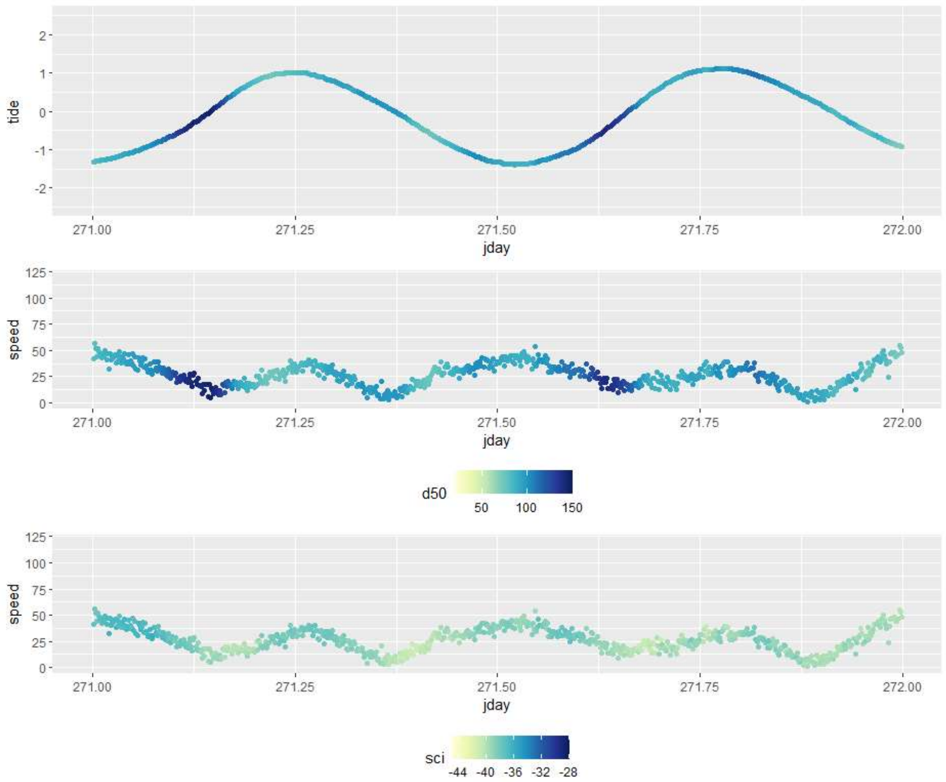

Figure 2.11: Representation of the d50 changes over 1 day during the neap tide (small tidal range of 2.5 m) which are rather small compared to spring tide (figure E3). Bottom graph is the current speed (cm/s) and SCI values (dB).

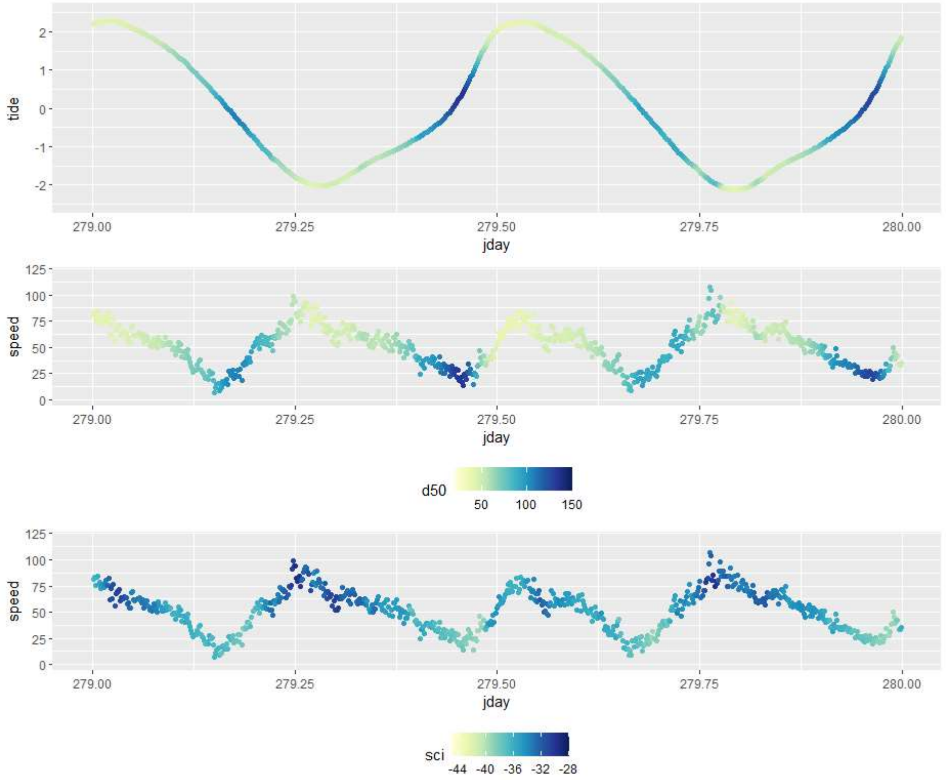

Figure 2.12: Representation of the d50 changes during the spring tide (small tidal range of 2.5 m) which are bigger compared to neap tide (figure E2). Bottom graph is the current speed (cm/s) and SCI values (dB).

3. Samenstelling van het suspensiemateriaal: Organische fractie

3.1. Reactiviteit van de organische fractie

Een eerste transdisciplinaire studie die de interactie tussen SPM en TEP (transparent exopolymer particles), POC (particulate organic carbon) en PON (particulate organic notrogen) verklaard werd gepubliceerd in 2022 (Fettweis et al., 2022). Hierin wordt beschreven dat het organisch materiaal (inclusief TEP) opgedeeld kan worden in twee fracties: een mineraal-geassocieerde en een verse fractie, die andere biogeochemische eigenschappen hebben. Wat TEP betreft heeft dit vooral betrekking op de kleverigheid, met name dat de mineraal-geassocieerde fractie beduidend minder kleverig is. Op dit moment kunnen deze twee fracties enkel gekwantificeerd worden met behulp van een semi-empirisch model (Schartau et al. 2019, Fettweis et al. 2022). De resultaten tonen aan dat het verse TEP de grotere vlokken verklaard die optreden in de lente en de zomer. Het mineraal-geassocieerde TEP, is hoog in de winter en in de kustzone en speelt geen belangrijke rol bij de vlokvorming. Om de partikel dynamica in troebele kustzones te begrijpen, moet er een onderscheid gemaakt worden (met behulp van een model) tussen het verse en het mineraal-gebondene TEP. Verder onderzoek zou kunnen zijn om deze twee fracties te identificeren en kwantificeren in een experiment.

3.2. Transitiezones tussen kust- en offshore zones

Pelagische partikels ondergaan andere biogeochemische transformaties langsheen het kust-offshore transect. Hun sedimentatie en resuspensie dynamica vertonen opvallende verschillen tussen de kustzone en de offshore zones, dit ten gevolge van veranderingen in bathymetrie (en dus in turbulentie), het aandeel van de minerale fractie in het SPM en de biologische activiteit. Deze twee laatste parameters beïnvloeden beiden de samenstelling van de deeltjes. Deze variabiliteit in ruimte en tijd werd bestudeerd met behulp van satellietbeelden en werd berekend met de maandelijkse parameters uit de modelberekeningen (Fettweis et al., 2022). De vergelijkingen worden hieronder gegeven, de parameters zijn m_{POM}, en K_{POC}, $f_{1,POC}$, $f_{2,POC}$ (POC) en K_{PON}, $f1_{,PON}$, $f_{2,PON}$ (PON), zie Tabel 3.1.

$$PON_f = f_{1,PON} * \frac{K_{PON}}{\frac{K_{PON}}{SPM_{observed}} + 1} * \frac{1}{m_{POM} + 1}$$

$$PON_m = f_{2,PON} * SPM_{observed} * \frac{m_{POM}}{m_{POM}+1}$$

Het model werd toegepast op de maandelijks gemiddelde SPM concentraties afkomstig van satelliet observaties en de verschillen tussen mineraal-gebonden en vers PON (PON_m-PON_f) worden getoond in Figuur 3.1 voor april 2021. We tonen enkel de PON fractie van het organisch materiaal, omdat het beter gecorreleerd is met de phytoplankton productie dan POC of TEP. De maandelijks verschillen tussen PON_m-PON_f voor heel de Noordzee (jaar 2017) kunnen in Appendix 1 worden gevonden. De in het rood gekleurde gebieden in Figuur 3.1 (April 2021) hebben een negatief PON_m-PON_f omdat PON_f domineert door de sterke phytoplankton productie. Het valt op dat op het BCP (Belgisch Continentaal Plat) het rood gebied niet tot aan de kust reikt en dat het relatief smal is. In de kustwateren is de concentratie aan minerale deeltjes hoog alsook van PON_m. Maar in April vertoont ook PON_f hoge concentraties zodat het verschil PON_m-PON_f minder negatief tot positief wordt. Een beetje meer offshore (rood gekleurd gebied) is PON_f lager dan aan de kust maar domineert

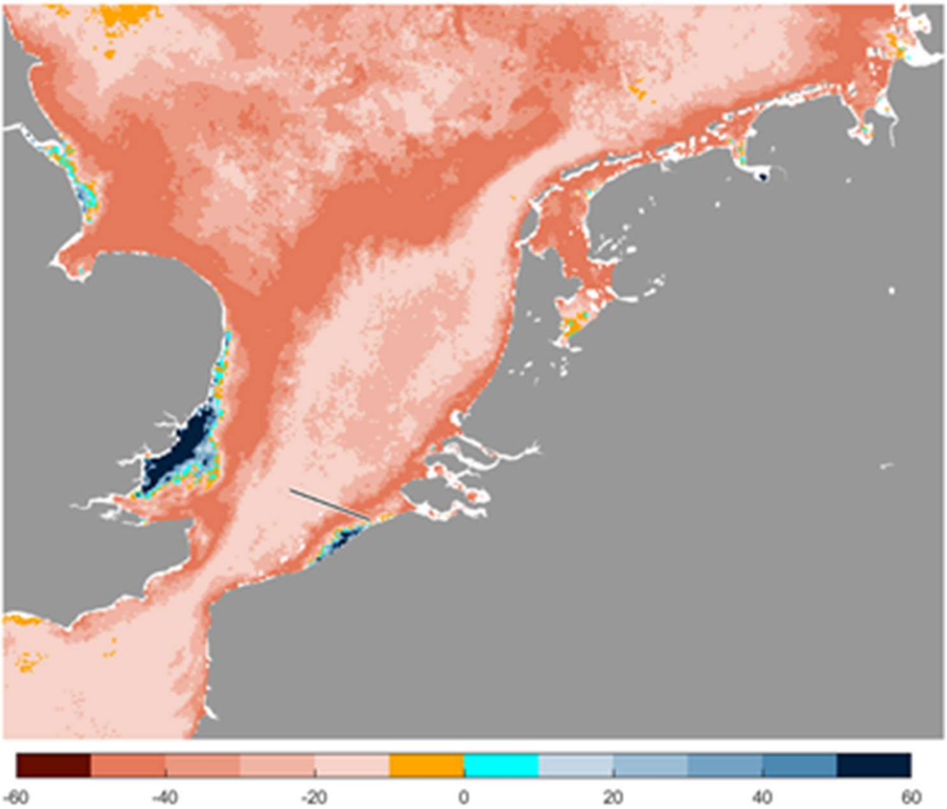

Figure 3.1: Satellite-derived map of PON_m-PON_f (mg-N m^{-3}) in the southern North Sea (April average of 2021), with a transect line linking stations MOW1-W05-W08 on the BCS.

zodanig over PON_m dat het verschil een minimum bereikt van ongeveer -45 mg-N m^{-3}. Dit wijst op een plotse en scherpe (enkele kilometers) afname van PON_m en doet het idee rijzen van een transitiezone waar de samenstelling van de deeltjes wijzigt, mogelijks door een verandering van de valsnelheid (Maerz et al. 2016). Onze hypothese is dat de phytoplankton bloei vers TEP produceert dat leidt tot een effectievere flocculatie en de vorming van grotere vlokken. De stroming nabij de bodem transporteert de vlokken richting kust, zodat deze gevangen worden en niet kunnen worden geëxporteerd naar offshore, zeer vergelijkbaar met processen in een estuariene circulatie (Maerz et al. 2016). Dit wordt ook geïllustreerd in Figuur 3.2, waar de warden van PON_m-PON_f negatief zijn en een minimum hebben rond 20 km van de kust.

Echter, Figuur 3.3 toont dat de partikels het hele jaar door, ook in de winter, een tendens vertonen om op ongeveer 20 km van de kust te sedimenteren. Dit suggereert dat, ook al doet de phytoplankton productie in de lente en de zomer de valsnelheid stijgen, andere fysische processen de flocculatie mee beïnvloeden in deze transitiezone. Bathymetrie is een goede proxy voor turbulentie, een toename in bathymetrie gaat gepaard met een afname in turbulentie en dus een beter behoud van groter vlokken omdat deze door de geringere turbulentie minder snel uiteenvallen. Figuur 3.2 toont dat de transitiezone gelegen is op ongeveer 20 km offshore, de ligging van de zone is van jaar tot jaar verschillend. Deze interannuele variabiliteit is vermoedelijk veroorzaakt door veranderingen in de indringing van oceanisch water in de zuidelijke Noordzee.

Samenvattend kan gesteld worden, dat er een transitiezone bestaat tussen kust en offshore, waar de sedimentatie van partikels een maximum kent. Het maximum in valsnelheid houd ogenschijnlijk verband met de toename in bathymetrie en de verandering in samenstelling. De interannuele verplaatsing van de transitiezone kan het gevolg zijn van meteorologische en oceanografische effecten die de menging van zoet- en oceanisch water beïnvloeden, als ook van de estuariene circulatie. Uiteindelijk zal ook de variabiliteit in phytoplankton productie de bezinking van de partikels beïnvloeden door de productie van TEP, en dit volgt de seizoenale cyclus.

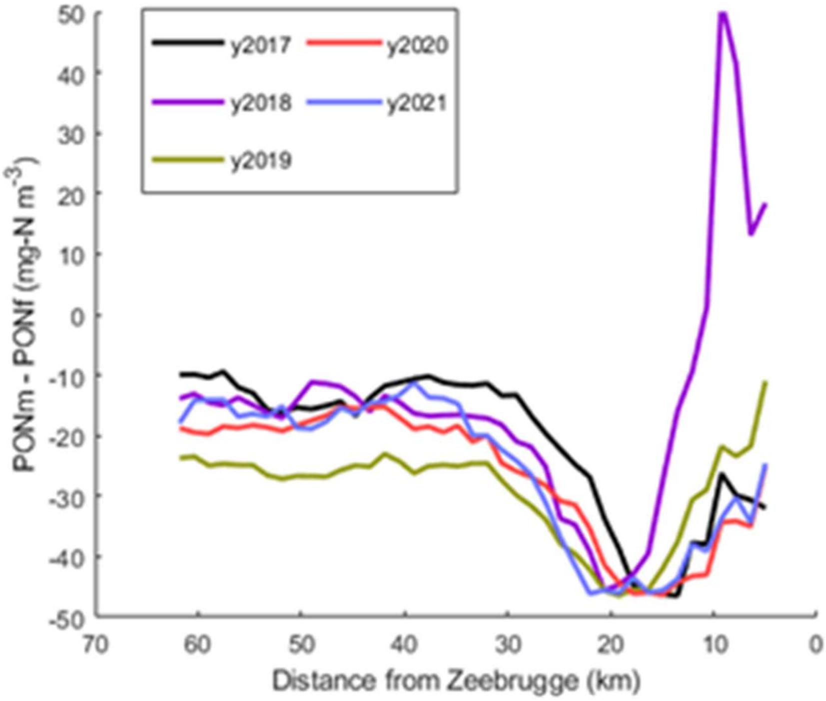

Figure 3.2: April values of PON_m-PON_f along the transect for years 2017 to 2021.

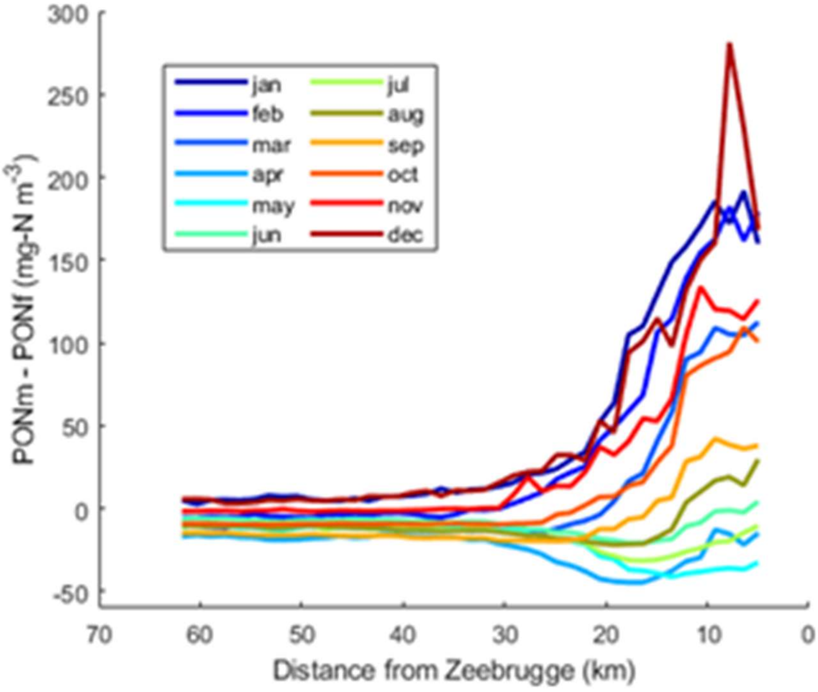

Figure 3.3: Monthly values of PON_m-PON_f as a function of the distance from the coast (Zeebrugge) along the transect of Figure 2.1 (monthly values are a multiyear average from 2017 to 2021).

