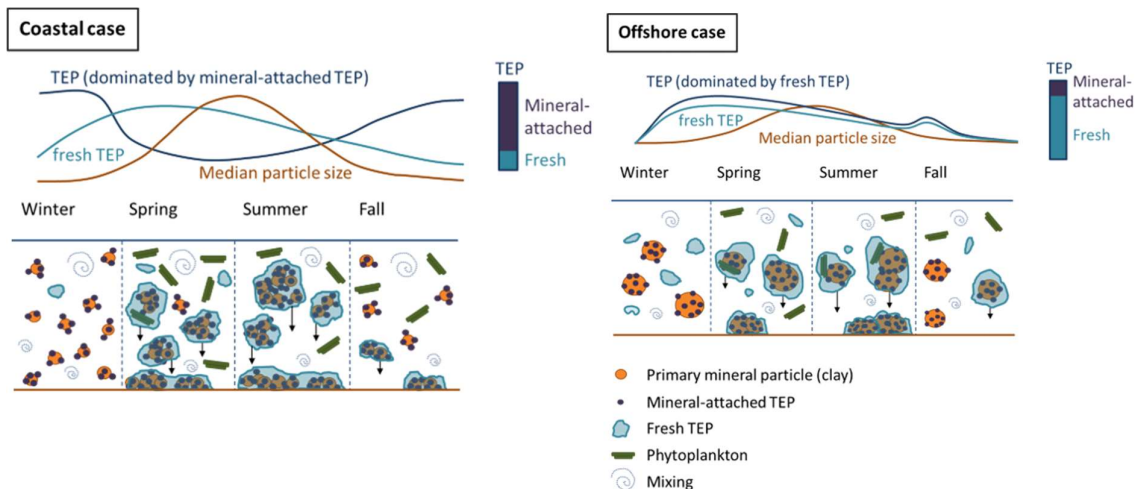


MONITORING en MOdellering van het cohesieve sedimenttransport en evaluatie van de effecten op het mariene ecosysteem ten gevolge van bagger- en stortoperatie (MOMO)



Activiteitsrapport (1 juli – 31 december 2020)

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MOMO/9/MF/202103/NL/AR/4

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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 baggerspeciéstortingen” (Lauwaert et al. 2019) dat gepubliceerd 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. Een tussentijdsrapport voor de vergunningsperiode

1.2. Algemene doelstellingen

Het onderzoek kadert in de algemene doelstellingen om de baggerwerken op het BCP en in de kusthavens te verminderen 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 onderzoek naar knelpunten voor het plannen en schatten van de effecten van de baggerwerken vereist. Dit is specifiek gericht op het dynamische gedrag van silb in de waterkolom en op de bodem en zal uitgevoerd worden met behulp van modellen en in situ metingen. 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-sedimentologische 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 2017-2021

Voor de vergunningsperiode 2017-2021 werden volgende taken voorzien:

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

De monitoring van effecten van baggerspeciéstortingen gebeurt met behulp van een vast meetstation in de nabijheid van MOW1, en met meetcampagnes met de RV Belgica (een 4-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 baggerspeciéstortingen 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 voortvloeien 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 fysisch milieu.

1.4. Onderzoek Januari 2019 – December 2021

Het onderzoek uitgevoerd tijdens de periode 2017-2018 werd gerapporteerd in Fettweis et al. (2017, 2018a, 2018b, 2019). Voor de periode 2019-2021 werd in overleg met de ambtelijke werkgroep baggeren een nieuw takenpakket opgesteld waarbij 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 baggerspeciéstortingen (2016)” 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

Sinds eind 2009 worden er continue metingen uitgevoerd te MOW1 met behulp van een meetframe (tripode). Met dit frame worden stromingen, slibconcentratie, korrelgrootteverdeling 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.

Taak 1.2 Calibratie van sensoren tijdens in situ metingen

Tijdens 11 meetcampagnes per jaar met de R/V Belgica zullen een 13-uursmetingen uitgevoerd worden met doel het calibreren van optische of akoestische sensoren en het verzamelen van verticale profielen. De metingen zullen plaatsvinden in een drietal punten gelegen op het BCP (zie Taak 3.1). De optische metingen (Optical Backscatter Sensor) zullen gecalibreerd worden met de opgemeten hoeveelheid materie in suspensie (gravimetrische bepalingen na filtratie) om te komen tot massa concentraties. Naast de totale hoeveelheid

aan suspensiemateriaal (SPM) wordt ook de concentratie aan POC/PON, chlorophyl (Chl-a, Chl-b), phaeofytine (a, b) en Transparante Exoploimerische Partikels (TEP) bepaald. Stalen van suspensiemateriaal zullen genomen worden met de centrifuge om de samenstelling ervan te bepalen.

Taak 1.3: Data archivering en rapportage

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 geassocieerd met bv biofouling. De data en metadata worden gearchiveerd.

Taak 1.4: Verwerking en interpretatie van metingen

De metingen vergaard tijdens de 13-uursmetingen aan boord van de Belgica en met de tripod worden verwerkt en geïnterpreteerd. Hiervoor werden in het verleden reeds heel wat procedures (software) toegepast of ontwikkeld, zoals de berekening van de bodemschuifspanning uit turbulentiemetingen, entropieanalyse op partikelgrootteverdelingen, de splitsing van multimodale partikelgrootteverdeling in een som van lognormale verdelingen, het groeperen van de data volgens getij, meteorologie, klimatologie en seizoenen. Deze methodes (zullen opgenomen worden) zijn opgenomen in de standaardverwerking van de data. De aldus verwerkte data dienen als basis voor het verder gebruik binnenin wetenschappelijke vragen (zie taak 2.2, 2.3 en 4.2, 4.4).

Taak 2: Uitbouw en optimalisatie van het modelinstrumentarium

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

Ondertussen is de nieuwe implementatie van het Noordzeemodel (inclusief een submodel van de Belgische kustzone) gerealiseerd voor de hydrodynamica. In een volgende fase zal op basis van dit model het slibtransportmodel worden geïmplementeerd en gevalideerd. Verdere ontwikkelingen aan het model parallel met nieuwe inzichten die voortvloeien uit de metingen en de process gerichte interpretatie van de metingen zullen worden geïmplementeerd in het model.

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.

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.

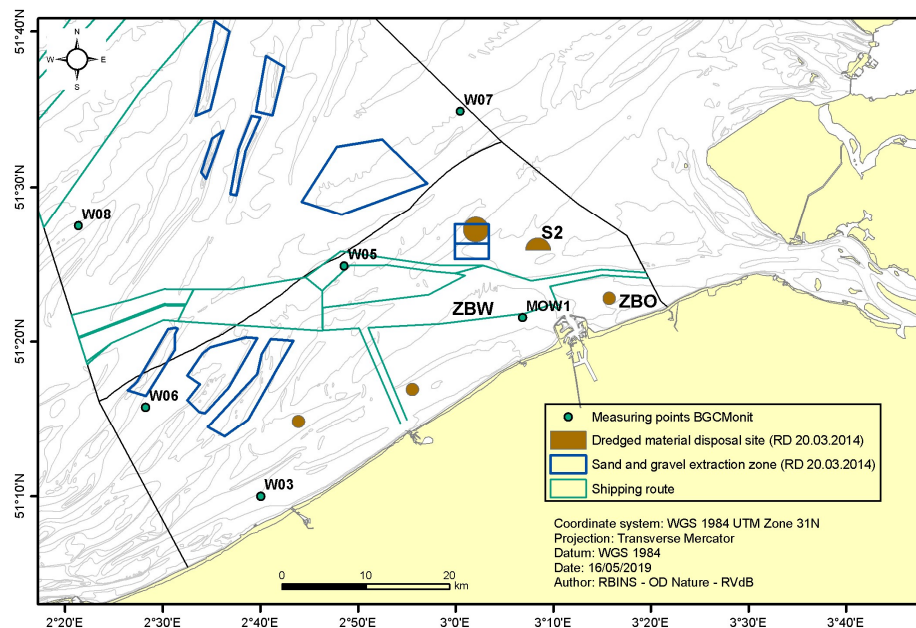
Taak 3.1: Intensieve bio-geo-chemische monitoring van het SPM in de overgangszone kust – offshore in 2019