Table 3.1: Monthly model parameters for POC and PON (m_{POM}=0.13).

	K_{POC} (mg/l)	$f_{1,POC}$	$f_{2,POC}$	K_{PON} (mg/l)	$f_{1,PON}$	$f_{2,POC}$
Jan	3.02	0.059	0.261	3.95	0.007	0.031
Feb	3.65	0.105	0.254	4.32	0.014	0.031
Mar	4.30	0.152	0.246	4.69	0.022	0.031
Apr	4.93	0.198	0.239	5.06	0.029	0.031
May	4.04	0.196	0.254	4.37	0.028	0.032
Jun	3.13	0.194	0.270	3.66	0.027	0.034
Jul	2.24	0.192	0.285	2.97	0.026	0.035
Aug	2.17	0.186	0.282	2.56	0.029	0.033
Sep	2.11	0.181	0.280	2.15	0.031	0.032
Oct	2.04	0.175	0.277	1.74	0.034	0.030
Nov	2.36	0.137	0.272	2.47	0.025	0.030
Dec	2.70	0.097	0.262	3.22	0.016	0.031

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COLOPHON

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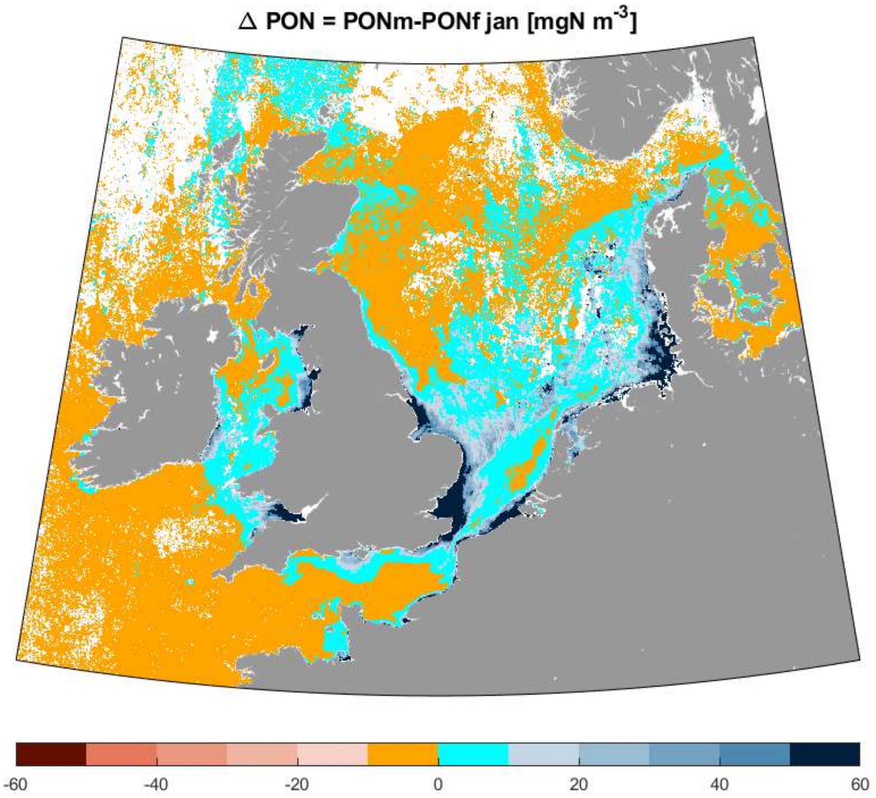
BEHEERSEENHEID VAN HET
MATHEMATISCH MODEL VAN DE NOORDZEE

APPENDIX 1

Maandelijks verschil tussen PON_m-PON_f voor 2017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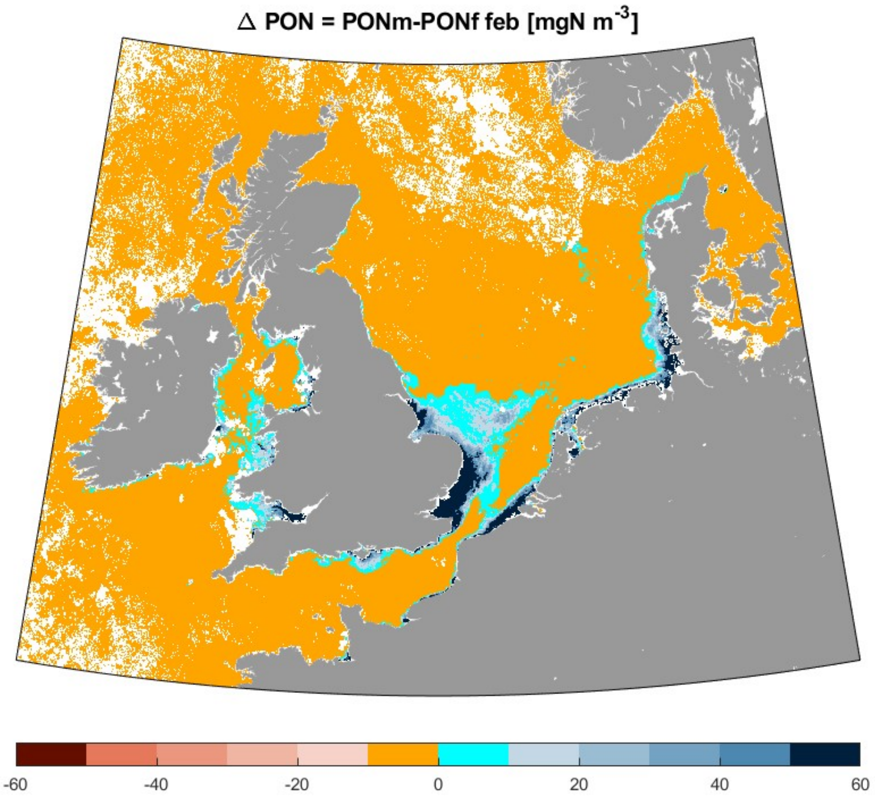
-60
-40
-20
0
20
40
60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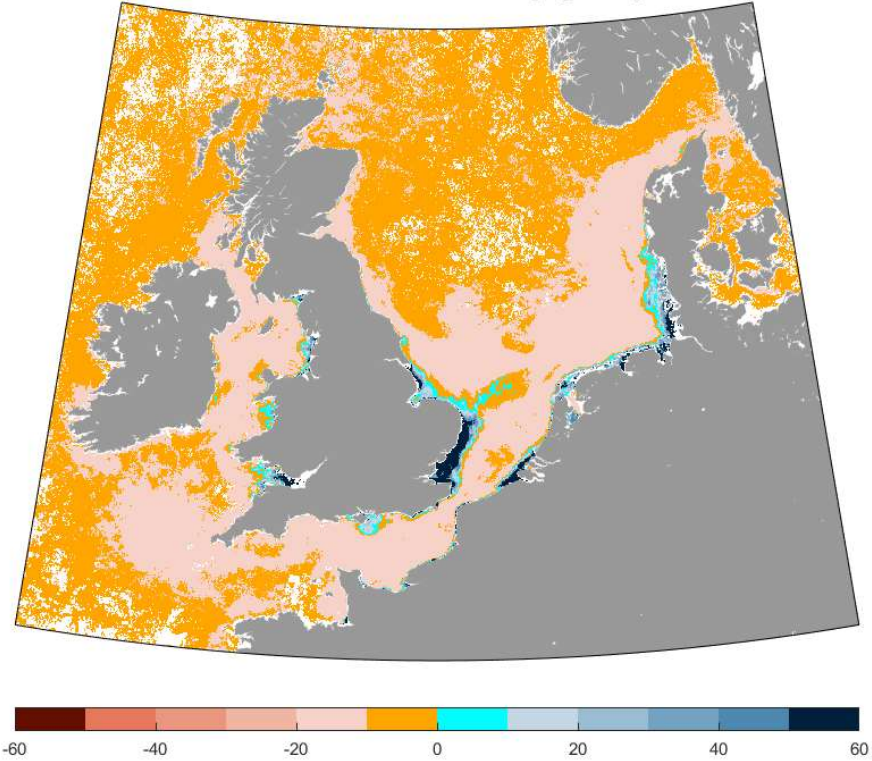
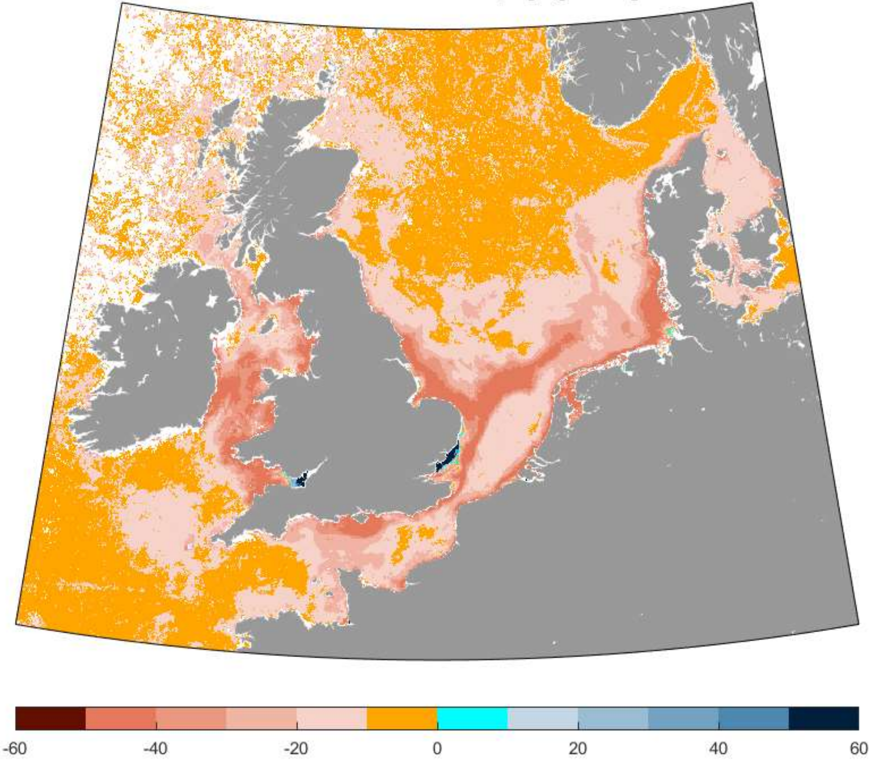
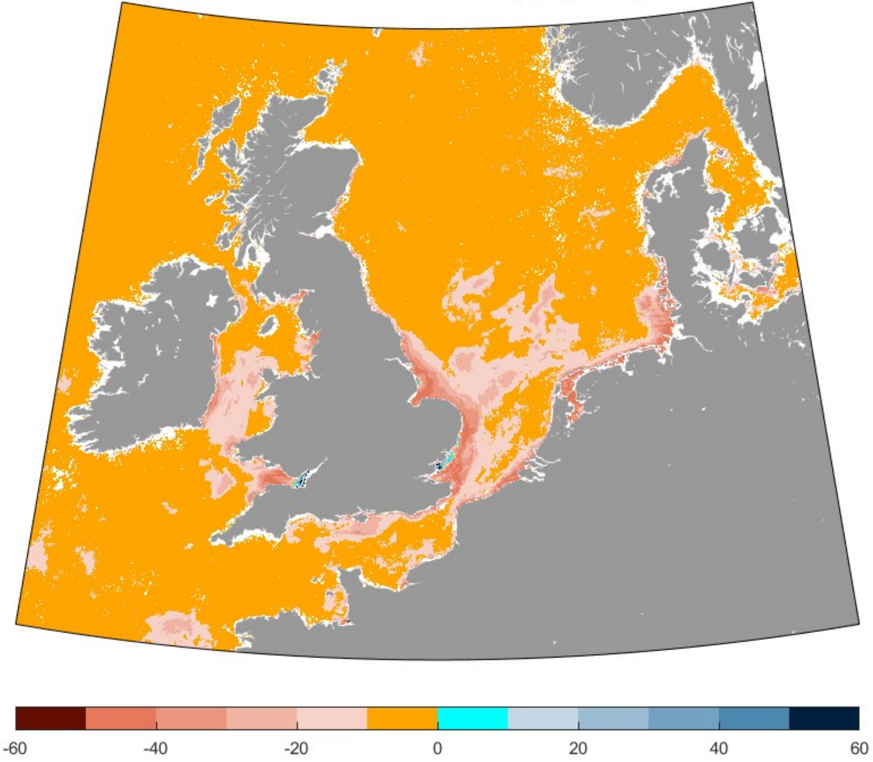
-40
-20
0
20
40
60



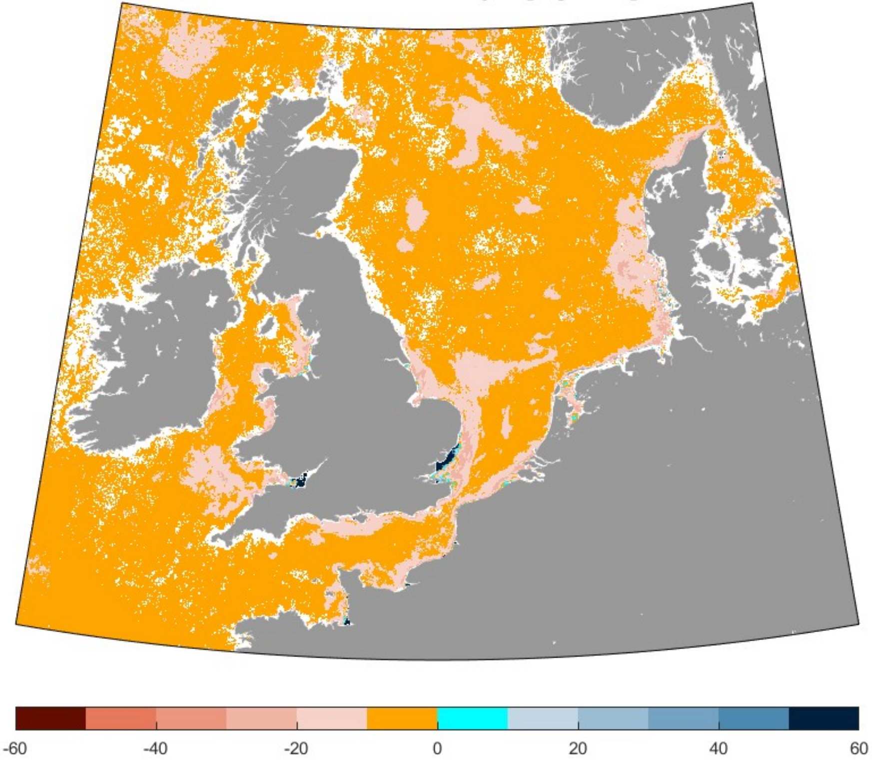
△ PON = PONm-PONf mar [mgN m^{-3}]



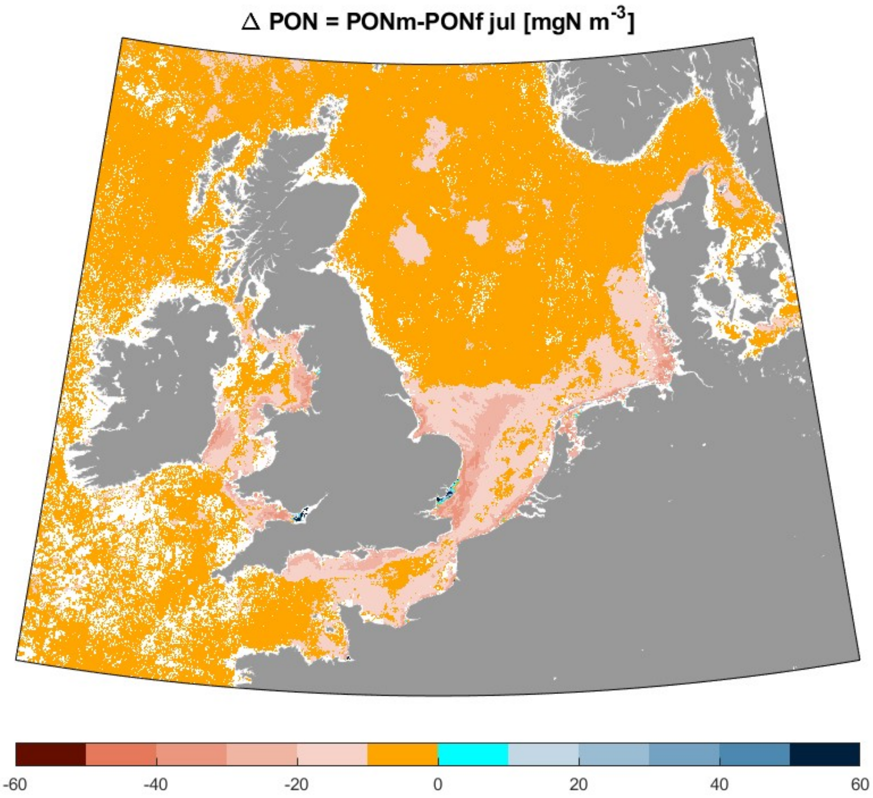
△ PON = PONm-PONf apr [mgN m^{-3}]

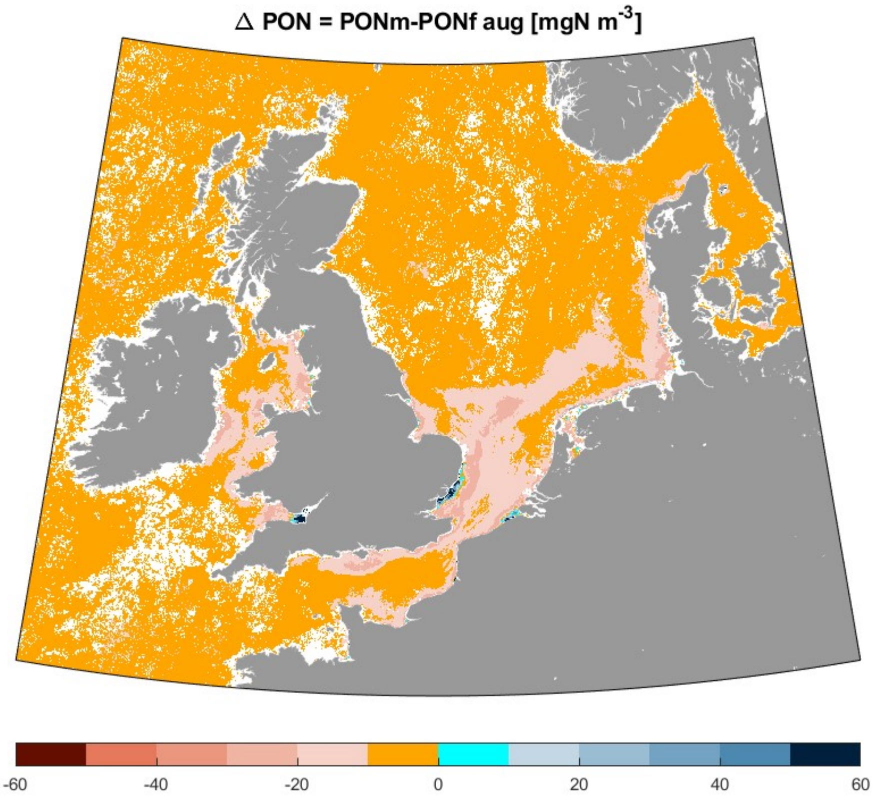


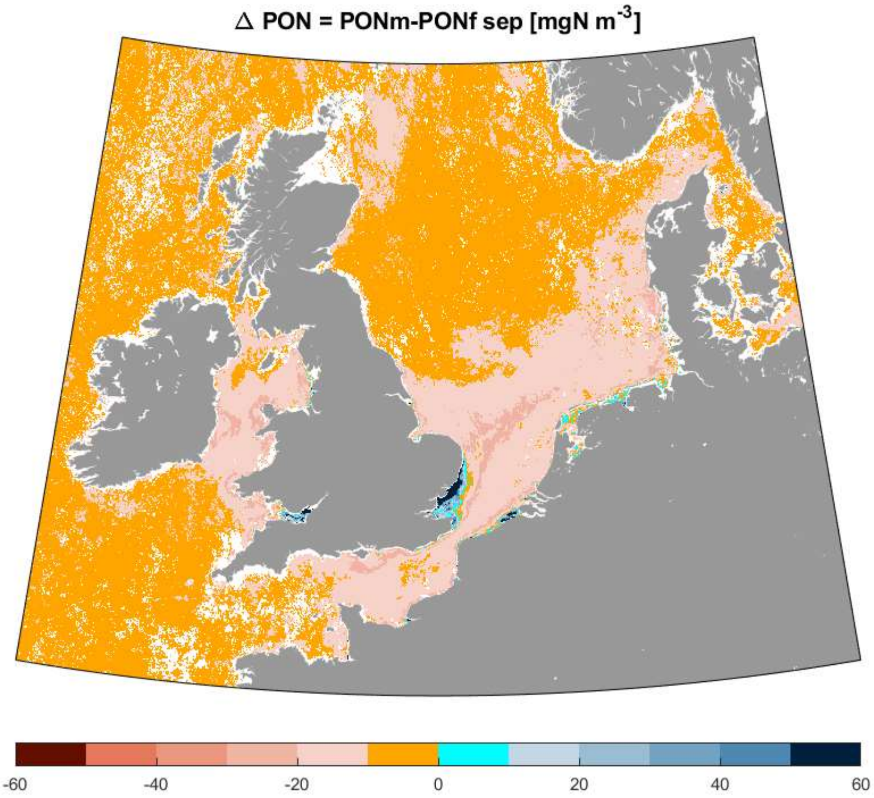
△ PON = PONm-PONf may [mgN m^{-3}]

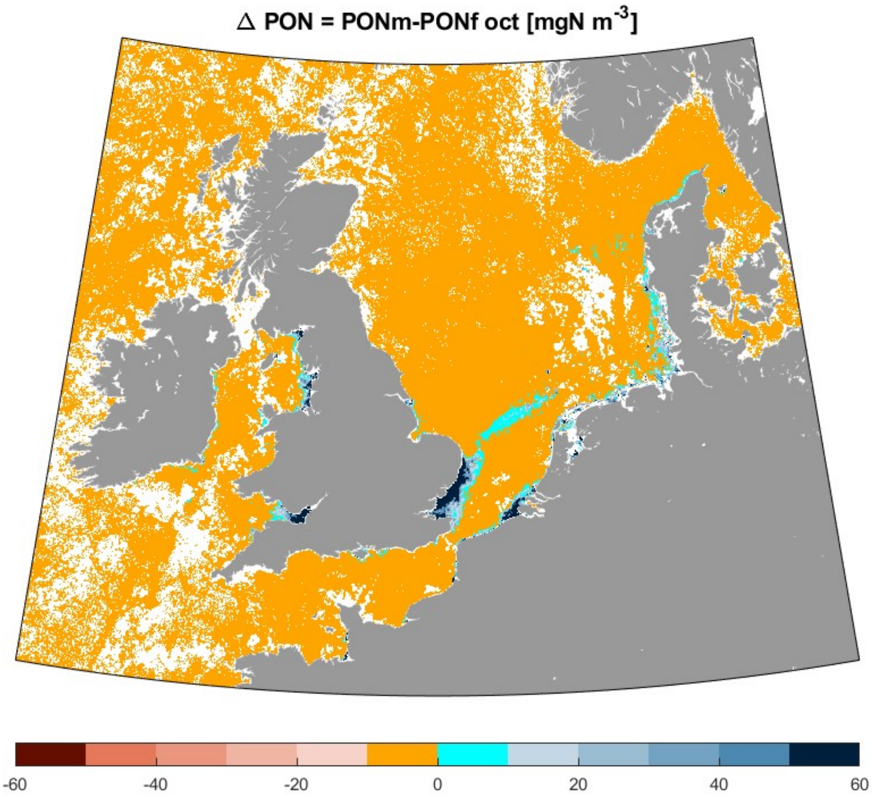


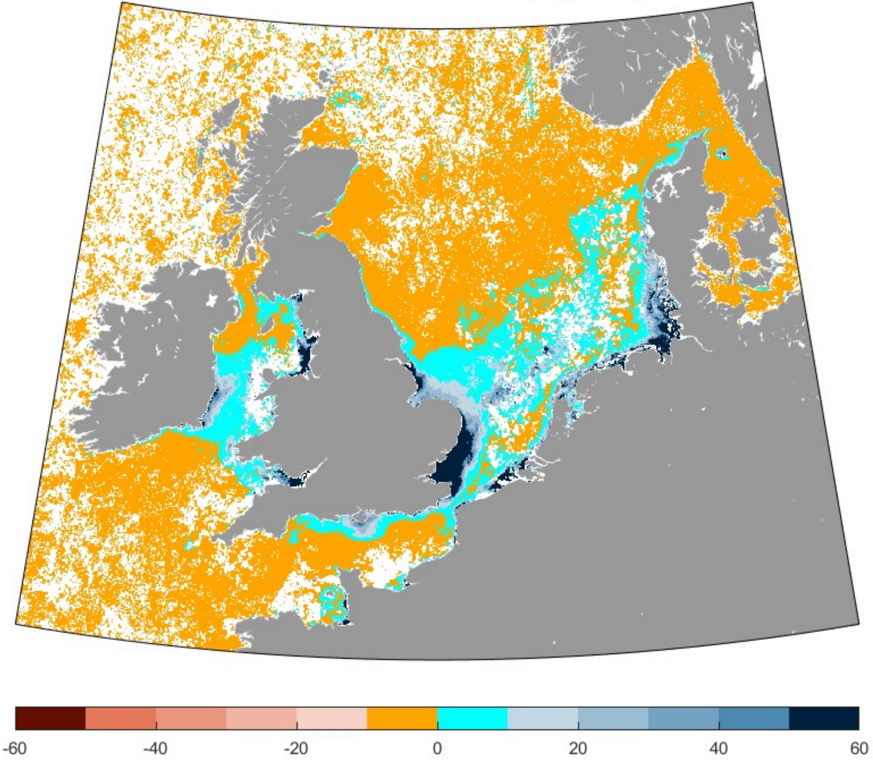
△ PON = PONm-PONf jun [mgN m^{-3}]

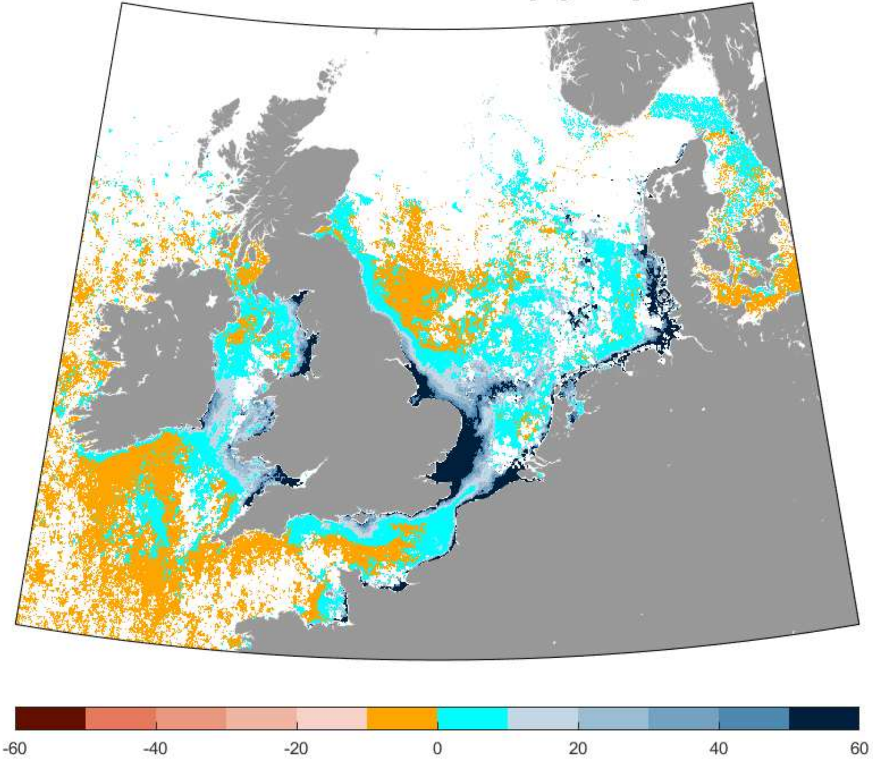

△ PON = PONm-PONf jul [mgN m^{-3}]
-60
-40
-20
0
20
40
60


△ PON = PONm-PONf aug [mgN m^{-3}]
-60
-40
-20
0
20
40
60


△ PON = PONm-PONf sep [mgN m^{-3}]
-60
-40
-20
0
20
40
60


△ PON = PONm-PONf oct [mgN m^{-3}]
-60
-40
-20
0
20
40
60


Δ PON = PONm-PONf nov [mgN m^{-3}]


Δ PON = PONm-PONf dec [mgN m^{-3}]

APPENDIX 2: Abstract Ocean Science Meeting, 24 February – 4 March, Honolulu (USA).

Organic Matter Composition of Biomineral Flocs and its Influence on Suspended Particulate Matter Dynamics along a Nearshore to Offshore Transect

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The seasonal variation in concentration of transparent exopolymer particles (TEP), particulate organic carbon (POC) and nitrogen (PON) were investigated together with floc size and the concentration of suspended particulate matter (SPM) along the cross-shore gradient, from the high turbid nearshore towards the low-turbid offshore waters in the southern Bight of the North Sea. Our data demonstrate that biophysical flocculation cannot be explained by these heterogeneous parameters, but requires a distinction between a more reactive labile (“fresh”) and a less reactive refractory (“mineral-associated”) fraction. Based on all data, we separated the labile and mineral-associated POC, PON and TEP using a semi-empirical model approach. The model’s estimates of fresh and mineral-associated OM show that great parts of the POC, PON and TEP are associated with suspended minerals, which are present in the water column throughout the year, whereas the occurrence of fresh TEP, POC and PON is restricted to spring and summer months. In spite of a constantly high abundance of total TEP throughout the entire year, it is its fresh fraction that promotes the formation of larger and faster sinking biomineral flocs, thereby contributing to reducing the SPM concentration in the water column over spring and summer. Our results show that the different components of the SPM, such as minerals, extracellular organic matter and living organisms, form an integrated dynamic system with direct interactions and feedback controls.

APPENDIX 2: Poster EuroSea/OceanPredict workshop, 29 June – 1 July, Exeter (UK)

Acoustic and optical turbidity response to altering particle size distribution during extreme events

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INTRODUCTION

Acoustic and optical devices are commonly used to measure suspended sediments in the water column. However, these two types of instruments have different responses (Fig. 1), this difference is generally recognised as depending on the composition of the sediment. **Acoustic devices are better at "hearing" sand** while **optical ones are better at "seeing" mud**.

In this poster, we present preliminary results to attempt to differentiate sand from mud composition based on the correlation between optical and acoustic responses (Fig. 2).

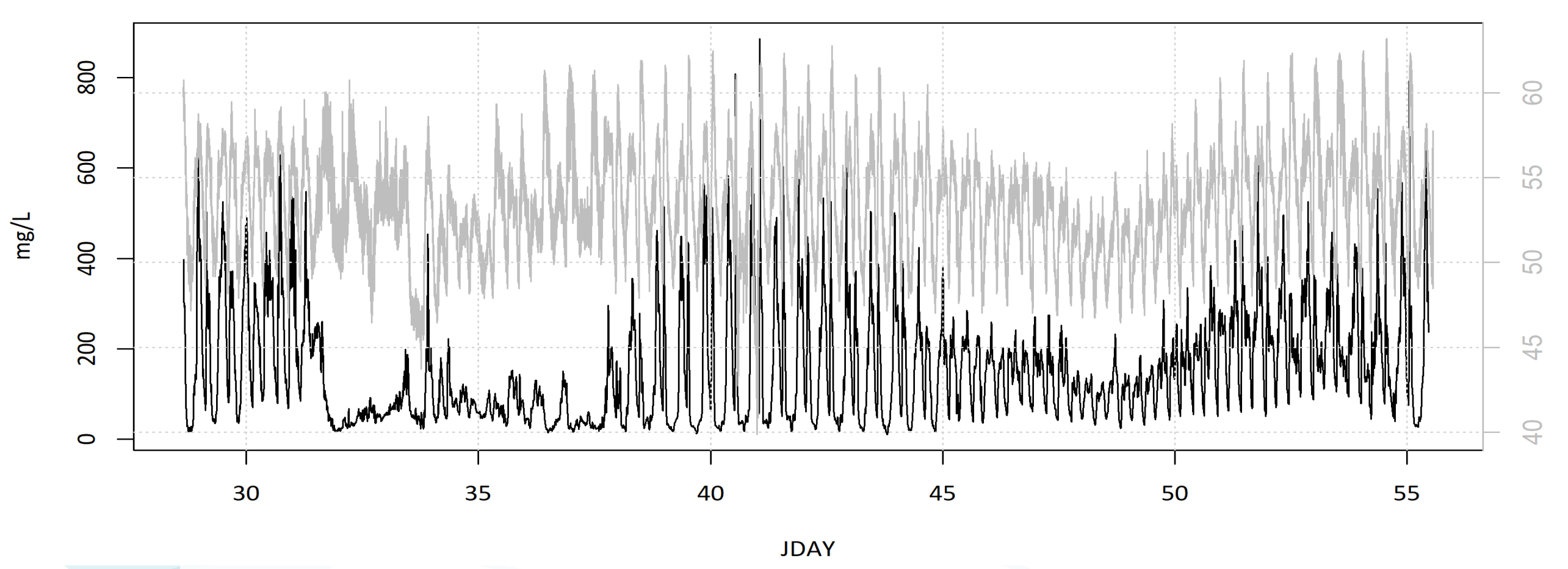

Fig. 1. Time-series of the acoustic and optical responses against the Julian day.