Een sleutelement in het functioneren van kust nabije ecosystemen is de aanwezigheid van biotische en abiotische partikels. Verticale en dus ook horizontale fluxen van particulier suspensiemateriaal (verder afgekort als SPM) worden bepaald door hun valsnelheid, die afhangt van de capaciteit van de deeltjes om te flocculeren. Flocculatie beïnvloedt de grootte van de gesuspendeerde deeltjes en bepaald daardoor ook de depositie van het slib in onder andere havens en vaargeulen. Op zijn beurt wordt flocculatie gestuurd door turbulentie,

SPM concentratie en de oppervlakte eigenschappen van de deeltjes, die van electrochemische of biologische oorsprong kunnen zijn.

SPM bestaat uit minerale deeltjes van fysicochemische (b.v. kleimineralen, kwarts, veldspaat) en biogene oorsprong (b.v. calciet, aragoniet, opaal), levend (bacteriën, fyto- en zooplankton) 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 en de metalen 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 en polluenten, bagger- en stortactiviteiten, offshore constructies). Het doel van deze taak is om een integrale monitoring uit te voeren in 2019 van de belangrijkste parameters die betrokken zijn bij de SPM-dynamica.

Een nieuw geïntegreerd monitoringsprogramma zal worden opgezet in vier stations (MOW1, W03, W05, W08), zie Figuur 1.1. Deze stations worden aanzien als zijnde representatief voor de belangrijkste gradiënten vanaf de kustzone (invloed van de Schelde) naar offshore (invloed van het Engels Kanaal) en zullen maandelijks bemonsterd worden. Gedurende 13 uur zullen om het uur waterstalen genomen worden aan de oppervlakte en bodem in stations MOW1, W05 en W08. De monitoring bevat alle parameters die nu reeds worden bepaald (maar niet noodzakelijk samen) op waterstalen (SPM, POC/PON, DOC/DON, Chl, TEP, nutriënten, pH) en met behulp van sensoren (CTD, OBS, ABS, LISST), en zullen aangevuld worden met Chl in sedimenten, de hydrofobe chemische polluenten (b.v. PAHs, PCBs) Verder wordt een monitoring voorzien van fysische parameters (ADCP/tripode) in de stations W05 en W08.



Figuur 1.1: BGC monitorings stations MOW1, W03, W05 en W08.

Door de verschillende monitoringsactiviteiten van OD Natuur/BMM (MOMO, WFD, MSFD, OSPAR en satellietvalidatie) te combineren en de monitoringsfrequentie en stations aan te passen worden de inspanningen geoptimaliseerd, blijven de legale verplichtingen en validatieprotocollen verzekerd, komen state-of-the-art wetenschappelijke vragen aan bod en wordt een bevattelijk dataset bekomen die alle gemeten parameters met elkaar verbindt. Na een eerste jaar van intensieve monitoring in 2019 zal het staalname schema geëvalueerd worden voor alle parameters om aldus tot een kwalitatieve sprong in monitoringsstrategie te komen die tijdsgebonden veranderingen, invariante eigenschappen en ruimtelijke gradiënten kan identificeren. De belangrijkste wetenschappelijke vragen die aan

de grondslag liggen van deze monitoring zijn:

1. Hoe variëren de fysische, biologisch en chemische parameters in de waterkolom tijdens een getijcyclus en tijdens de seizoenen.
2. Waarom is het kustgebied troebel en wat is hierbij de link met de cross-shore gradiënten in fysische, biologische en chemische parameters.
3. Hoe beïnvloedt de SPM-concentratie de algenbloei (lichtreductie) en vice versa (TEP-productie)? Hoe moet het modelinstrumentarium (flocculatiemodule) worden aangepast om deze seizoensaliteit te kunnen modelleren.
4. Wat is de variabiliteit van de concentratie aan chemische polluenten in het SPM? Hoe beïnvloedt de variabiliteit in SPM-concentratie en samenstelling de variabiliteit van de chemische polluenten?
5. Verbetering van remote sensing producten (SPM, Chl) door in situ validatie.

Taak 3.2: Monitoring stortplaats ZBW

De concentratie en samenstelling van het suspensie- en bodemmateriaal zal gemonitord worden in de nabijheid van de nieuwe stortplaats ZBW. Afhankelijk van de keuze van de stortplaats kan de langdurige meetlocatie MOW1 hiervoor in aanmerking komen of kan een andere locatie gekozen worden als de veiligheid van de meetapparatuur kan gegarandeerd worden. Details hiervan zullen op een vergadering van de technische werkgroep besproken worden.

Taak 3.3: Ondersteuning kader rond Passende Beoordeling van stortactiviteiten

Ondersteuning zal gegeven worden voor het opstellen van de passende beoordeling voor de vergunningsplichtige stortactiviteiten. Dit houdt in het meewerken aan een schriftelijk verslag waarin aan de hand van gemotiveerde argumenten uitgelegd wordt of de Europese natuurwaarden in het vogelrichtlijngebied nabij Zeebrugge al dan niet betekenisvol worden aangetast door het storten van baggerspecie in zee. Meer specifiek zal onderzoek worden uitgevoerd over de verstoring van het eetgedrag van zeevogels door de verhoging van de turbiditeit die gepaard gaat met de baggerspeciéstortingen.

Taak 3.4: Trends in SPM concentratie

Om significante statistische trends te kunnen documenteren in SPM concentratie over de laatste decades, zijn kwalitatief hoogstaande metingen nodig die een lange tijdspanne omvatten en over een groot gebied verdeeld zijn. 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 verzamelt 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.

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 2019 – Juni 2019

Taak 1.1: De meetreeks te MOW1 werd verdergezet.

Taak 1.2: Calibratie van OBS sensoren werd uitgevoerd tijdens RV Begica campagnes 2019/01, 2019/03, 2019/07, 2019/11, 2019/14 en 2019/17.

Taak 2.1: Het 2 klassen population balance model van Lee et al. (2011) werd geïmplementeerd in Coherens V2 en gevalideerd met testcases.

- Taak 3.1: Intensieve bio-geochemische monitoring werd uitgevoerd te MOW1 (RV Belgica campagnes 2019/01, 2019/03, 2019/07, 2019/11, 2019/14, 2019/17), W03 (RV Belgica campagnes 2019/03, 2019/11, 2019/14, 2019/17), W05 (2019/01, 2019/03, 2019/11, 2019/14, 2019/17) en W08 (2019/01, 2019/03, 2019/14, 2019/17).
De methode voor de TEP-analyse werd opgesteld en gevalideerd.