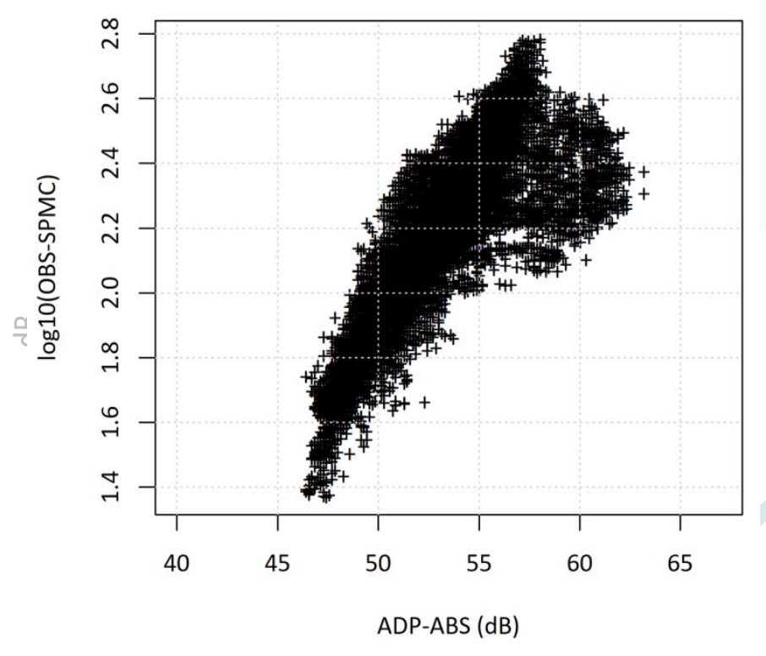

***Fig. 2.** Correlation between acoustic and optical responses.*

MATERIALS & METHODS

150 days of data were collected with a benthic tripod at one sampling location in the Belgian part of the North Sea (Fig. 3) in 2008 and 2009. Measurements with optical backscatterance sensor (OBS Campbell Sc.), acoustic Doppler profiler (ADP Sontek 3MHz) and laser in-situ scattering and transmissometry (LISST-100X Sequoia) took place at 2.3 meter above the seabed.

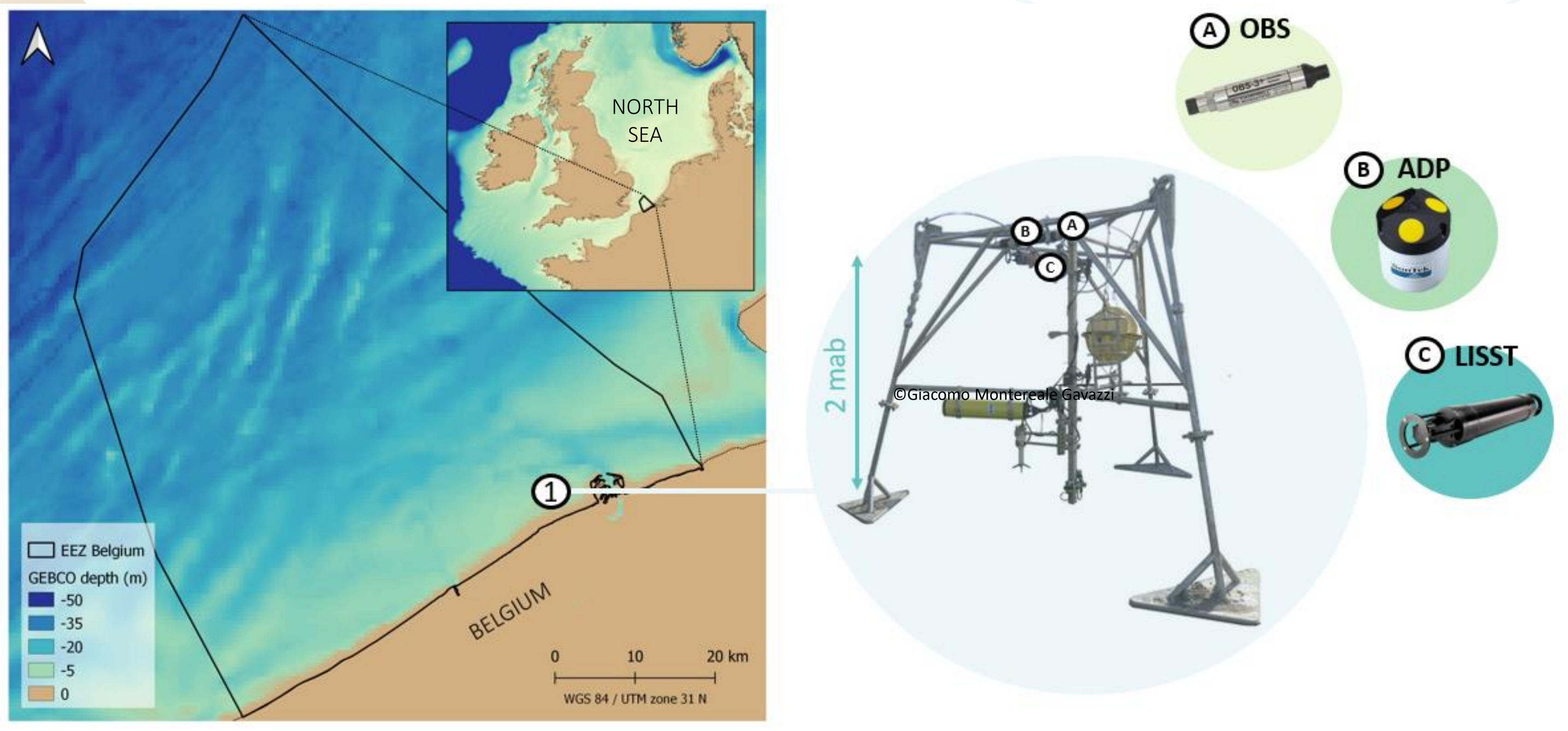

Fig. 3. Sampling location and instruments used for the collection of the data.

A regression line was then fitted between the acoustic (ADP) and optical (OBS) sensor responses over a moving 12.4-hour window (i.e. 1 tidal cycle). **It is then assumed that the slope varies under altering hydrodynamic conditions**.

A **positive** slope (and strong R²) corresponds to calmer periods (no wave activity and low TKE), while a **negative** slope (and weak correlation) corresponds to more extreme events of high TKE and waves (Fig. 5). Based on regression slope distribution, three cases were defined (higher turbulence: <mean-1 SD, medium state: mean-1SD to mean+1SD; calm conditions: >mean+1SD)

The turbulent kinetic energy (TKE) was calculated as follow:

$$k = \frac{1}{2}\left(\overline{(u')^2} + \overline{(v')^2} + \overline{(w')^2}\right)$$

When looking now into the percentage size fraction >62.5 µm, measured by the LISST, higher percentages occur for the positive slope values cases. This is associated to the well-known process of flocculation in the area (Fettweis et al. 2012). However, there is also a significant amount of sand-sized particles in suspension during the higher turbulence, implying solid (quartz) particles and not anymore mud flocs in suspension. The latter explains the poor correlation as the acoustic and optical sensor do behave differently.

REFERENCES

Fettweis et al. 2011. "Hydro-meteorological influences and multimodal suspended particle size distributions in the Belgian nearshore area (southern North Sea)", Geo-Marine Letters.

Pearson et al. 2021. "Characterizing the Composition of Sand and Mud Suspensions in Coastal and Estuarine Environments Using Combined Optical and Acoustic Measurements". Journal of Geophysical Research: Oceans, 126(7).

RESULTS

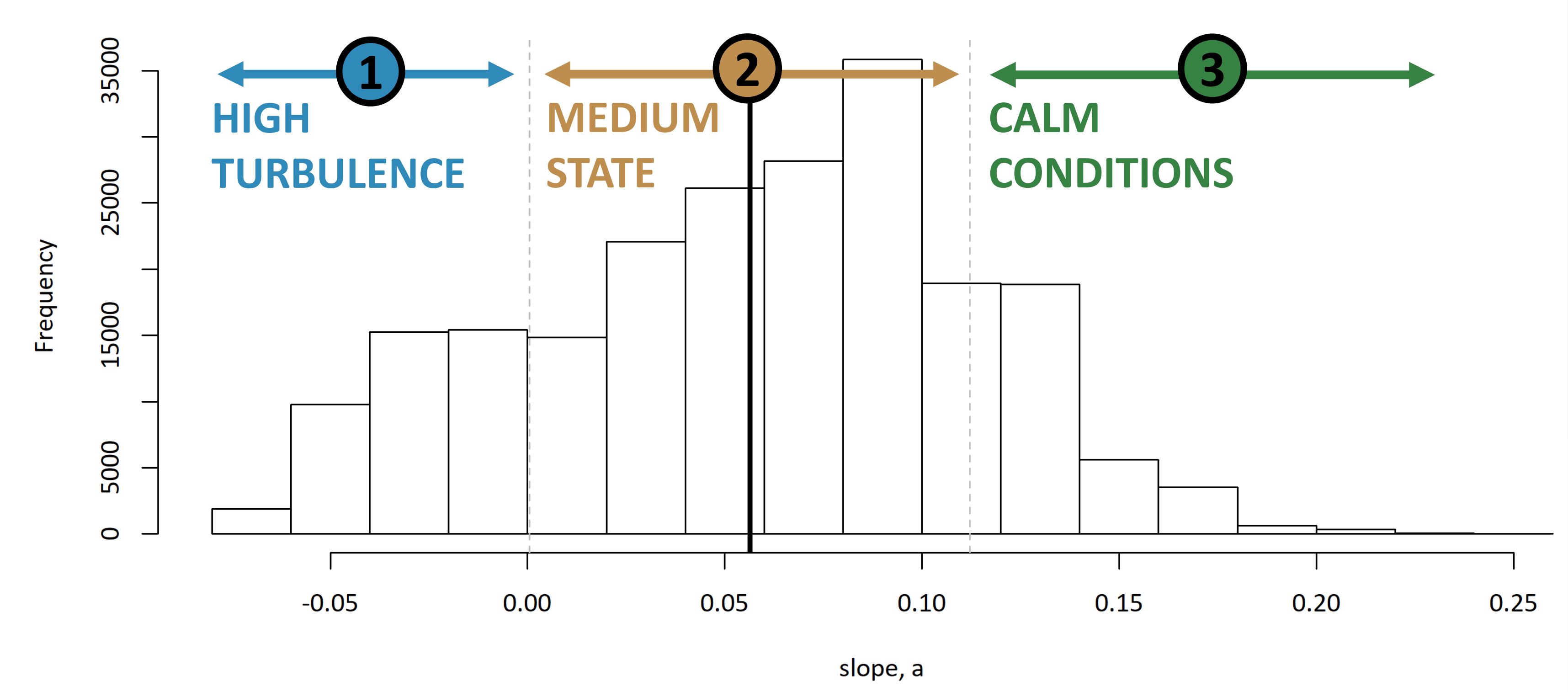

***Fig. 4.** Histogram of the slope values distribution.* Dashed vertical lines refer to 1 standard deviation (SD), and solid black line to the mean slope.

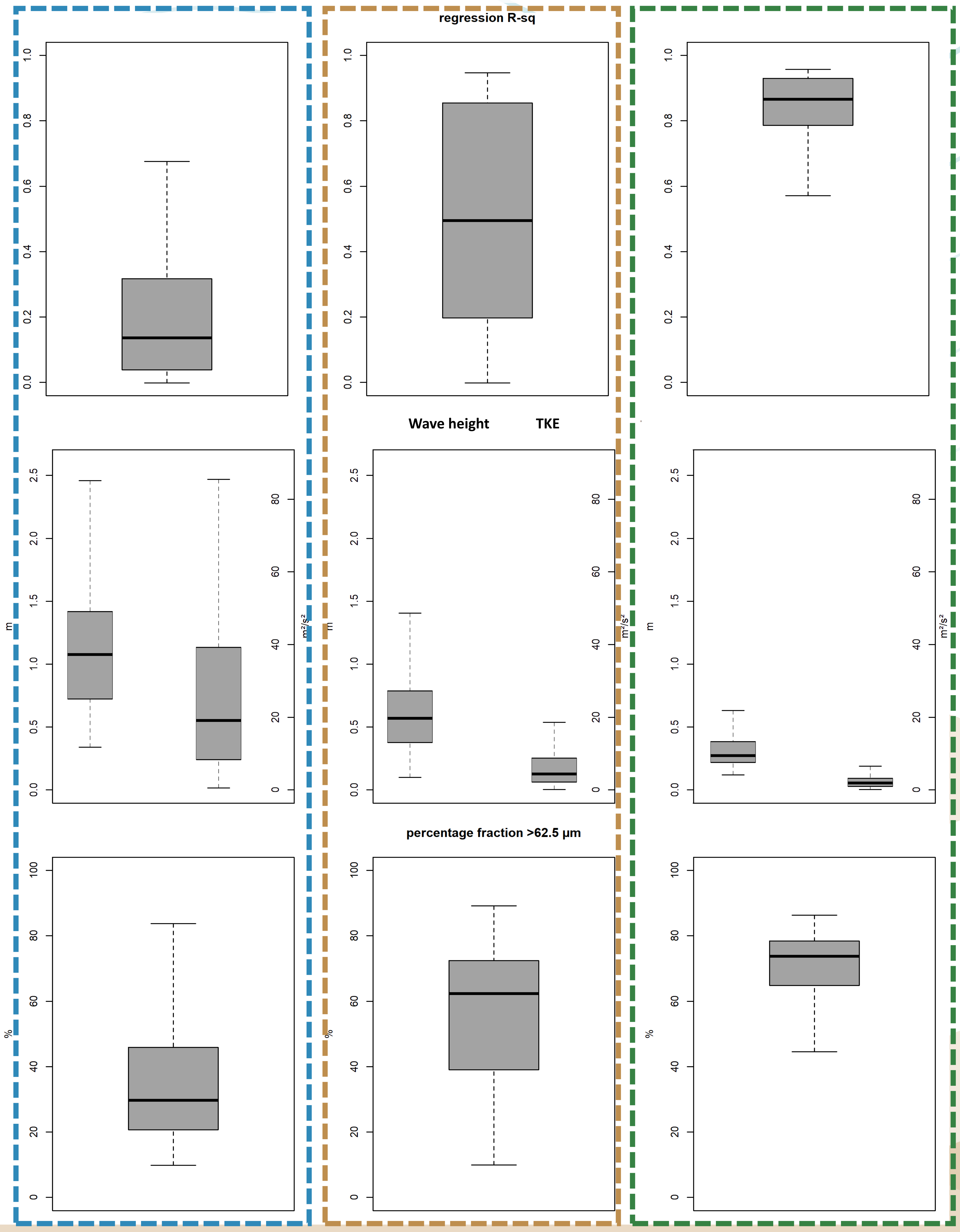

***Fig. 5.** Boxplots of the R², wave height, TKE and percentage fraction >62.5 µm for the high turbulence, medium state and calm conditions.*

Higher turbulence	Medium state	Calm conditions
Poorer correlation	More variability	Better correlation
Silt-clay and sand in suspension	Mix of silt-clay and sand	Only silt-clay (flocculation)
No mud flocs		

CONCLUSIONS & PERSPECTIVES

This work presents only preliminary results showing the importance and complexity of the correlation between acoustics and optics in a turbulent and turbid environment in order to obtain reliable suspended sediment values as well as to be able to distinguish sand from mud.

We show that turbulent conditions display a generally poorer correlation between both instruments and presents a higher concentration of sand and the absence of mud flocs.

Future works include the study of the total dataset (2005-2021) as well as the integration of the SCI as described by Pearson et al. 2021.

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APPENDIX 4: Ho QN, Fettweis M, Spencer KL, Lee BJ. 2022. Flocculation with heterogeneous composition in water environments: A review. *Water Research*. 118147. doi:10.1016/j.watres.2022.118147

Water Research 213 (2022) 118147

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Review

Flocculation with heterogeneous composition in water environments: A review

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CBB, Coomassie Brilliant Blue
CSPs, Coomassie stainable particles
DOM, Dissolved organic matter
ENPs, Engineered nanoparticles
EPS, Extracellular polymeric substances
FA, Fulvic acids
HA, Humic acids
Hm, Humin
HS, Humic substances
LB-EPS, Loosely bound EPS
MPs, Microplastics
OM, Organic matter
OWFs, Offshore wind farms
POM, Particulate organic matter
SPM, Suspended particulate matter
TB-EPS, Tightly bound EPS
TEP, Transparent exopolymer particles
TOC, Total organic carbon

ABSTRACT

Flocculation is a key process for controlling the fate and transport of suspended particulate matter (SPM) in water environments and has received considerable attention in the field of water science (e.g., oceanography, limnology, and hydrology), remaining an active area of research. The research on flocculation has been conducted to elucidate the SPM dynamics and to diagnose various environmental issues. The flocculation, sedimentation, and transportation of SPM are closely linked to the compositional and structural properties of flocs. In fact, flocs are highly heterogeneous in terms of composition. However, the lack of comprehensive research on floc composition and structure has led to misconceptions regarding the temporal and spatial dynamics of SPM. This review summarizes the current understanding of the heterogeneous composition of flocs (e.g., minerals, organic matter, metals, microplastic, engineered nanoparticles) and its effect on their structure and on their fate and transport within aquatic environments. Furthermore, the effects of human activities (e.g., pollutant discharge, construction) on floc composition are discussed.

1. Introduction

Flocculation involves a combined process of the aggregation and breakage of suspended particulate matter (SPM) in the water environment, as shown in Fig. 1. Here, aggregation induces particles to attach to each other to form larger flocs, while breakage disaggregates large flocs into smaller flocs or into primary particles (Lee et al., 2012; Maggi, 2005). Flocculation determines the structure, density, and settling velocity of flocs and thus the overall governing fate and transport of SPM. Alongside the recent changes in climate conditions and land use, flocculation, sedimentation, and transportation can alter the SPM dynamics and budget in water environments.

The water environment is full of dissolved substances and living and nonliving particles that are suspended in the water column. In the continuum from river and estuary to coast, flocs largely consist of minerals in estuarine and nearshore turbidity maximum zones, while they contain more organic matter and low-density aggregates (e.g., marine snow) in offshore zones. The size, density, and settling velocity

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of these flocs determine their fate and transport under tidal currents, while their concentration affects the water clarity. Clearly then, the mineralogical and biological components of flocs are important parameters for understanding the SPM dynamics in water environments.