Periode Juli 2019 – December 2019

- Taak 1.1: De meetreeks te MOW1 werd verdergezet.
Taak 1.2: Calibratie van OBS sensoren werd uitgevoerd tijdens RV Belgica campagnes 2019/18, 2019/22, 2019/25, 2019/29 en 2019/32.
Taak 1.3: Data archivering en rapportage werd uitgevoerd.
Taak 1.4: Verwerking en interpretatie van de tripode meetdata 2016-2018.
Taak 2.1: Een op Baesiaanse statistiek gebaseerde methode werd toegepast op de MOW1 data om de parameters van het 2 klassen populatiemodel te bepalen en voorgesteld op de INTERCOH conferentie.
Taak 3.1: Intensieve bio-geochemische monitoring werd uitgevoerd te MOW1 (RV Belgica campagnes 2019/20, 2019/22, 2019/25, 2019/29, 2019/32), W03 RV Belgica campagnes 2019/20, 2019/22, 2019/25, 2019/29, 2019/32), W05 (2019/20, 2019/22, 2019/25, 2019/29, 2019/32) en W08 (2019/20, 2019/22, 2019/25, 2019/29, 2019/32).
Een eerste interpretatie van de bio-geochemische meetresultaten werd voorgesteld op de INTERCOH conferentie.

Periode Januari 2020 – Juni 2020

- Taak 1.1: De meetreeks te MOW1 werd verdergezet, zover dit mogelijk was onder Covid maatregelen. Metingen met de tripode zijn beschikbaar van januari t.e.m. ongeveer maart en van 12 juni t.e.m. 8 juli.
Taak 1.2: Calibratie van OBS sensoren werd uitgevoerd tijdens RV Belgica campagnes 2020/01 (21-24/01), 2020/04 (18-20/02) en 2020/19a. Wegens Covid maatregelen konden de campagnes 2020/08 (16-20/03), 2020/12 (27-30/04), 2020/14 (25-29/05) niet worden uitgevoerd. Campagne 2020/19a (22-24/06) is de eerste campagne na de lockdown. Staalnames werden beperkt tot 3 ½ getijcycli.
Taak 2.1: Ondanks de grote hoeveelheid aan data en modellerstudies, zijn de mechanismen die het turbiditeitstmaximum in de Belgisch-Nederlandse kustzone ter hoogte van Zeebrugge instand houden nog onvoldoende gekend. Om de dynamica ervan beter te begrijpen werd de rol van barocline (saliniteit en sediment geïnduceerde) processen en lokale sedimentbronnen onderzocht met een numeriek model, zie van Maren et al. (2020).
Taak 3.1: Intensieve bio-geochemische monitoring werd uitgevoerd te MOW1 (RV Belgica campagnes 2020/01, 2020/04, 2020/19a), W03 (RV Belgica campagnes 2020/01), W05 (2020/01, 2020/19a) en W08 (2020/01, 2020/19a), zie ook taak 1.2.
Een overzicht van de biogeochemische data verzameld vanaf 2018 tot heden wordt gegeven in Hoofdstuk 2.
De analyse van stalen genomen met sedimenttraps bevestigd aan de tripode (MOW) worden beschreven en geëvalueerd in Hoofdstuk 3.

Periode Juli 2020 – December 2020

- Taak 1.1: De meetreeks te MOW1 werd verdergezet. Metingen met de tripode zijn beschikbaar 12 juni t.e.m. 8 juli en vanaf 19 augustus 2020 t.e.m. eind december.
Taak 1.2: Calibratie van OBS sensoren werd uitgevoerd tijdens RV Belgica campagnes 2020/19c (7-8/07), 2020/20 (19-21/08), 2020/22 (7-11/09), 2020/26 (20-22/10), 2020/30 (23-26/11/2020) en 2020/33 (14-18/12/2020).
Taak 3.1: Intensieve bio-geochemische monitoring werd uitgevoerd te MOW1 (RV Belgica campagnes 2020/20, 2020/22, 2020/26, 2020/30, 2020/33), W03 (RV Belgica campagnes 2020/20, 2020/22, 2020/30, 2020/33), W05 (2020/19c, 2020/20, 2020/22, 2020/26, 2020/30, 2020/33) en W08 (2020/19c, 2020/20,

2020/22, 2020/30, 2020/33), zie ook taak 1.2.

Taak 3.1: Een interpretatie van de biogeochemische monitoring met betrekking tot de wetenschappelijke vragen opgesomd in Taak 3.1 werd uitgevoerd met de data verzameld in 2019-2020, zie Hoofdstuk 2.

1.6. Publicaties (januari 2019 – december 2020)

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, Desmit X, Terseleer N. 2021 MOMO activiteitsrapport (1 juli - 31 december 2020). BMM-rapport MOMO/9/MF/202103/NL/AR/4, 45pp + app.

Fettweis M, Adamapoulou A, Baeye M, Parmentier K, van den Eynde D. 2020. MOMO activiteitsrapport (1 januari – 30 juni 2020). BMM-rapport MOMO/9/MF/202010/NL/AR/3, 42pp + app.

Fettweis M, De Ville de Goyet N, Francken F, Van den Eynde D. 2020. MOMO activiteitsrapport (1 juli – 31 december 2019). BMM-rapport MOMO/9/MF/202005/NL/AR/2, 59pp + app.

Fettweis M, Baeye M, Francken F, Jaspers N, Knockaert M, Montereale-Gavazzi G, Parmentier K, Van den Eynde D. 2019. MOMO activiteitsrapport (1 januari – 30 juni 2019). BMM-rapport MOMO/9/MF/201911/NL/AR/1, 21pp + app.

Lauwaert B, Fettweis M, De Witte B, Van Hoei G, Timmermans S, Hermans L. 2019. Vooruitgangrapport (juni 2019) over de effecten op het mariene milieu van baggerspeciestortingen (Vergunningsperiode 01/01/2017 – 31/12/2021). RBINS-ILVO-AMT-CD rapport. BL/2019/01, 28pp.

Backers J, Hindryckx K, Vanhaverbeke W. 2019. Rapport van de RV Belgica Meetcampagnes en Verankering van Meetsystemen MOMO – 2018. BMM-rapport BMM-MDO/2019-05/MOMO/2018, 169pp.

Conferenties/Workshops

Fettweis M, Riethmüller R, Schartau M, Verney R, Lee BJ. 2019. The composition of suspended particulate matter in coastal areas. JJ Mehta Award lecture at IntercoH, 13-17 October, Istanbul (Turkey).

Lee BJ, Bi Q, Toorman E, Fettweis M, Lee BK, 2019. Application of a Bayesian Method for Investigating the Probability and Uncertainty of a Two-Class Flocculation Kinetic Model. IntercoH, 13-17 October, Istanbul (Turkey).

Shen X, Toorman E, Fettweis M, Lee BJ. 2019. A population balance model for multi-class floc size distributions of cohesive sediments in Belgian coastal zones. EGU, 7-12 April, Vienna (Austria).

Fettweis M. 2019. Schwebstoff in Küstenmeeren – Flockige Fracht in ständigem Wandel: Gut zu sehen und doch schwer genau zu messen. Invited lecture at HZG Institute for Coastal Research, 31 January, Geesthacht (Germany).

Peer reviewed artikels

Fettweis M, Riethmüller R, Verney R, Becker M, Backers J, Baeye M, Chapalain M, Claeys S, Claus J, Cox T, Deloffre J, Depreiter D, Druine F, Flöser G, Grünler S, Jourdin F, Lafite R, Nauw J, Nechad B, Röttgers R, Sotollichio A, Vanhaverbeke W, Vereecken H. 2019. Uncertainties associated with in situ long-term observations of suspended particulate matter concentration using optical and acoustic sensors. *Progress in Oceanography*, 178, 102162. doi:10.1016/j.pocean.2019.102162

Montereale-Gavazzi G, Roche M, Degrendele K, Lurton X, Terseleer N, Baeye M, Francken F, Van Lancker V. 2019. Insight into short term tidal variability of multibeam backscatter from field experiments on different seafloor types. *Geosciences* 2019, 9, 34; doi:10.3390/geosciences9010034

Shen X, Toorman EA, Lee BJ, Fettweis M. 2019. Effects of aquatic biofilms on flocculation processes of cohesive sediments: A modeling approach. *Journal of Geophysical Research*, 124, 4098-4116. doi:10.1029/2018JC014493

Vanlede J, Dujardin A, Fettweis M, Van Hoestenbergh T, Martens C. 2019. Mud dynamics

in the port of Zeebrugge. *Ocean Dynamics*, 69, 1085-1099. doi:10.1007/s10236-019-01273-3

van Maren DS, Vroom J, Fettweis M, Vanlede J. 2020. Formation of the Zeebrugge coastal turbidity maximum: The role of uncertainty in near-bed exchange processes. *Marine Geology* 425, 106186. doi:10.1016/j.margeo.2020.1061

Thesis, eindwerk

Demilde C. 2019. Analyse van transparante exopolymeerpartikels (TEP) optimaliseren en valideren. Bachelorproef, Bachelor in de agro- en biotechnologie, Afstudeerrichting biotechnologie, VIVES Hogeschool, 66pp + bijlagen

2. De samenstelling van het gesuspendeerd organisch material en de SPM dynamica langsheen een kust-offshore transect¹

Interactions and feedback loops between organic and mineral particles have an impact on sediment dynamics as well as on primary production in nearshore marine ecosystems (Droppo, 2001; Muylaert et al., 2006; Jago et al., 2007; Fettweis et al., 2014; Maerz et al., 2016; Liénart et al., 2017; Neumann et al., 2019; Schartau et al., 2019, Skinnebach et al., 2020; Fall et al., 2021). The suspended particulate matter (SPM) concentration can be highly variable in these areas due to hydrodynamic (tidal currents) and atmospheric (waves and solar radiation) energy entrainment, weather and climate, biological activity and terrestrial export (Schlünz & Schneider, 2000; Pietrzak et al., 2011; Fettweis et al., 2012; Wang et al., 2013), as well as human activities such as trawling, dredging and dumping operations, and major engineering works (e.g. Milliman et al., 1987; Manning et al., 2011; Baeye & Fettweis, 2015). SPM controls marine ecosystems through, for example, its influence on water clarity, filter-feeding animals, mineral and organic seabed composition or as carriers of pollutants (van Hoey et al., 2005; Regnier et al., 2013; Capuzzo et al., 2015; Zhang et al., 2017; Hendriks et al., 2020). The interactions between physical forcing, biological and chemical processes, and human activities result in highly variable spatial and temporal scales of SPM concentration and composition (Eisma & Kalf, 1979; Ittekkot & Laane, 1991; Mayer, 1994; Fettweis et al., 2006; Van Beusekom et al., 2012; Adriaens et al., 2018; Blattmann et al., 2019). SPM is composed of particulate inorganic (PIM) and particulate organic matter (POM). Flocculation processes combine these particles into biomineral flocs (Shen et al., 2018; Lee et al., 2019), which overcompensates the resulting decrease in overall density and therefore yields higher settling velocities compared to most of their individual constituents (e.g. Engel & Schartau, 1999; Mietta et al., 2009). In tidally dominated, mostly shallow environments, floc break-up dominates during periods of high currents and waves with strong shear. In contrast, the formation of larger flocs prevails during slack water periods (e.g. Winterwerp, 1998). The size of the flocs is theoretically determined by the smallest turbulent eddies (Braithwaite et al., 2012). But floc size can exceed those of the turbulent eddies in the presence of biogenic particles whose surfaces can become exceedingly sticky (Cross et al., 2013).

SPM concentration in the North Sea is higher in winter and lower in summer (Howarth et al., 1993). This seasonality appears to be caused mainly by biological cycles and only to a minor part by the higher storm frequencies in winter (Fettweis et al., 2014; Lai et al., 2018). Biological processes influence flocculation, seabed erodibility and transport of the suspended particles, because of the emergence of polysaccharides such as exopolymeric substances (EPS; e.g. Verdugo et al., 2004), including gel-like particles like transparent exopolymer particles (TEP; e.g. Alldredge et al., 1993; Logan et al., 1995) and Coomassie stainable particles (e.g. Long & Azam, 1996). Dissolved EPS are the precursors of these particles and refer to any extracellular dissolved organic matter released from phytoplankton and bacteria, either actively by exudation or passively via viral lysis, sloppy feeding or through bacterial degradation (Passow, 2000; Engel & Passow, 2001; Engel et al., 2020). TEP are known to be a common component of the organic matter (OM) in marine environments, having specific characteristics such as adhesiveness, transparency, flexibility and may form biofilms (Zhou et al., 1998; Passow, 2002; Mari & Robert, 2008).

¹ Fettweis M, Schartau M, Desmit X, Lee BJ, Tereleer N, Van der Zande D, Riethmüller R. Organic matter composition of biomineral flocs and its influence on suspended particulate matter dynamics along a nearshore to offshore transect (submitted to *Journal of Geophysical Research Biogeosciences*)

The interactions between TEP and SPM have mainly been studied in open ocean environments where mineral concentrations are low and the hydrodynamics is weaker than in coastal regions. Typically, under open ocean conditions TEP concentrations are correlated with the rise and decline of phytoplankton blooms (Fukao et al. 2010; Mari et al., 2017). But for nearshore and estuarine environments TEP data in combination with SPM measurements are scarce. Here, hydrodynamical forces are strong, the SPM dynamics is complex and the mineral fraction of the SPM is dominant. Published data show that in winter, when SPM concentration frequently reaches high values, also concentrations of OM, including TEP, become high, displaying maxima within high turbid areas (Malpezzi et al. 2013; Morelle et al., 2018). Thus, a correlation between total TEP concentration and floc size is inextricable. Extensive mixing events in spring and summer can generate SPM concentrations similar to those found in winter, but with floc sizes that are significantly larger. This apparent contradiction indicates that TEP concentration alone cannot sufficiently explain biophysical flocculation.

The aim is to gain deeper insight into the connection of TEP as a driver of flocculation with the temporal and spatial variation in SPM and floc size dynamics. This is based on numerous water samples collected between 2004 and 2020 in the Belgian part of the North Sea. We investigate the seasonal variations of the interrelation between concentration and OM composition of SPM. Further, we provide insight to unraveling apparent discrepancies in observations with respect to SPM concentration, floc size and the qualitative composition of the particulate organic matter (POM), notably the fresh and labile vs mineral-associated and more recalcitrant fraction. This chapter is structured as follows: First, the fresh and mineral-associated POM concentration in the particulate organic carbon (POC), nitrogen (PON) and TEP fractions is differentiated, refining the POM-SPM modelling approach of Schartau et al. (2019). Then, the seasonality of the size and density of biomineral flocs along the coastal to offshore gradient, using in situ data, is related to fresh and mineral-associated POM. Finally, the model is applied to estimate fresh and mineral-associated POM from in situ and satellite SPM measurements to discuss the temporal and geographical variability of SPM concentration and composition across the onshore-offshore gradient.