Various physical and biochemical processes result in some variation in floc structure and SPM dynamics. In terms of a short timescale, tides, waves, and winds come into play, while in terms of a long timescale, seasonal, climatological, and interannual dynamics are significant. Seasonal dynamics are primarily caused by the seasonality of solar forcing that drives the physical (e.g., weather conditions, thermal stratification, and light) and biochemical (e.g., primary production) processes. The result of human activities related to both land and water resources, such as agriculture, construction, pollutant discharge, eutrophication, sediment deposition, and dredging, can also affect floc structure and SPM dynamics.

The flocs in aquatic systems are highly heterogeneous in terms of composition (Droppo et al., 1997; Droppo, 2001; Maggi, 2013) as shown in Table 1. In fact, flocs can be regarded as individual microecosystems with autonomous and interactive chemical, physical, and biological reactions and processes activating within the floc matrices (Droppo et al., 1997). They contain three major groups of heterogeneous components, including inorganic components that contain cohesive (e.g., clay) and noncohesive minerals (e.g., sand, quartz, carbonates), biological components that include living (e.g., phytoplankton, bacterial) and nonliving components (e.g., extracellular polymeric substances [EPSs], transparent extracellular polymers [TEPs]), and chemical components that include ions (e.g., metals) and organic compounds (e.g., glucose, humic substances) (Tang, 2016). As noted above, flocs can vary in their heterogeneous composition, both temporally and spatially (Fettweis and Lee, 2017).

The heterogeneous composition of flocs affects their structure, porosity, density, and size, and, as such, ultimately the SPM dynamics in water environments. This paper provides a review of the current understanding of the heterogeneous composition of flocs and its effect on floc structure and the SPM dynamics in water environments. A better understanding of the heterogeneous composition of flocs will ultimately enhance our knowledge regarding their compositional and structure properties as well as the SPM dynamics in water environments.

2. THE heterogeneous composition of flocs

2.1. *Inorganic matter*

The inorganic matter in flocs can be categorized into minerals and naturally occurring metals. Inorganic matter meditates not only physical processes (e.g., floc density, settling, and transportation) (Droppo, 2001) but also chemical processes (e.g., the adsorption and transportation of pollutants and nutrients) (Horowitz, 1991), whereas this form of matter, especially minerals, can also provide habitats and reactive sites for bacterial colonization and chemical and biological reactions (Droppo and Ongley, 1994; Liss et al., 1996).

2.1.1. *Minerals*

Minerals are a major component of flocs. Mineral particles aggregate with one another and incorporate other dissolved and suspended substances into flocs, ultimately determining the floc composition and structure. For example, as building materials, mineral particles combine with particulate organic matter (POM) to assemble large settleable biomineral flocs (Chen et al., 1994). Here, mineral particles and POM are arranged in an irregular and complex manner, with pore spaces in the floc occupied by water (Droppo et al., 1997). Moreover, mineral particles also provide habitats and sites for bacterial colonization and biochemical reaction (Droppo and Ongley, 1994; Liss et al., 1996).

The suspended and deposited sediment in water environments is categorized according to size in terms of clay (< 2 μm), silt (2–63 μm), and sand (63–2000 μm), as well as larger particles with a variety of mineral compositions (McCave and Hall, 2006; Walsh and Nittrouer, 2009). A large number of clay-sized particles consist of clay minerals (e.g., kaolinite, montmorillonite, illite) as well as other minerals, such as quartz, carbonates, or feldspars. Meanwhile, quartz, carbonates, and other silicates typically appear in the silt- and sand-sized particles. Clay minerals are cohesive due to certain physicochemical attractive forces (e.g., van der Waals and electrostatic forces), while silt- and sand-sized particles are less cohesive or even noncohesive. Clay and silt particles are the most abundant in a floc, with sand particles seldomly found in this form of matter due to their heaviness and noncohesiveness. Clay minerals are tightly bound in the flocculi, a compound word of floc and nuclei (Lee et al., 2012), via electrostatic attraction, with the flocculi subsequently aggregating further to form flocs through the gluing action of EPSs, as shown in Fig. 2. (Yin, 2013). This stepwise growth from primary particle to flocculi and floc tends to accelerate in aggregation-favorable conditions with a high clay concentration and moderate turbulence.

Silt can present a heterogeneous composition in a clay-dominant floc, while it is less cohesive (Tran and Strom, 2017). Tran et al. reported that when silt and clay minerals are in suspension, clay-dominant flocs can incorporate silt particles within the floc structure, thereby increasing the floc density and settling velocity and changing the floc

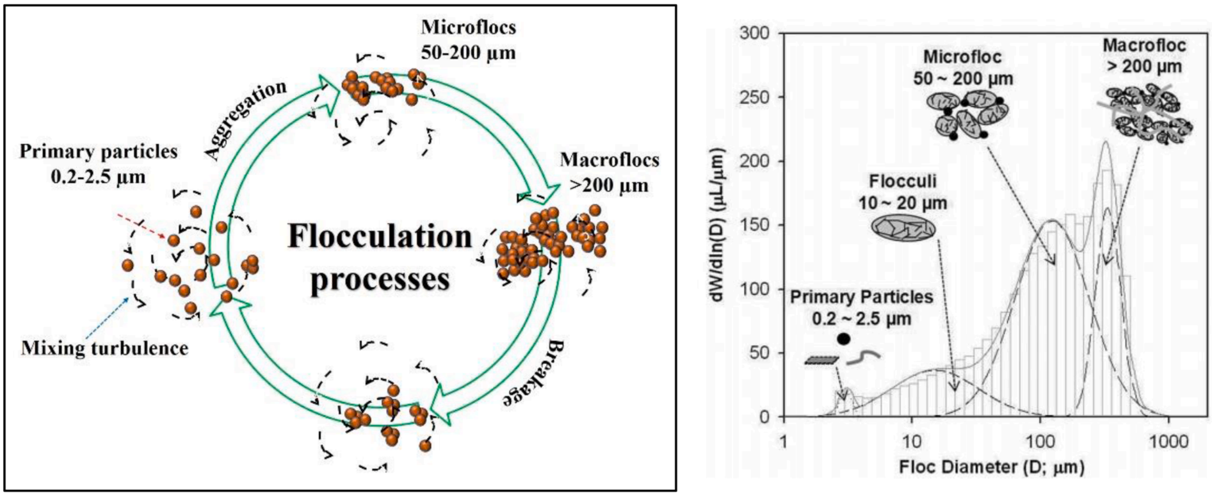

Fig. 1. Left: schematic of the flocculation processes of aggregation and breakage, right: hierarchical floc structures composing floc size distribution (Kuprenas et al., 2018, Lee et al., 2012).

Table 1
Heterogeneous composition of flocs in aquatic environments.

Compositions	States	Sources	Functions/Contributions	References
Inorganic Matter				
Mineral particles	- Particulate - Colloidal	- Nature (e.g., erosion, weathering) - Human activities (e.g., agriculture, construction, dredging)	- Mineral particles aggregate into flocs and incorporate other dissolved and suspended substances into floc matrices - Minerals provide reactive sites for bacterial colonization and biochemical reactions	(Chen et al., 1994; Droppo and Ongley, 1994; Liss et al., 1996)
Naturally occurring metals	- Particulate - Colloidal - Dissolved	- Nature (e.g., weathering)	- Chemical precipitation aids in the transformation of metal ions into crystals or composites, which are also important heterogeneous ingredients in flocs	(Jonas and Millward, 2010; Palanques et al., 1995)
Organic Matter				
Microorganism	- Particulate - Colloidal	- Nature (e.g., phytoplankton and bacteria) - Human activities (e.g., aquaculture, diffuse pollution, eutrophication)	- Phytoplankton and bacteria form flocs and biomineral flocs in combination with minerals - Phytoplankton and bacteria produce biopolymers, as sticky binders between biomineral particles	(Alldredge and Gotschalk, 1989; Kranck and Milligan, 1980; Tran et al., 2020; Winterwerp and Van Kesteren, 2004)
Nonliving organic particles	- Particulate - Colloidal	- Nature (e.g., cell debris, fecal pellets) - Human activities (e.g., aquaculture, diffuse pollution, eutrophication)	- Detrital POM, produced by the decaying of terrestrial and aquatic organisms, can contribute to the heterogeneous composition of flocs - Fecal pellets, secreted by filter feeders, can also contribute to the heterogeneous composition of flocs	
Extracellular polymeric substances (EPS)	- Particulate - Colloidal - Dissolved	- Nature (e.g., production by algae or bacteria)	- EPSs can be either POM or DOM, depending on their molecular weights - EPSs act as polymeric bridges between particles and build large, settleable flocs - EPSs and the associated cations mitigate the overall negative surface charge of particles, thereby increasing the flocculation potential of particles	(Nouha et al., 2018; Schmidt and Ahring, 1994; Shen et al., 1993)
Transparent exopolymer particles (TEP)	- Particulate - Colloidal	- Nature (e.g., production by algae or bacteria)	- TEPs are quantified using polysaccharide-specific Alcian Blue staining - Highly viscose and sticky TEPs can facilitate flocculation in terms of combining various particles of solid, nonsticky particles, cells, debris, and dissolved substances	(Passow, 2002b)
Coomassie stainable particles (CSPs)	- Particulate - Colloidal	- Nature (e.g., production by algae or bacteria)	- CSPs are enumerated by a protein-specific staining - CSPs are less viscose and sticky than TEPs but are considered as a component of flocs given their abundance in aquatic environments	(Cisternas-Novoa et al., 2015; Long and Azam, 1996; Thornton, 2018)
Humic substances (HS)	- Colloidal - Dissolved	- Nature (e.g., excretion and decomposition of plankton and aquatic bacteria) - Human activities (e.g., agriculture, decomposition of land plants)	- HS can adsorb on SPM, it promotes HS-mediated flocculation and incorporation of HS into floc matrices in the brackish and saline water of the estuarine and coastal zones. - HS associated within flocs were found to scavenge trace inorganic elements in estuaries	(Kholodov et al., 2014; Komy et al., 2014; Mahler et al., 2021)
Water and Pore Space				
Water in/around flocs		- Nature (e.g., river, lake, coast)	- Water runs around/through flocs can exchange inorganic and organic matter into floc matrices	(Droppo et al., 1997; Droppo, 2001)
Pore Space		- Nature (space in a floc)	- Pore space, occupied by water, affects floc structure, density and creates drag when settling. - Pore water mediates the physical and biochemical processes in floc matrices and thereby modifies floc composition and structure.	(Droppo, 2001; Li and Ganczarczyk, 1988; Logan and Hunt, 1987; Sherman, 1953)
Xenobiotic Substances				
Microplastics (MPs)	- Particulate - Colloidal	- Human activities (e.g., food packaging, household waste, agriculture)	- MPs are an important component of flocs, given their affinity to SPM and their abundance in aquatic environments	(Lobelle and Cunliffe, 2011; Oberbeckmann et al., 2014; Taylor et al., 2016; Van Cauwenberghe et al., 2013)
Engineered nanoparticles (ENPs)	- Particulate - Colloidal	- Human activities (e.g., cosmetics, painting and coating compounds, catalysts, lubricants)	- ENPs are easily trapped in the pore space of flocs in association with EPS - ENPs interact with the EPSs in floc matrices and can be part of the heterogeneous composition of flocs	(Adeleye and Keller, 2016; Fernando et al., 2020)
Oil Droplets				
Oil droplets	- Emulsion - Colloidal	- Artificial and human activities (e.g., ship refueling, pipeline breakage, drilling operation failure). - Natural oil-bearing sediments	- Hydrophobic oil droplets can easily attach to SPM, thereby becoming a part of flocs with a heterogeneous composition. - Oil droplets and EPSs can attach to each other to form flocs - hydrophobic sediments containing naturally occurring oils have small floc size affecting transport behavior	(Droppo et al., 2016; Lee, 2002; Quigg et al., 2016)

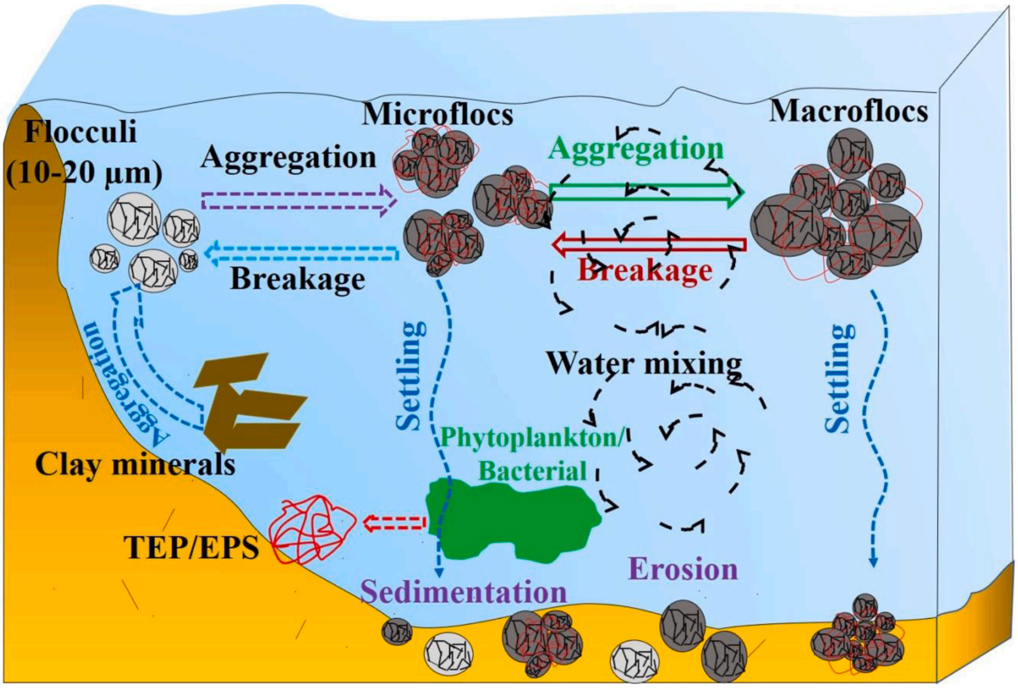

Fig. 2. Schematic diagram of suspended particulate matter (SPM) dynamics in a water environment (Yin, 2013).

structure (Tran and Strom, 2017). As such, silt-sized particles can contribute to the heterogeneous composition of flocs; however, silt-dominant flocs with less clay composition are highly porous and are readily broken down by turbulence (Li et al., 1993).

2.1.2. *Naturally occurring metals*

The metals that appear in nature can be incorporated into floc matrices. Metals undergo biogeochemical cycling and ultimately surface in aquatic environments, having been released from rocks and top soil via erosion and weathering (Garrett, 2000), at which point they are transported to waterbodies as dissolved ions, chemically precipitated particles or sorbed to other particulate species. Metal-rich precipitates are often found in flocs with a heterogeneous composition (Jonas and Millward, 2010; Palanques et al., 1995). For example, the red-colored precipitates of iron oxide easily attach to clay particles in soil and water, while EPSs can also contribute to binding metals on flocs and to increasing the heterogeneity of the floc composition (Decho and Gutierrez, 2017).

2.2. *Organic matter*

Organic matter can be integrated into flocs in the forms of POM and dissolved organic matter (DOM). While the latter is able to pass through a filter (0.45 μm), the former is generally retained on the filter (Hartnett, 2018), with its composition including living microorganisms (e.g., bacteria, phytoplankton) and nonliving compounds (e.g., TEPs, Coomassie stainable particles [CSPs], plant or animal debris), and xenobiotic particles from human activities (e.g., microplastics) (Lee et al., 2019). The quantity of POM in suspension can be determined by various methods. Loss-on-Ignition, for example, involves the combustion of POM on a filter, and will give the percentage of OM in the SPM (Wang et al., 2011). Other methods, such as element analysis (Ehrhardt and Koeve, 1999) will give the concentration of particulate organic carbon and nitrogen, while HPLC method (Wright et al., 1991) will provide the concentration of pigments, such as chlorophyll a. Bacteria and phytoplankton can be quantified using conventional counting methods. For example, bacterial cells are generally counted via light or epifluorescence microscopy, while phytoplankton cells tend to be enumerated using an electronic particle counter (Muthukrishnan et al., 2017; Picazo et al., 2013; Willén, 1976). Meanwhile, TEPs and CSPs are generally quantified through staining with Alcian Blue (AB) and Coomassie Brilliant Blue (CBB), respectively (Cisternas-Novoa et al., 2014; Passow and Alldredge, 1995). The DOM in aquatic systems consists of numerous allochthonous and autochthonous organic compounds with a wide-ranging molecular weight from micro- (e.g., organic acids) to macromolecule (e.g., fulvic and humic acids) (Amy et al., 1987; Leenheer and Jean-Philippe, 2022; Rashid and King, 1969). EPSs can be an important part of either DOM or POM, depending on their molecular size, significantly contributing to the heterogeneous composition of flocs, with EPS concentration generally quantified using total carbohydrates and protein analysis (Hung and Santschi, 2001; Panagiotopoulos and Sempéré, 2005; Smith et al., 1985).