2.1. Measurements

2.1.1. *Water and seabed samples*

Water samples were taken in the Belgium part of the North Sea from March 2018 until July 2020 at three locations along a cross-shore section (MOW1, W05 and W08; Figure 2.1). It ranges from the nearshore coastal turbidity maximum (MOW1) to the offshore under complete Channel water influence (W08). W05 is located in between at the outer margin of the coastal turbidity maximum. Lacroix et al. (2004) deduce from model tracer experiments backed-up by long-term salinity observations that at W05 and MOW1 Channel waters still dominate and that at MOW1 fresh waters from the Rhine-Meuse and the Scheldt contribute with about 6%. The present-day SPM in the Belgian-Dutch nearshore area originates mainly from the erosion and resuspension of the existing mud deposits situated in the Belgian nearshore and the present-day Scheldt estuary can be excluded as source of fine-grained sediments (Adriaens et al., 2018).

Sampling was carried out every 1 or 1.5 hours during a tidal cycle (12.5 hours) at 2 m below the surface and about 2 m above the seabed using 5 l Niskin bottles attached to a rosette CTD system. During this period about 6 Van Veen grab samples have been taken in each station for the analysis of POC and PON content in the <63 μm fraction. In total 17 tidal cycles have been sampled at the nearshore station MOW1, 10 at the intermediate station W05, and 9 at the offshore station W08. The water samples were filtered on board and

analysed in the laboratory to obtain the concentration of SPM, POC, PON, pigments (Chlorophyll-a: Chl; Pheophytin-a: Pheo-a) and, from December 2018 onward, TEP. The Particulate Organic Matter (POM) content was determined by loss-on ignition until November 2019. The sample turbidity (in FNU) was measured with a Hach TL2360 LED Turbidimeter and salinity was analysed from the water samples. Samples for dissolved inorganic nutrients and Dissolved Organic Carbon (DOC) were taken from the filtrate. From 2004 until 2011, 25 tidal cycle measurements of SPM, POC, PON, and from 2012 until March 2018, 25 additional cycles including pigment concentration have been sampled at station MOW1. During the period March 2004 to March 2018, 7 tidal cycles have been sampled at two offshore stations, in the intermediate zone and 18 in the high turbidity zone for SPM, POC, PON and pigment (the latter from 2012 onward) concentration. The sampling strategy was different before March 2018 as samples have only been taken at about 2 m above the bed and not at the surface. The total amount of samples collected with at least SPM and POC concentration amounts to 1841; the other parameters have respectively 1663 (PON), 1810 (Chl-a), 1716 (Pheo-a), 1414 (Salinity), 935 (Hach turbidity) and 659 (TEP) good data.

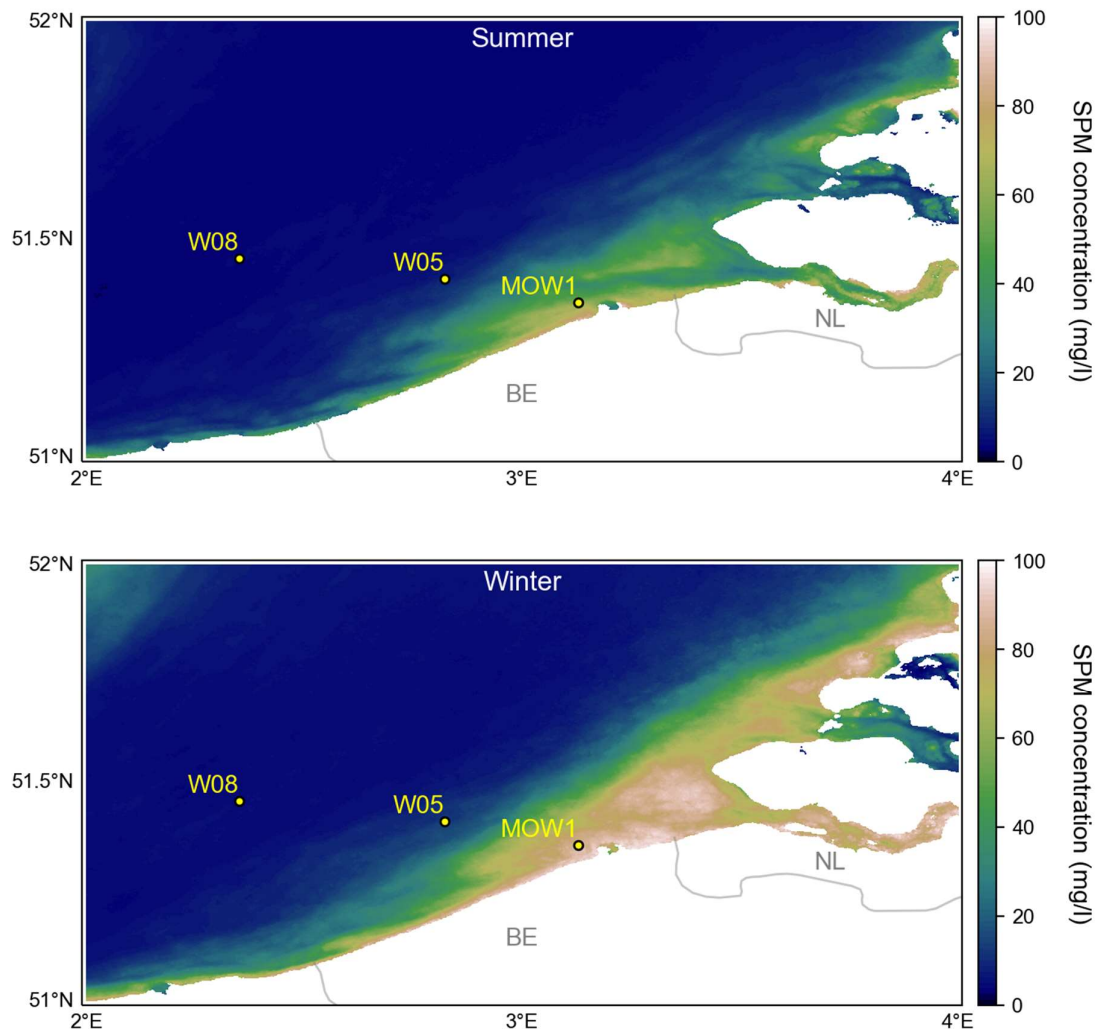


Figure 2.1: Map of sampling stations MOW1, W05 and W08 (BE: Belgium, NL: The Netherlands). The background displays the averaged near surface SPM concentrations in the Belgian coastal zone (southern North Sea) computed from satellite images taken by Sentinel-3/OLCI from April 2019 to September 2019 (above) and from November 2019 to March 2020 (below).