The different analysis methods measure all or parts of the OM in suspension and combine living and non-living types of OM that can be labile, semi-labile or refractory. As a simple distinction, POM can be separated into a freshly produced, free floating and a mineral-associated, more refractory OM fraction (Schartau et al., 2019). The mineral-associated and the freshly produced POM have different susceptibilities towards microbial degradation (Arndt et al., 2013). The mineral-associated OM content is a function of the available mineral surface area and is particularly bound with phyllosilicates (Blattmann et al., 2019; Keil et al., 1994; Mayer, 1994). The relative fractions of freshly produced labile OM along with the rather recalcitrant mineral-associated OM of the SPM change with SPM concentration and season (Fettweis et al. 2022, Schartau et al. 2019). Below a more specific classification of the POM and DOM is given, based on the above mentioned methods and on its origin.

2.2.1. *Microorganisms*

Some microorganisms, especially phytoplankton, form biological flocs in aquatic systems, often adhering to mineral particles and building large biomineral flocs. Many phytoplankton species have extruding spines or hairs that enhance flocculation via the mechanical adhesion or entanglement of the particles (Kiørboe et al. 1990). Microorganisms are thus important heterogeneous components of flocs and can be used to determine their morphological aspects, including size, porosity, and density (Alldredge and Gotschalk, 1989; Kranck and Milligan, 1980). The stickiness and flocculation potential of phytoplankton cells are based on the frequency and efficiency of cell collision and attachment, which depends on the cells' physicochemical and biological properties (Kiørboe et al., 1990; Kiørboe and Hansen, 1993). The stickiness and flocculation potential become particularly high in nutrient-depleted conditions (Smetacek, 1985). Notably, the stickiness and flocculation potential depend on the generic species of phytoplankton. For example, in lake environments, colonial phytoplankton species (e.g., *Aphanotece*) attach better to mineral particles and form larger flocs than filamentous species (e.g., *Aphanizomenon*) (de Lucas Pardo et al., 2015; Verspagen et al., 2006).

Marine snow is a special type of organic-rich floc that appears in offshore areas with a floc size of over 500 μm and a composition of detritus, living organisms, and inorganic matter (Alldredge and Silver, 1988; Turner, 2015). Marine snow has a fluffy structure with high porosity and a heterogeneous composition (Maerz et al., 2020), with phytoplankton and phytodetritus as the main components (Turner, 2015). A high population of phytoplankton in aquatic environments increases the occurrence of marine snow. As such, the presence of marine snow indicates the high productivity of the aquatic ecosystem.

The interaction between heterotrophic bacteria and phytoplankton also promotes a bacteria-mediated aggregation of microbial cells. The stickiness and flocculatio potential of bacteria vary depending on the bacterial taxa or exopolymers (Tran et al., 2020). Certain species of bacteria influence phytoplanktonic physiology and enhance the stickiness and flocculation of phytoplankton cells (Decho, 1990; Heissenberger and Herndl, 1994). Other species of bacteria have also attach directly to phytoplankton and enhance flocculation (Gärdes et al., 2010; Grossart et al., 2006).

2.2.2. Nonliving organic particles

Detrital POM is produced via the decaying of various aquatic and terrestrial organisms (e.g., plant litter, cyanobacterial, fungi, algae) and becomes suspended in the water column and ultimately contributes to floc formation as a heterogeneous ingredient. The main sources of detrital POM include zooplankton, phytoplankton, terrestrial plants, and animals, with the matter diversified in terms of properties depending on the source. Various detrital POM species can thus act as heterogeneous ingredients in floc formation.

Fecal pellets, generally secreted by filter feeders (e.g., mussels, oysters) can also contribute to flocs with a heterogeneous composition. For example, mussels enhance biological fouling and result in the conversion of slowly sinking organic and inorganic SPM into large and fast-sinking fecal pellets, which can be regarded as large biomineral flocs. Mussels can thus enhance the stability of SPM deposits on the sea floor, making them resistant to tidal currents. Furthermore, when fecal pellets are decomposed via biological and tidal actions, they are subject to resuspension and flocculation in the water column (Winterwerp and Van Kesteren, 2004).

2.2.3. Extracellular polymeric substances

The production of EPSs is a general feature of microorganisms in water environments, which occurs in eukaryotic and prokaryotic microorganisms (Wingender et al., 1999). In simple terms, EPSs are polymeric substances biosynthesized from several strains of microorganisms (Flemming and Wingender, 2010). EPS formation from microbial cells has many origins, including cell surface material shedding, active secretion from microorganisms, cell lysis, and sorption from the environment (Liu and Fang, 2003, Wingender et al., 1999). However, when microorganisms exist within nitrogen-limiting conditions, they produce more EPSs as the intracellular carbon cannot be allocated for growth (Bhaskar and Bhosle, 2005; Engel et al., 2004). The nitrogen concentration is often used as an indicator of EPS production in water/sediment environments.

The EPSs act as polymeric bridges between particles to build large, settleable flocs. Here, multivalent cations can further enhance the formation of polymeric bridges by connecting between the functional sites of EPSs and the negatively charged sites of bacterial and mineral particles (Zhang et al., 2015). The EPSs and binding cations mitigate the overall negative surface charge of particles, thereby increasing the flocculation potential of particles (Nouha et al. 2018; Schmidt and Ahring, 1994, Shen et al., 1993). Clearly, EPSs play an important role in flocculation and are a key component in the heterogeneous composition of flocs.

In general, EPSs are classified into soluble and bound substances, as shown in Fig. 3. Soluble EPSs include macromolecules, slimes, and colloids, while bound EPSs include capsular polymers, loosely bound polymers, condensed gels, sheaths, and attached organic compounds (Comte et al., 2006; Laspidou and Rittmann, 2002, Nielsen and Jahn, 1999; Yu et al., 2008). Soluble EPSs are also termed soluble microbial products (SMP) and can move freely among the microbial flocs and the surrounding liquid. Meanwhile, bound EPSs exhibit a dynamic double-layer-like structure and can be roughly grouped into loosely bound EPS and tightly bound EPS (Liang et al., 2010; Ramesh et al., 2006). These substances also differ in terms of chemical composition under different environmental conditions of microbial communities, with the most abundant chemical compounds of EPS being polysaccharides and proteins (Leppard, 1997; More et al., 2012; Nouha et al., 2015; Santschi et al., 1998; Subramanian et al., 2010), while more minor compounds include humic substances (HS), nucleic acids, uronic acids, humic acids, and lipids (d'Abzac et al., 2010a; D'Abzac et al., 2010b; Nguyen et al., 2016; Sutherland, 2001b; Wingender et al., 1999).

2.2.4. Transparent exopolymer particles

As a special particulate species of EPS, TEPs are ubiquitous in water environments, while this has only been known since the development of quantification methods from 1993 onward (Alldredge et al., 1993). The average size of TEPs has been determined to be larger than 0.4 μm, while they tend to present various forms, including clouds, amorphous blobs, sheets, filaments, or clumps (Alldredge et al., 1993; Berman and Passow, 2007). This form of particle can be regarded as a "sticky" building material in flocs, since it exists in particle form rather than as a cell coating or dissolved slime, as shown in Fig. 4 (Alldredge et al., 1993).

The quantity of TEPs varies spatially in the continuum from river and estuaryto coast. In low turbid environments, the quantity of TEPs in marine and fresh waters is similar to that of phytoplankton, with the highest occurrence appearing in phytoplankton blooms. In contrast, in turbid environments (e.g., a turbidity maximum zone), a large quantity of minerals can adsorb TEPs on their surface, and hence TEP-coated (or TEP-associated) minerals are deposited on the bed layer. Therefore, the quantity of TEPs tends to decrease in turbid waters during the summer bloom season. The clay minerals in turbid environments can thus facilitate the stabilization and burial of organic matter (i.e., TEP), depending on their abundance (Blattmann et al., 2019; Fettweis et al., 2022; Keil et al.; 1994; Mayer, 1994).

The TEPs enhance flocculation and are an important heterogeneous component of flocs due to their adhering capacity as polymeric binders or glue. Highly viscose and sticky TEPs can enhance flocculation as they combine numerous solids, nonsticky particles, cells, debris, and dissolved substances (Passow, 2002b). An abundance of TEPs will also enhance the probability of particle collision in the water environment (Jackson, 1995; Passow et al., 1994), thereby increasing the particle aggregation rate. However, it is important to note that not all the TEP species have the same adhesive quality, with TEPs from nondiatom microorganisms not as sticky as those from diatom species (Kiørboe and Hansen, 1993; Logan et al., 1995, Passow and Alldredge ,1994).

While TEPs and EPSs have been categorized into the same biopolymer group in scientific communities, in the authors' opinion, TEPs should be classified into a subgroup of EPSs (Li et al., 2016; Morelle et al., 2017; Passow, 2002b). In fact, while both TEPs and EPSs contain a large proportion of acidic polysaccharides (Passow, 2002a,

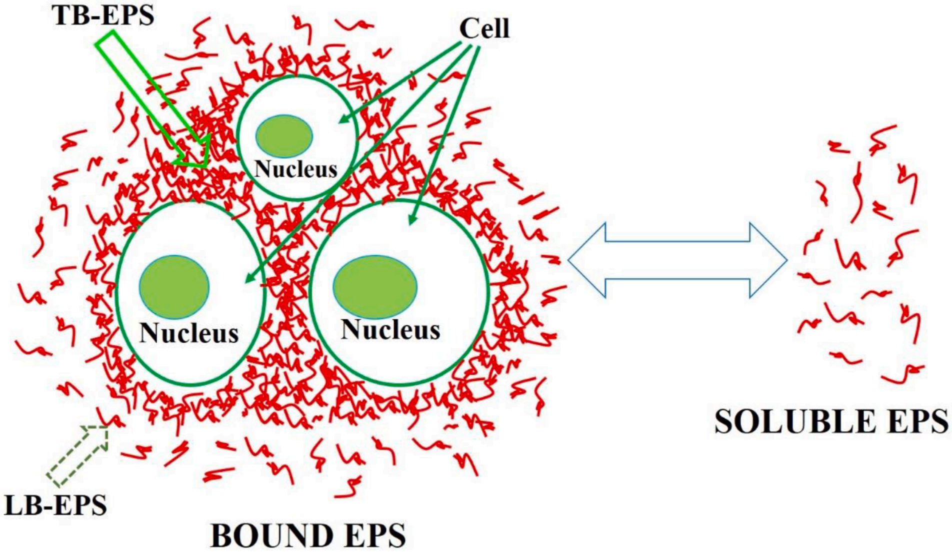

Fig. 3. Schematic of extracellular polymeric substances (EPS) structure around microbial cells. TB-EPS and LB-EPS indicate tightly and loosely bound EPS, respectively (Shi et al., 2017).

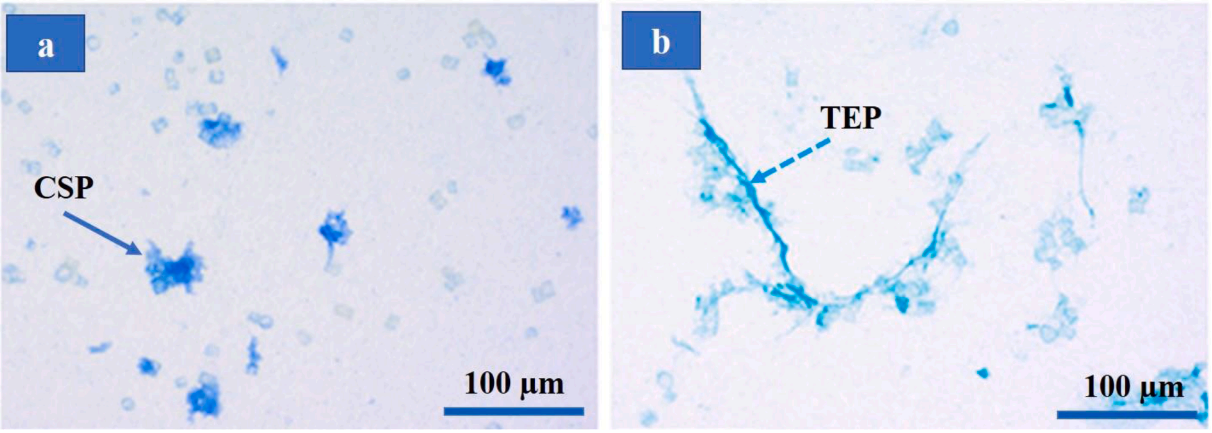

Fig. 4. Photographic images of representative exopolymer particles: (a) Coomassie stainable particles (CSPs) and (b) Transparent exopolymer particles (TEPs) (Thornton, 2018).

2002b), they do not include exactly the same substances, while not all EPSs are a TEP precursor nor do they develop into TEPs (Passow, 2002b). Furthermore, TEPs and EPSs should ideally be measured using different analytical methods since they present different physicochemical properties (Xu et al., 2018). In short, TEPs and EPSs should be regarded as independent indices and should be investigated as such to ensure a better understanding of the heterogeneous composition of flocs.

2.2.5. Coomassie stainable particles

Coomassie stainable particles are transparent gel-like particles and can be characterized as protein-including particles, as shown in Fig. 4. They are present everywhere in water environments and are abundant in cultures of cyanobacteria, diatoms, and heterotrophic bacteria, indicating that microorganisms are a significant source (Cisternas-Novoa et al., 2015; Huang et al., 2016, Long and Azam, 1996; Thornton, 2018). In a study on phytoplankton mesocosm, the quantity of CSPs was found to be similar to that of TEPs (Prieto et al., 2002). However, CSPs are generally more labile and less sticky than TEPs (Thornton, 2018). In seawater, CSPs are 3–13 times more numerous and have a surface area of up to two orders of magnitude greater than TEPs. Thus, while a fraction of CSPs may overlap TEPs, the remaining fraction of the former will tend to differ from the latter (Long and Azam, 1996). However, there is a lack of information on CSPs compared with TEPs (Engel et al., 2020).

In fact, CSPs can be an important heterogeneous component in flocs given their abundance in aquatic systems. However, the flocculation and sedimentation of CSPs in water environments have not been comprehensively investigated (Cisternas-Novoa et al., 2015), and few studies have found that CSPs have less effect on flocculation than TEPs. The role of TEPs in flocculation and sedimentation has been better identified than that of CSPs (Prieto et al., 2002).

2.2.6. Humic substances

Humic substances (HS) are an important pool of transient refractory organic carbon in the geosphere, and they are present everywhere in soil and water environments. HS is produced mainly through the decay of terrestrial and aquatic plants. HS is classified into humic acids (HA), fulvic acids (FA), and humin (Hu) (Beck et al., 1974; Black and Christman, 1963; Schnitzer and Khan, 1972; Sipler and Bronk, 2015). In freshwater, HS comprises 50%–80% of the total DOM (Black and Christman 1963, Rocker et al. 2012). In contrast, HS in the ocean comprises only a small fraction of the total DOM (0.7%–2.4%) because a large part of HS is removed in the estuarine and coastal zone (Opsahl and Benner, 1997). HS can thus be an important component of the OM in flocs in fresh or estuarine water environments.

Adsorption of HS on SPM, such as clay minerals, is common in both fresh and saline waters (Chotzen et al., 2016; Kloster and Avena, 2015; Rashid et al., 1972). HS adsorption on SPM enhances particle stabilization in freshwater, whereas it promotes flocculation of HS and particles and incorporation of HS into floc matrices in brackish and saline water, such as estuarine and coastal zones. HS adsorption on SPM and HS-mediated flocculation are usually higher in brackish and saline water than in freshwater due to the compression of the electrical double layer and reduction of the electrostatic repulsion between HS and SPM (Rashid et al., 1972; Sieburth and Jensen, 1968; Swanson and Palacas, 1965). Besides high salinity, low pH and abundant metal ions increase HS adsorption and HS-mediated flocculation (Kholodov et al., 2014; Komy et al., 2014). HS associated with flocs also scavenges trace inorganic elements in estuaries (Nissenbaum and Swaine, 1976; Sholkovitz, 1976). Therefore, HS is not only an important heterogeneous component of flocs but also a mediator that scavenges other components into floc matrices, especially in brackish and saline water.

2.3. Water and pore space

2.3.1. Water in flocs

Water in and around flocs consists of bound, surface, interstitial, and free waters, which reside in or flow around the flocs (Vesilind and Martel, 1990). Such waters affect floc formation and biota (Droppo, 2001), with the water running through the flocs potentially incorporating inorganic and organic particles into the floc matrices (Droppo et al., 1997). Furthermore, when water flows through flocs, it acts as a food stream supplying nutrients and trace elements to the existing biota and exchanging waste products.

Bound water is chemically bound to solid particles (Kopper, 2017). Bound and surface waters are barely detached via fluid shear force (Vesilind, 1994) since they are tightly bound via chemical bonding, physical adsorption, and mechanical capture in both micro- and macro-capillaries of porous media (Wu et al., 2018). Surface water, occasionally referred to as vicinal water, includes water attached to the surface of solid particles via adsorption and adhesion forces (Vaxelaire and Cézac, 2004). Meanwhile, free water is bound by capillary forces acting between flocs and the surrounding water; thus, it does not reach the inner particles and pore space directly. Free water can also be washed away by fluid shear force (Kopp and Dichtl, 2001). Finally, interstitial water occupies the pore space of flocs. It is retained inside the floc by capillary forces but turns into free water when the flocs are broken (Vesilind and Martel, 1990).

2.3.2. Pore space in flocs

The pore space plays an important role in determining floc structure and density. When particles aggregate to form large flocs, they create pore space in the floc matrices (Droppo, 2001). The pore space, generally occupied by water (i.e., pore water), necessarily affects floc structure and density (Li and Ganczarczyk, 1988; Logan and Hunt, 1987; Sherman, 1953). Flocs are assembled in a hierarchical manner in terms of the arrangement of particles and pore space. For example, a tight assemblage of particles can result in dense flocculi with nanoscale pore space, with the assemblage of flocculi subsequently developing microflocs with a moderate pore. Meanwhile, a loose assemblage of microflocs results in macroflocs with a large pore, as shown in Fig. 5. The hierarchical assemblage of flocculi, microflocs, and macroflocs determines the porosity, density, settling velocity, and transportation of the flocs within the water environment (Gorczyca, 2000).

Pore space also serves as active media hosting physical and biochemical reactions of the various chemicals and nutrients present in flocs. These reactions within the floc, especially those in the pore space, can cause a modification of floc structure and density and can affect floc hydrodynamics and transportation in aquatic environments (Droppo, 2001). For example, if flocs consist of several of EPSs due to microbial growth in the pore space, they will contain numerous fibrils and will thus develop a fluffy, less dense floc structure. Liss et al. reported that EPS fibrils could enlarge the pore space and change the flocs' morphology and settling velocity (Liss et al., 1996).

2.4. Xenobiotic substances

Among several varieties of xenobiotic substances, microplastics and engineered nanoparticles are the most prominent and threatening substances. These xenobiotics are usually well dispersed in aquatic environments due to electrostatic repulsion and hydrophobicity, but they are often subject to flocculation and become heterogeneous components of flocs under favorable conditions. EPS, as natural tackiness agents, enhance attachment between xenobiotics and other particles and flocculation (Bacosa et al., 2018; Cunha et al., 2019; Gao et al., 2019; Shiu et al., 2020). Other types of organic matter (e.g., HS) may also enhance xenobiotics-associated flocculation, but they may have less effect on flocculation than EPS because of their low molecular weight and tackiness. The EPS role in xenobiotics-associated flocculation is reviewed in the following sections.

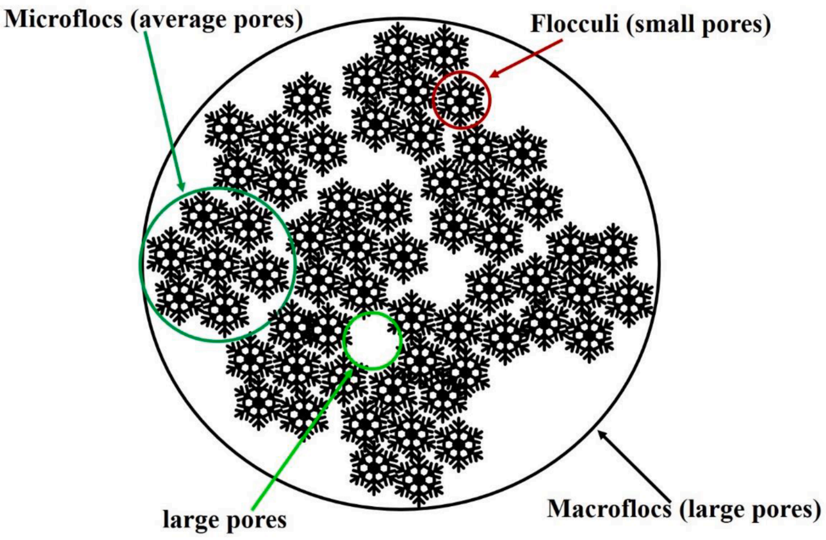

Fig. 5. Schematic of the hierarchical structure of flocculi, microflocs, and macroflocs (Li and Logan, 1997).

2.4.1. Microplastics

Microplastics are small plastic particles ($<$ 5 mm) that are ubiquitous in aquatic environments (Taylor et al., 2016; Van Cauwenberghe et al., 2013). They have been found everywhere from the poles to the tropics and from surface waters to seafloors (Van Sebille et al., 2015). They are released into various water bodies and are ultimately transported into the oceans (Andrady, 2011; Lebreton et al., 2017; Woodall et al., 2014). As a result, the sediment deposits on the seafloor are often recognized as a major sink of MPs (Chen et al., 2020). The population density of MPs in coastal sediments was found to range from 259 to 1743 items/L of sediment (Bashir et al., 2021), while they have also been found in the guts of over 300 different marine species (Kühn et al., 2015). Thus, MPs are regarded as emerging and threatening pollutants for both aquatic ecosystems and humans.

Meanwhile, while data are limited, MPs, particularly those $<$ 300 μm in diameter, are likely to associate with SPM and be transported within heterogeneous flocculated materials (Nizzetto et al., 2016). Stickiness is a key characteristic of flocs that facilitates the scavenging of MPs in the water column and results in an accumulation of MPs on river or sea floors and the benthic food web (Cunha et al., 2019; de Haan et al., 2019; Sakhon et al., 2019). While MPs transport, deposit, and resuspend, they can become associated with SPM and become incorporated into floc matrices (Michels et al., 2018). It is also important to note that the stickiness between MPs and SPM has been found to depend on the size and shape of the MPs, which are governed by weathering, including abiotic (physicochemical) and biotic processes, as well as mechanical degradation and fragmentation (Arp et al., 2021).

However, MPs are not only building materials of flocs but also a controlling factor in flocculation and sedimentation. For example, if MPs adhere to flocs via the action of sticky EPSs or TEPs, they change the floc morphology and density (Michels et al., 2018; Nguyen et al., 2020). Furthermore, large MPs ($>$ 100 s micron) can provide a habitat for microorganisms and exudate substrates or become precursors for biofilm formation: 'the Plastisphere' (Eich et al., 2015; Lobelle and Cunliffe, 2011; Oberbeckmann et al., 2014; Oberbeckmann et al., 2016; Yang et al., 2020; Zettler et al., 2013). Since biofilm is essentially a sticky EPS matrix on MPs, it is likely to increase the stickiness of the MPs and MP-associated flocs and, consequently, the scavenging capacity in terms of other suspended particles (Petrova and Sauer, 2012; Sutherland, 2001a).

Beside EPS, other natural organic matter, such as HS, can be a component of MP-associated flocs (Wells and Stretz, 2019). HS can also adsorb on the surface of MPs and become a heterogeneous component of MP-associated flocs, and it eventually changes the fate and transport of MPs and HS in aquatic environments (Abdurahman et al., 2020; Alimi et al., 2018; Tourinho et al., 2019). Notably, MPs are not only heterogeneous components of flocs but also mediators or scavengers of other components of flocs, thereby changing the compositional and structural characteristics of flocs.

2.4.2. Engineered nanoparticles

Engineered nanoparticles (ENPs) are now often found in water environments following the development of nanotechnology industries in recent years. The ENPs are released into these environments from various industrial sources, including paints, coatings, cosmetics, catalysts, lubricants, food, packaging, water and wastewater treatments, plant protection products, and human and veterinary medicines. For example, the use of personal care and cosmetic products in the city of Macao was estimated to release over 37 billion ENPs per year into water environments via wastewater treatment plants (Bashir et al., 2021). The fate and transport of ENPs in water environments are driven by physical and biochemical processes, such as advection and dispersion, partitioning to sediment, and biotic and abiotic degradation (Boxall et al., 2007), with the ENPs ultimately increasing the toxicity to organisms through the food webs (Maurer-Jones et al., 2013). However, the knowledge on ENPs remains largely lacking in terms of their fate and transport in water environments due to the diversity of ENP species and the complexity of the ENP-associated physical and biochemical processes in aquatic environments (Dunphy Guzman et al., 2006; Fabrega et al., 2011; Oberdörster et al., 2005). Furthermore, little consideration of ENPs has been adopted in studies on the heterogeneous composition of flocs.

ENPs associate with EPS in floc matrices through electrostatic interaction resulting in the incorporation of ENPs into heterogeneous floc matrices (Adeleye and Keller, 2016; Fernando et al., 2020). For example, metal or metal oxide ENPs with a positive surface charge, such as Al_2O_3, ZnO, Fe_3O_4, and CeO_2, easily attach to the negatively charged functional groups of EPSs and enhance flocculation via charge neutralization. In contrast, ENPs with a negative surface charge, such as SiO_2, CuO, and carbon composites, do not interact with EPSs inhibiting floc formation (Huangfu et al., 2019; Miao et al., 2015; Zhang et al., 2017).

ENPs also interact with HS, which has lower molecular weights than EPS. Previous studies have shown that HS can stabilize ENPs through patchy coatings on ENPs (Baalousha et al., 2011; Gibson et al., 2007; Hou et al., 2017). However, the presence of divalent ions (such as Ca^{2+} and Mg^{2+}) could promote attachment between HS and ENPs and the formation of HS-ENP flocs (Chen and Elimelech, 2007), as shown in Fig. 6. In other words, the negative charge of HS on ENPs can be neutralized by divalent cations, which then reduce the electrostatic repulsion and cause the flocculation of ENPs (Liu et al., 2010; Saleh et al., 2008; Zhang et al., 2009). Thus, HS is also an important factor in ENP-associated flocculation, depending on the environmental conditions (e.g., the presence of mono- or divalent ions).

2.5. Oil droplets

Oil spills occur at various sources in the oil industries, often due to small incidents, such as spills from ship refueling or large accidents, such as pipeline breakage, oil tanker stranding, drilling operation failure, or transportation-related accidents. Oil droplets can easily adhere to SPM due to their hydrophobicity and are thus incorporated into flocs with a heterogeneous composition.

The collision and attachment of oil droplets and SPM can enhance flocculation, which facilitates the scavenging and deposition of oil droplets from the water column to the river/sea bed (Lee, 2002). A previous study demonstrated that 87%–98% of spilled oil is transformed into either oil globules or oil–SPM aggregates (Gordon Jr et al., 1973), and Boehm reported that a high SPM concentration enhances the formation and deposition of oil droplet–SPM flocs due to the increase in the collision and attachment between droplets and SPM (Boehm, 1987). The size and shape of both droplets and SPM are also critical for oil–SPM floc formation, as shown in Fig. 7 (Lee and Stoffyn-Egli, 2001).

Oil droplets can also interact with EPSs, with the two substances potentially attaching to each other to form flocs with a heterogeneous composition, much like EPS-enriched marine snow, as shown in Fig. 8 (Quigg et al., 2016). Gutierrez et al. reported that the EPS-producing bacteria that are abundant in oil-spill sites could enhance floc formation, which will ultimately lead to the degradation of hydrocarbons (Gutierrez et al., 2013). In the current authors' opinion, since oil droplets, SPM, and EPSs are highly mutually interactive, they undoubtedly contribute to flocs with a heterogeneous composition.

Oil droplets in aquatic environments often attach to POM and minerals (Cloutier et al., 2002; Lee, 2002). Lee et al. showed that POM (e.g., phytoplankton) readily form oil–organic aggregates (Lee et al., 1985). Grazing by zooplankton also enhances the transportation of oil droplets through the excretion of fecal pellets (Conover, 1971; Mackie et al., 1978). Subsequently, the fecal pellets can be trapped in the net of sticky components of flocs. There are thus various pathways for oil droplets to be incorporated into flocs.

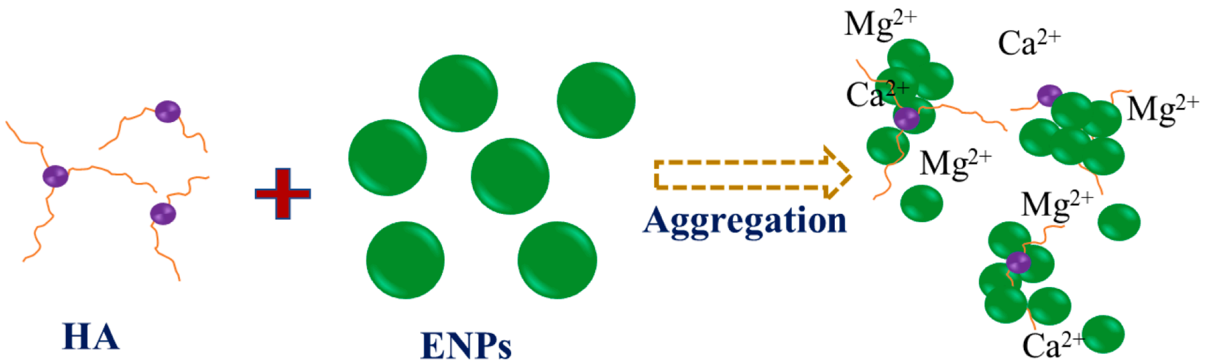

Fig. 6. Flocculation of engineered nanoparticles (ENPs) in the presence of humic substances (HS) and divalent cations (Chen and Elimelech, 2007).

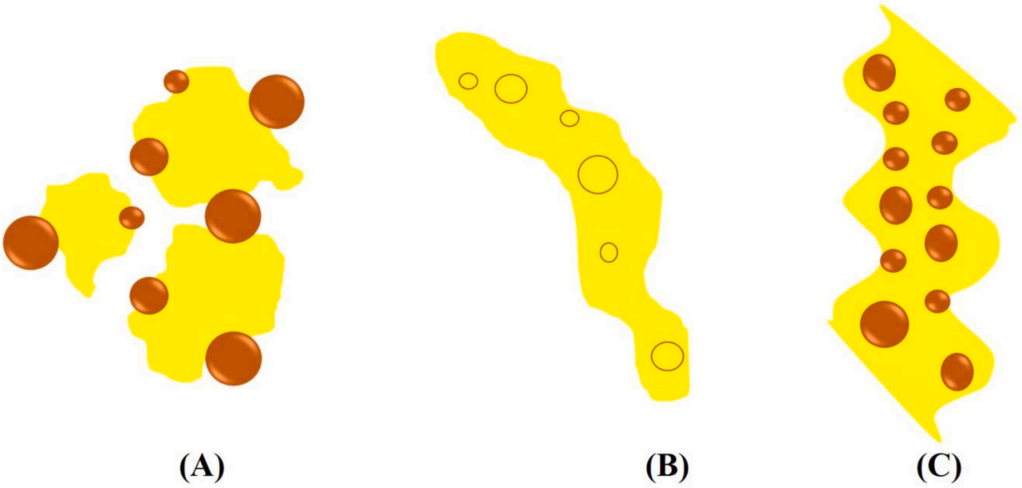

Fig. 7. Different types of oil-incorporated floc: (A) aggregate of multiple oil droplets; (B) solid aggregate of large, generally elongated mass of oil with interior particles (open circles); (C) flake aggregate of thin membranes of clay aggregates that incorporate oil and fold up. The brown spheres represent particles, and the yellow parts represent oil (Lee and Stoffyn-Egli, 2001).

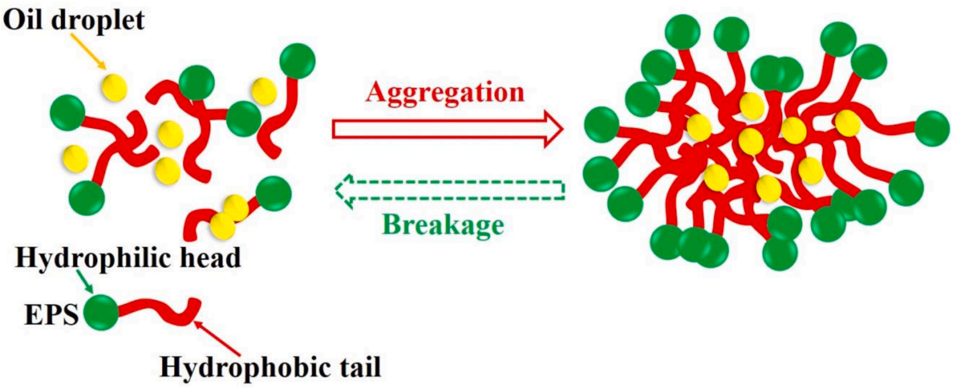

Fig. 8. Interaction between extracellular polymeric substances (EPSs) and oil droplets. As surfactants, EPSs consist of a hydrophilic head and a hydrophobic tail (Quigg et al., 2016).

3. Insight into flocs with heterogeneous composition and structure

Fractal dimensions have been used as a traditional, empirical index of floc composition and structure in the past few decades. The fractal dimension of a floc describes its space-filling capacity for primary particles and ranges from 1 to 3. The higher the value, the more compact and uniform the floc will be (Wheatland, 2017). A dense floc has a relatively high fractal dimension of around 2.3–2.5 or higher, while a fluffy floc has a low fractal dimension of around 1.7–1.8 (Lee et al., 2005). The fractal dimension was found to increase with a higher suspended sediment concentration in intertidal mudflats, implying that the floc structure becomes more dense and compact with abundant suspended sediments (Dyer and Manning, 1999). In contrast, the fractal dimension tends to decrease with higher organic matter content, indicating that the floc structure becomes less dense and more fluffy in biologically enriched conditions, much like the marine snow in an offshore zone (Chen and Eisma, 1995; Dyer and Manning, 1999). For example, Larsen et al. found that flocs with high organic matter content are more porous, less dense, and less settleable, and are thus more mobile in water environments than flocs with low organic matter content (Larsen et al., 2009a). However, recent studies have revealed the non-fractal nature of flocs in the water environment, while investigating detailed floc composition and structure (Spencer et al., 2021).

Recent developments in 3D volumetric imaging of flocs (Wheatland et al., 2017; Wheatland et al., 2020) enables new insight into flocs with heterogeneous composition and structure. Based on their 3D analysis, Wheatland et al. revealed that the geometries of individual components are far more complex than suggested by traditional 2D imaging techniques. Here, the authors analyzed a 3D dataset and could recognize five basic elements of flocs: pore space, clay minerals, nonclay minerals, microbial cells, and organic detritus (Fig. 9). Here, irregularly shaped objects with high gray-level values were deemed to be organic detritus, while the nonclay minerals were differentiated based on their distinct blocky/irregular morphology and uniform gray-scale value. Within 3D datasets, the volumes of each component and pore space in a given floc could be successfully quantified, and the authors could also identify EPSs linking multiplatelet clay particles within the primary structure of flocculi and could discern micrometer-sized pores between the substructures of flocs (Wheatland et al., 2017; Wheatland, 2017).