2.1.2. *Sensor measurements*

A LISST 100X was attached to the rosette to measure volume concentrations in 32 logarithmically spaced size groups over the range of 2.5–500 μm using laser diffraction (Agrawal & Pottsmith, 2000). Long-term measurements with a LISST 100X and an OBS are available at the station MOW1 from tripod deployments over the period 2005-2019. In the beginning, the tripod was moored for 3 to 6 weeks and then recovered. From December 2009 an advanced tripod system allowed continuous time series. The LISST 100X was mounted at 2 m above bed (mab) and the OBS at 0.2 and 2 mab. In total about 1716 days of “good” LISST data have been collected and about the double of “good” OBS data. “Good” LISST data are defined by a smooth (i.e., no sudden decrease) optical transmission within a range between 0.15 and 0.98, a smooth floc size distribution (FSD) and no biofouling. The latter two disturbances have regularly been observed in the long-term data series. Disturbed FSDs occur when the laser beam is misaligned. Biofouling occurs mainly in spring and summer and is identified by a gradual decrease in transmission or optical backscatter and increase in SPM volume concentration. OBS data have been discarded when the sensor output changed over time unrelated to changes in inherent particle properties or SPM concentration. This was caused by variations in voltage supply, changes in the transmittance of the window that is the interface between the sensor and the water and the signal was attenuated by biofouling (Fettweis et al., 2019). The OBS output has first been calibrated against a laboratory standard (AMCO clear) in order to convert the sensor output to a backscatter turbidity unit, before being calibrated in situ with SPM concentration derived from water samples in order to obtain a mass concentration.

2.1.3. *Remote sensing measurements*

Surface SPM and Chl concentration have been derived from the Ocean and Land Colour Instrument (OLCI). OLCI is a multispectral radiometer carried on board Sentinel-3A (launched in 2016) and B (launched in 2018) with 21 bands on the 400-1200 nm spectral range and a spatial resolution of 300 m. The two satellites provide a daily revisit time over the southern North Sea. Sentinel-3/OLCI baseline water products (L2-WFR) were retrieved from the Copernicus Online Data Access (CODA) service hosted by EUMETSAT (coda.eu-metsat.int). The baseline products were processed with IPF-OL-2 version 06.13 (EUMETSAT, 2019) with standard masking applied, i.e. excluding INVALID, LAND, CLOUD, CLOUD_AMBIGUOUS, CLOUD_MARGIN pixels. Additionally, a custom quality control was applied to remove outlier pixels with a spectrally flat signal. The SPM product was generated by an artificial neural network as a multiple non-linear regression technique to deal with the optically complex waters in the study area. The artificial neural network, originally developed by Doerffer and Schiller (2007), was updated to become the Case 2 Regional (C2RCC) processor suitable for Sentinel-3 (EUMETSAT, 2019). Generating reliable satellite estimates of Chl-a in optically complex coastal waters is still challenging. Many algorithms exist and give quite different performance for different optical conditions. For this reason we applied the approach of Lavigne et al. (2021) who clearly defined the limits of applicability of three popular and complementary algorithms: 1. the OC4 blue-green band ratio algorithm which was designed for open ocean waters; 2. the OC5 algorithm which is based on look-up tables and corrects OC4 overestimation in moderately turbid waters; and 3. a near infrared-red (NIR-red) band ratio algorithm designed for high turbid waters. This approach allows automatic pixel-based switching between the most appropriate algorithms for a certain water type. For the measuring stations these are depending on the season, OC4 and OC5 for W08, OC5 and NIR-red for W05 and NIR-red for MOW1.

2.2. Sample and data analysis

2.2.1. Water samples

At every sampling occasion, three subsamples for SPM concentration were taken and filtered on board using annealed (24 hours in a muffle furnace at 400°C) and pre-weighted 47mm GF/C filters. The filters were then rinsed with MilliQ water and immediately stored at -20°C, before being dried during 24 hours at 50°C and weighted to obtain the concentration. The absolute detection limit is 0.4 mg and the uncertainty (expressed as the RMSE of the triplicates divided by the mean value) decreases with increasing concentration from 8.5% (SPM concentration < 5 mg/l) to 6.7% (<10 mg/l), 3.5% (10–50 mg/l) and 2.1% (>100 mg/l) and represent the random error related to the lack of precision during filtrations. Especially in clearer water, systematic errors due to the offset by salt or other errors become much larger than the random errors (Neukermans et al., 2012; Fettweis et al., 2019). These are not included, and have been estimated based on Stavn et al. (2009) and Röttgers et al. (2014) as 1 mg/l. One of the SPM filters was used to determine the POM content, through Loss-on-Ignition (LoI) in a muffle furnace at 500°C during a few hours and reweighing. The samples for POC and PON were filtered on board using 25mm glass fibre filters, stored immediately at -20°C and analysed in the laboratory through catalytic oxidation and gas chromatography using a FLASH EA 1112 – Element analyser. The analytical uncertainty for POC and PON are 12% and 18% and the detection limits 0.018 mg/l and 0.009 mg/l respectively. The sample for pigment concentration was filtered on 47mm GF/C glass fibre filters, stored in liquid Nitrogen and determined in the lab using ultra high-performance liquid chromatography. The analytical uncertainty for Chl-a and Pheo-a is 23% and 31% and the detection limits are 0.023 µg/l and 0.015 µg/l. We added to these analytical uncertainties the random errors due to filtration, which we assumed to be equal to the ones of SPM concentration. The method for TEP analysis follows the one described in Nosaka et al. (2017). This method is, as many other semi-quantitative methods, based on Aldredge et al. (1993) and Passow and Aldredge (1995). Three subsamples for TEP concentration have been taken and filtered using 25mm 0.4 µm polycarbonate filters with low under-pressure. The filters have been coloured immediately after filtration with 1 ml of Alcian blue, rinsed with 1 ml of MilliQ water and stored at -20°C. The stained particles are related to a weight equivalent for the anion density of TEP and standardized using xanthan gum (Passow and Alldredge, 1995; Passow 2002). The units for TEP are expressed as mg xanthan gum equivalents per litre (mg XG eq./l). The filtrates were collected in sample tubes for DOC, inorganic nutrients and analysed using standard spectrophotometric methods with a Skalar autoanalyzer. The detection limit for DOC is 0.09 mgC/l.

2.2.2. Sediment samples

The POC and PON content of the bed surface samples was determined for the fraction < 63 µm using the same method as described above.

2.2.3. Floc size distribution and effective floc density

The volume concentration of each size class is used to build the floc size distributions (FSD), and thus the median floc size (D50) and total SPM volume concentration are computed from the FSDs. The uncertainties and limitations of the LISST 100X detectors are related to the shape, size and inherent optical properties of the particles occurring in nature, and to the measuring principle (Mikkelsen et al., 2006; Andrews et al., 2010; Davies et al., 2012; Schwarz et al., 2017) and will influence the FSD. In case of a too low turbidity (transmission >90%) the data becomes less accurate. The diameter of a particle is an exact proxy of its size if the particle is a sphere. Natural particles, such as flocs, have irregular shapes and generally follow Junge or multimodal log-normal distributions (e.g. Liley, 1992; Buonassisi

& Dierssen, 2010). Measurements by laser diffraction result thus intrinsically in a particle size distribution that is generally lognormally distributed. The effective floc density (ρ_{eff}) is the ratio of floc mass (M_f) over floc volume (V_f) minus the water density (ρ_w). The floc mass, M_f , can be calculated as:

$$M_f = M_p + M_w = M_p + \rho_w(V_f - V_p) = M_p + \rho_w \left(V_f - \frac{M_p}{\rho_p} \right) \quad (1)$$

where ρ_p is the primary particle density, M_w is the mass of water and M_p the mass of primary particles in the flocs. The latter can be obtained from the SPM filtrations, the water density was fixed at 1025 kg/m³, the primary particle density was estimated as 2500 kg/m³ (Fettweis, 2008) and the floc volume is the volume concentration measured by the LISST.

2.2.4. Long-term measurements of the FSD and SPM concentration

The structure of the long-term FSD time series at MOW1 has been investigated using the entropy analysis (e.g. Mikkelsen et al., 2007). Applied to FSDs, entropy analysis allows grouping the size spectra without assumptions about the shape of the spectra. It is therefore suited to analyse unimodal as well as multimodal distributions. Firstly, the 60 minutes averaged FSD time series were normalized by dividing each of the 32 size classes by the total volume concentration of the FSD and then pl64 low-pass filter (Beardsley et al., 1985) removed the tidal signal. Next, a climatological FSD over the period 2006-2019 was generated by averaging the data of each time stamp related to the start of the respective year. Finally, a climatological entropy classification was carried out using the FORTRAN routine of Johnston and Semple (1983). In accordance with Fettweis et al. (2014) four entropy groups have been chosen for the classification. The pl64 low-pass filter was also applied to the long-term SPM concentration time series before a climatological SPM concentration was calculated over the period 2005-2016 similar as the climatological FSD time series.

2.3. Model based differentiation of the OM

The inorganic and organic components of the SPM have different origins. The mineral particles may have a detrital or biogenic origin. The detrital PIM typically incorporates clays, quartz and other minerals, while biogenic PIM consists of minerals such as carbonates and amorphous silicates. In the further considerations, we will only consider PIM as a whole. The POM is a mixture of compounds derived from marine photosynthesis or terrestrial sources. It is a combination of diverse detrital organic substances as well as of living organisms such as bacteria, phyto- and zooplankton. The POM can be refractory, mineral-associated, or fresh. The first two have a low susceptibility and the last one a high susceptibility towards microbial degradation (Arndt et al., 2013). We will use the adjectives 'mineral-associated' (POM_m) for the more recalcitrant and 'fresh' (POM_f) for the labile and semi-labile fraction. The POM_m is incorporated in the mineral fraction where it is particularly bound with clay minerals (Mayer, 1994).

2.3.1. Model assumptions

For the differentiation between the POM_f and POM_m we follow the approach of Schartau et al. (2019), who considered Loss-on-Ignition (LoI) measurements for describing the POM:SPM ratio as a function of SPM concentration using a semi-empirical model. The conceptual basis of the POM-SPM model is that the POM concentration can be written as the sum of the POM_f and POM_m concentrations and that POM_m is assumed to be linearly correlated with the PIM concentration by a constant proportionality factor m_{POM} :

$$POM = POM_f + POM_m = POM_f + m_{POM} PIM \quad (2)$$

The assumption is that the seasonal built up of POM_f can be described as a saturation function of the SPM concentration:

$$POM_f = \frac{K_{POM}}{\frac{K_{POM}}{SPM} + 1} \quad (4)$$

with the parameter K_{POM} (in the same units as SPM concentration) being the second parameter of the POM-SPM model. The function reaches a saturation at high SPM concentrations where POM_f equals K_{POM} , while at low SPM concentration POM_f concentration tends to zero. This approach assumes that the production of POM_f is eventually limited by nutrients, temperature and light availability. Optimized values of K_{POM} were shown to be subject to seasonal variations, whereas values estimated for m_{POM} turned out to be fairly constant and independent of seasonal conditions (Schartau et al., 2019). According to the POM-SPM model, the POM content of SPM can be approximated by:

$$\frac{POM}{SPM} = \frac{POM_f}{SPM} \frac{1}{m_{POM} + 1} + \frac{POM_m}{SPM} \quad (4)$$

A non-linear dependency between POM content and SPM concentration is obtained by including eq. (3) in eq. (4). The combined equation has some meaningful and desired convergence characteristics. For SPM concentration approaching zero, POM content converges to 1 (and POM_f fraction dominates POM) and for high SPM it approaches $\frac{m_{POM}}{m_{POM} + 1}$ (and POM_m fraction dominates POM). Instead of using Lol data for POM content, we considered three different types of organic matter data, namely the concentrations of POC, PON, and TEP. The POM-SPM model was refined by introducing two parameters (f_1 and f_2) for every observational type X_i (POC, PON, and TEP) to the POM-SPM model (Eq. 5):

$$\frac{X_i}{SPM} = f_{1,X_i} \frac{POM_f}{SPM} \frac{1}{m_{POM} + 1} + f_{2,X_i} \frac{POM_m}{SPM}; X_i [POC, PON, TEP]; \quad (5)$$

These additional parameters f_{1,X_i} and f_{2,X_i} represent relative proportions of X_i to POM, e.g. f_{1,X_2} and f_{2,X_2} express the ratios of fresh- and of mineral-associated PON to POM (or f_{1,X_1} and f_{2,X_1} for respective ratios of POC to POM) in units of molecular weight ($g\ g^{-1}$) or TEP to POM in units of ($g\ XG\ eq.$)/(g POM), respectively. In this manner, consistent and meaningful estimates of f_{1,X_i} and f_{2,X_i} could be derived. Values assigned to or estimated for K_{POM} and m_{POM} should be largely independent of the observational type, no matter whether POC, PON, or TEP concentrations are considered. Overall, the refined model requires values to be assigned to four parameters (m_{POM} , K_{POM} , f_1 and f_2). Consequently, and somewhat different from the POM:SPM model, the respective fraction of X_i converges to f_{1,X_i} at SPM concentration approaching zero. For high SPM concentrations the portion X_i of SPM approaches $f_{2,X_i} \frac{m_{POM}}{m_{POM} + 1}$.

2.3.2. Parameter optimization

The mineral-associated POM_m of the SPM is entirely determined by the value assigned to the parameter m_{POM} (eqs. 2 and 4). The parameters m_{POM} and f_2 are collinear and therefore they cannot be estimated independently. For maintaining consistency between the previous parameter estimates of m_{POM} , and the added parameters of f_2 ($f_{2,POC}$, $f_{2,PON}$, and $f_{2,TEP}$) we used the optimized value ($m_{POM} = 0.13$) of Schartau et al. (2019). This estimate was obtained by using data of all seasons within the German Bight and German part of the Wadden Sea in the south-eastern region of the North Sea. The uncertainty of this estimate for m_{POM} is small (<3%) and the seasonal variations between estimates turned out to be small as well (0.12 - 0.14). With a fixed value assigned to m_{POM} we only require values of three parameters to be optimized. The values of f_1 , f_2 , and K_{POM} were estimated by minimizing the negative logarithm of a likelihood and a prior (cost function) that was used as a metric for assessing the deviation between observational data and the model counterparts. In general, for the likelihood (description of the data, given the model) and prior (deviation between estimated and some prescribed characteristic parameter value) we assumed respective probability

densities to be normal, represented as Gaussian functions of the data-model residuals and of the deviation of parameter estimates from a prior value assigned to K_{POM} . Reasons for why we had to account for prior information will be explained in the following paragraph. We explicitly accounted for uncertainties in the observations and in the prior value of K_{POM} . Optimal combinations of parameter values were determined for seasonally sorted data sets of POC, PON, and TEP. The observational data reveal pronounced variability at low SPM concentrations, which becomes much reduced at high SPM concentrations. At high SPM concentrations (>100 mg/l), uncertainties in measurements were much lower than the variations due to spatio-temporal variability. Like in the approach of Schartau et al. (2019), we added the variance of the observed POC:SPM, PON:SPM, and TEP:SPM to the measurement uncertainties for SPM concentrations >100 mg/l, otherwise individual data points at such high SPM concentrations can introduce severe biases in the estimates of the parameters f_1 and K_{POM} . For all data points we calculated variances for POC:SPM, PON:SPM, and TEP:SPM, following the law of error propagation, based on individual measurement errors of SPM, POC, PON concentrations. Errors for TEP were assumed to be 15% of the measured concentrations, which was approximately the highest relative error found for the POC concentration measurements.