State-of-the-art microscopic techniques could reconstruct a 3D image of a typical estuarine floc with heterogeneous composition (e.g., clay minerals and other organic substances). Spencer and coworkers further identified the hierarchical floc structures, associated with heterogeneous composition, in a stepwise particle/floc aggregation process (Droppo et al., 1997; Droppo and Ongley, 1994; Spencer et al., 2021). In the earlier stage of the aggregation process, clay minerals are organized into multiparticle units, aligned in either ‘stacked’ or ‘stepped’ arrangement (Fig. 10(a)). Then, heterogeneous components, such as clay and nonclay minerals, pores, unicellular organisms, filamentous cyanobacteria, decaying organic detritus, and organo-mineral debris, are organized in a more complex manner (Figs. 10(b)–(d)). Here, EPS plays an important role in combining heterogeneous components in floc structures (Liss et al. ,1996; Spencer et al., 2021). Such heterogeneous flocs further aggregate to macroflocs and megaflocs, which have large, tortuous pore channels in their floc structure, providing good habitats for bacteria populations (e.g., filamentous cyanobacteria). This observation on the hierarchical floc structure with heterogeneous composition agrees well with previous studies because OM (i.e., EPS/TEP) as heterogeneous composition enhances the flocculation and formation of less-dense biomineral flocs (Alldredge and Gotschalk, 1989; Chen and Eisma, 1995; Passow, 2002b).

4. Human activities affecting floc composition

4.1. Pollutant discharge and eutrophication

A wide variety of particulate and dissolved pollutants are dischared from urban and industrial areas to water environments (Müller et al., 2020; Siddique and Kiani, 2020). Such particulate pollutants include MPs, ENPs, soil particles, road dust, particles from various industries, and soot from combustion, whereas dissolved pollutants consist of various organic (e.g., petrochemical compounds) and inorganic (e.g., heavy metals, ionic species) pollutants (Cisneros, 2011; Müller et al., 2020). Agricultural areas also discharge various particulate and dissolved pollutants, including sediments, biomass, microorganisms, nutrients, pesticides, salts, metals, and so on (Mateo-Sagasta et al., 2017). Particulate pollutants from the urban/industrial and agriculture areas may contribute to formation of flocs with heterogeneous composition. Also, dissolved organic and inorganic pollutants may adsorb on SPM and finally become a part of flocs (Awad et al., 2019).

Certain components of the flocs in aquatic systems emanate from the runoff or discharge from landcover and the associated land use, as shown in Fig. 11. Here, the level of impact depends on the intensity of the activities, which include agriculture, timber harvesting, housing, industry, and road construction. These activities will provide various components of flocs, including minerals, organic matter, metals, MPs, ENPs, and oil droplets. In addition, the discharge of excessive nutrients via human activities (e.g., sewage, animal waste, atmospheric deposition, and fertilizer application) enhances phytoplankton blooms and changes the SPM dynamics (i.e., flocculation, sedimentation, deposition, and resuspension) in the water environment.

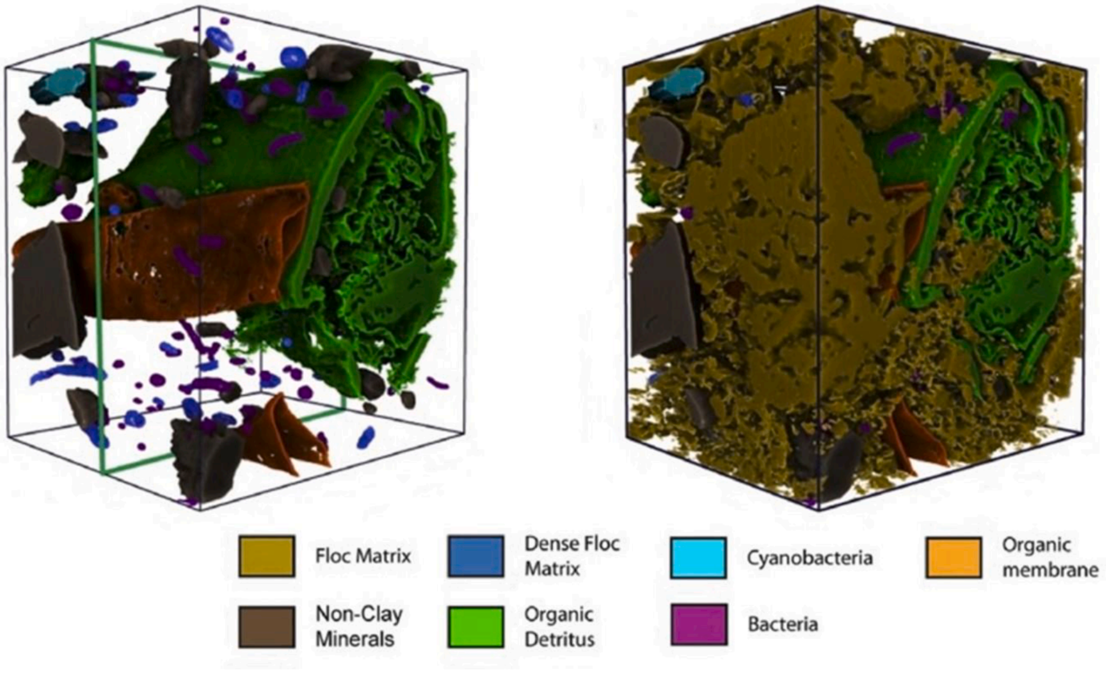

Fig. 9. Three-dimensional tomographic image of a floc consisting of different mineral and organic components (Wheatland et al., 2020).

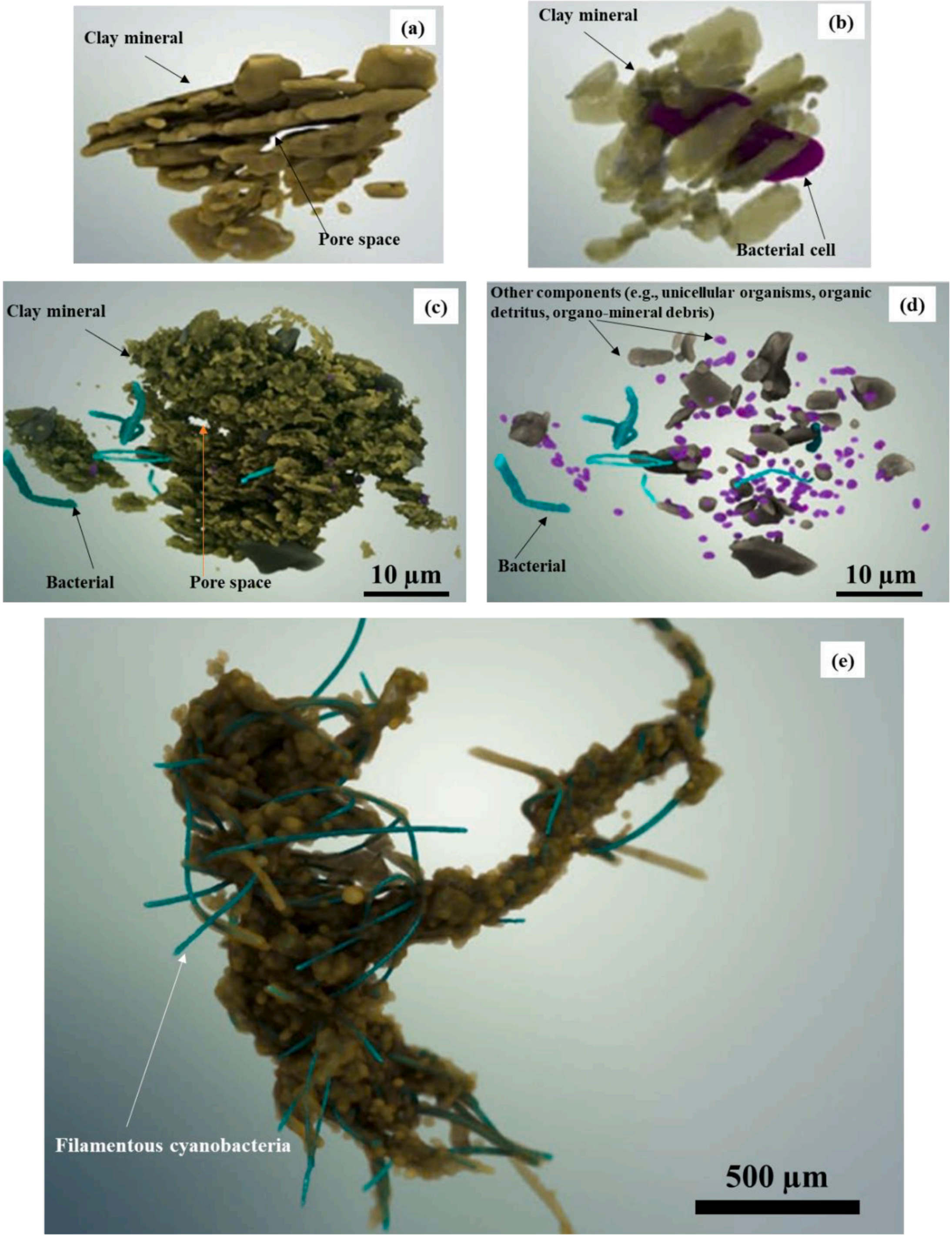

Fig. 10. Hierarchical structures of an Estuarine floc containing various mineralogical and biological components (Spencer et al., 2021).

Phytoplankton bloom can deteriorate due to climate changes, population increases, industrialization, and agribusiness development (Anderson et al., 2002; Rabalais et al., 2009). Specifically, the phosphorus and nitrogen loads from watersheds are known to be the main drivers of phytoplankton production and bloom (Anderson et al., 2002). Phytoplankton bloom increases the EPS/TEP concentration since certain phytoplankton species produce a large quantity of EPS/TEP precursors, typically in the decaying phase of algal bloom (Decho and Gutierrez, 2017; Lee et al., 2019; Lee et al., 2012). Increasing the quantity of phytoplankton and EPS/TEP in the eutrophic condition can ultimately enhance the formation of large and highly-settleable biomineral flocs and sedimentation and deposition on river, lake, estuarine, coastal, and sea floors (Droppo, 2001; Larsen et al., 2009b).

4.2. *Construction activities*

Alongside marine and inland navigation and construction, dredging can result in the resuspension of various mineral and organic particles/flocs from river or sea floors into water columns and can thus affect floc composition and structure. Such resuspended particles from a dredging site are subject to transportation (i.e., dispersion and advection), flocculation, sedimentation, and deposition, and they may ultimately cause harmful siltation in nearby benthic ecological systems (Dankers, 2002). Dredging may also cause the resuspension of particulate heavy metals

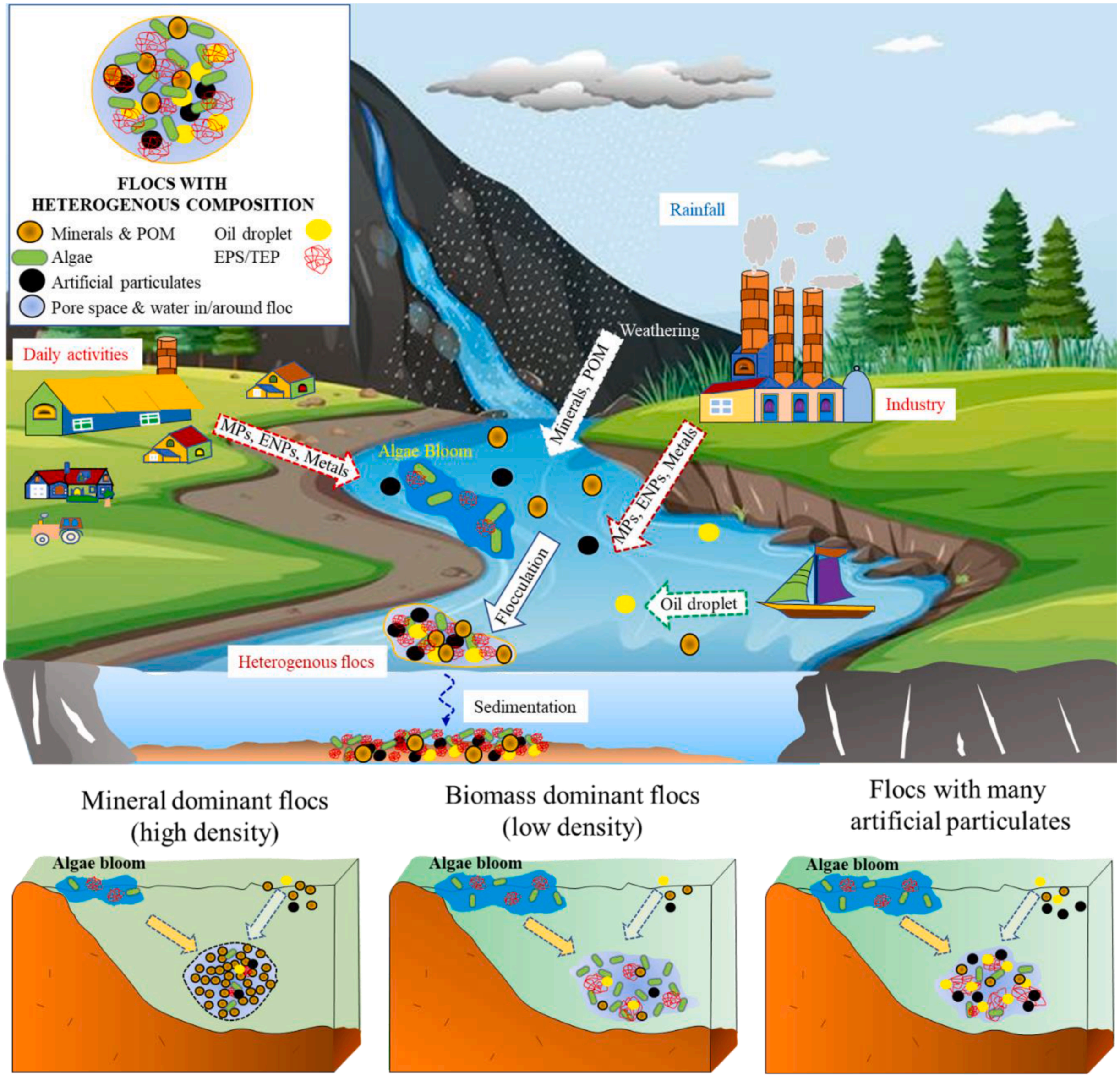

Fig. 11. Schematic of the fate and transport of flocs with a heterogeneous composition in aquatic systems. The upper panel presents the main sources of the floc components, while the lower panel presents different types of floc in terms of biomineral composition.

and other organic and inorganic pollutants (Sin et al., 1991; Tang et al., 1997).

River dam construction can also affect flocculation and the heterogeneous composition of flocs. Such dams can alter the ecological, hydrological, and biogeochemical conditions, which subsequently alter the organic matter and SPM composition in the river water. For example, a river with a constructed dam can become more lacustrine than riverine, with this lacustrine condition facilitating algae bloom and EPS/TEP production and ultimately enhancing flocculation with heterogeneous composition (Lee et al., 2019).

Meanwhile, offshore wind farms (OWFs) can also affect flocculation with a heterogeneous composition and the SPM dynamics in water environments. The construction, operation, and decommission activities of OWFs can enhance phytoplankton growth and organic matter (i.e., EPS and TEP) production while also changing the flow and turbulence near the sea floor (van Berkel et al., 2020). For example, Ivanov et al. demonstrated that the total organic carbon (TOC) concentration increased up to 50% in an area of 5 km around the monopiles of the OWFs (Ivanov et al., 2021). A high TOC concentration around OWFs indicates an abundance of organic matter, which could affect floc composition and structure. Moreover, the OWF structures act as artificial reefs, providing new habitats for filter feeders (e.g., clams, snails, oysters, mussels), with the fecal pellets secreted by the filter feeders potentially contributing to floc composition and structure, as was noted in section 3.2.

5. Conclusions

It is well-known that SPM is indispensable in water environments, with its fate and transport involved in various current environmental issues, including water pollution, ecosystem destruction, and natural disasters (i.e., siltation and erosion). Understanding flocculation with a heterogeneous composition, which is the core process in the fate and transport of SPM, must be the first step in protecting or reducing these environmental issues. The heterogeneous composition of flocs includes inorganic matter (e.g., inorganic particulate matter, heavy metals), organic matter (e.g., EPS, TEP, HS, POM), pore water, and xenobiotic particulate matter (e.g., MPs, ENPs, oil droplets). Each component has a unique function in floc formation with heterogeneous composition. For instance, clay minerals and POM are basic building materials for flocs.

EPS and TEP make bridges among particles and thus promote flocculation. HS also enhances the connection among particles under suitable conditions (e.g., the presence of divalent cations and high ionic strength). MPs provide habitats and substrates for microorganisms, which can create biofilms and scavenge various dissolved and particulate matter. The interaction between ENPs and HS can enhance flocculation under favorable physicochemical conditions. Human activities, such as pollutant discharge, eutrophication, and construction, can be additional drivers for facilitating flocculation with a heterogeneous composition. However, in the current authors' opinion, flocculation with a heterogeneous composition is, at present, not fully understood within the scientific communities. In short, more efforts should be made to investigate flocs with a heterogeneous composition, specifically in terms of their effects on the current environmental issues.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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