The cost functions' minima yield the best model representations of the POC:SPM, PON:SPM, and TEP:SPM data. Respective minima (best parameter values) were identified by exploring the parameter space including combinations of the three parameters of interest, f_1 , f_2 , and K_{POM} . Intervals and resolution differed between the observational types for f_1 and f_2 . For POC and TEP we chose f_1 and $f_2 \in [0.01, 1]$ with a resolution of $\Delta=0.01$ (with 100 elements respectively). For PON we had to increase the variational range and resolution for $f_1 \in [10^{-3}, 1]$ (resolution $\Delta=10^{-3}$) as well as for $f_2 \in [5 \times 10^{-4}, 1]$ ($\Delta=10^{-4}$). Possible values of K_{POM} span two orders of magnitude and we therefore assigned a constant resolution on logarithmic scale ($\Delta \log = 5 \times 10^{-3}$) within the interval $\log_{10}(K_{\text{POM}}) \in [\log_{10}(0.1), \log_{10}(10)]$, which approximates a precision of 1%. The parameter screening is fast enough for deriving confidence intervals of respective parameter estimates via subsampling. A range of best parameter estimates was confined from 100 individual optimizations, based on random data subsamples that each included 30% of respective total data points. Doing so we learned that estimates of f_1 can become poorly constrained (mainly when using autumn data) for some subsamples that yield estimates of $K_{\text{POM}} < 0.5$ mg/l. By introducing an additional term as a prior to the likelihood-based cost function, the optimization problem became well-posed for all subsample cases and we could obtain robust parameter estimates. For the prior we imposed a K_{POM} value of 2.0 mg/l, with a 100% uncertainty ($=2.0$ mg/l) for all seasons apart from autumn, for which we had to prescribe a 25% uncertainty ($=0.5$ mg/l) for the prior. Based on the 100 individual optimizations, each with a different set of subsampled data, we determined statistical properties of the estimates, including lower and upper limits of 95% confidence intervals respectively. Instead of the arithmetic mean, the median of the parameter estimates turned out to be a better representation of the overall model fit to the data. This is because curved collinearities appeared in few cases and respective mean values did not coincide with the curved (banana-shaped) spread of optimal parameter values. In all other cases the median was similar to the mean of the estimates.

For model descriptions of POC:SPM and PON:SPM we considered seasonal variations and distinguished between in parameter estimates accordingly, combining data from three months: winter (December, January, and February), spring (March, April, and May), summer (June, July, and August), and autumn (September, October, and November). Monthly parameter estimates were elaborated for model fits to TEP:SPM data. Instead of using data from a single month, we included data from the two adjacent months. For example, optimal

parameter values for January were constrained with data from December, January, and February. Likewise, in June the parameter estimates were determined with data from May, June, and July. We recommend such a procedure, because it facilitates the identification of gradual temporal changes in parameter estimates, similar to the low-pass filtering of a moving average.

2.4. Results

2.4.1. Temporal and spatial variabilities

Some of the measured data together with some physical parameters are shown in Figure 2.2. The tidal amplitude (Figure 2.2a) is for Zeebrugge and has been calculated from harmonic analysis, the significant wave height is from a wave buoy near MOW1 (Figure 2.2b) and has been downloaded from the Measurement Network Flemish Banks (<https://meetnetvlaamsebanken.be>) and the daily solar radiation at Zeebrugge (Figure 2.2c) has been obtained from the Royal Meteorological Institute (<https://www.meteo.be>). The dissolved and particulate matter data have been averaged over the measuring period (usually 12 hours) and over the vertical. The data averaged over four seasons for all available parameters (2004-2020) are given in the tables in Appendix 1. For completeness these tables comprise also parameters that are not further discussed in this study. Variations in parameters occur at tidal, lunar and seasonal scales. Winter (December - February) is the period with low solar radiation, high nutrient concentration and low primary production. In spring (March - May) increasing solar radiation and temperature initiate phytoplankton blooms under nutrient replete conditions. Summer (June-August) has the highest solar radiations (Figure 2.2c) and nutrients are largely consumed. In late summer - early autumn, a second phytoplankton bloom shows up, but from autumn (September-November) on phytoplankton activity ceases with the decreasing solar radiation and nutrients pile up again. It is interesting to note that for the majority of parameters the more offshore stations W05 (red) and W08 (blue) displayed the same overall course as in MOW1 (black) but with lower values and a lower seasonal variability. Exceptions are median floc size and salinity. Observed variability during a tidal cycle is also less pronounced in the offshore stations. The water column was well mixed in all stations, the variations in salinity between them are, in accordance with Lacroix et al. (2004), caused to a large part by different freshwater contributions from the Rhine-Meuse and the Scheldt rivers. Temperature varied during 2019 sampling between 6.0°C at MOW1 in January (6.3°C at W05, 8.7°C at W08) and 19.9°C in June (19.5°C at W05, 18.2°C at W08). At each station, the highest SPM concentrations occurred in winter and the lowest in summer (Figures 1 and 2d). The volume SPM concentration has a nearly 75% more pronounced seasonality than the mass SPM concentration (Figure 2.2d, 2.2e and tables in Appendix 1). The lower spring-summer volume SPM concentrations correspond to larger floc sizes (Figure 2f) and also to lower effective floc densities (Figure 2.2g). Median floc size increased towards offshore by about 2. POC and PON concentrations (Figure 2.2h and 2.2i) are correlated with SPM concentrations, although higher POC:SPM and PON:SPM ratios occurred during the spring phytoplankton bloom (see tables in Appendix 1). The yearly mean value of the POC/PON ratio is 6.61 molC molN⁻¹, practically equal with the Redfield ratio (6.62 molC molN⁻¹). Lower values occur in spring (6.37) and summer (6.06) and higher ones in winter (7.01) and autumn (6.75). According to Frigstad et al. (2011), this seasonal variation reflects variations in the water mass characteristics, nutrient concentrations, biomass and OM composition. TEP concentration (Figure 2.2j) at MOW1 varied between 0.31 and 17.2 mg XG eq./l in winter, 0.62 and 17.57 mg XG eq./l in spring and 1.53 and 6.97 mg XG eq./l in summer. At W05 these values were between 0.11 and 3.31 mg XG eq./l (winter), 0.76 and 4.13 mg XG eq./l (spring) and 0.61 and 1.74 mg XG eq./l (summer); and at W08

between 0.10 and 0.59 mg XG eq./l (winter), 0.52 and 1.09 mg XG eq./l (spring) and 0.28-1.60 mg XG eq./l (summer). The seasonal variation in TEP concentration was similar to POC, PON and SPM concentration and all were somewhat opposite to the DOC concentration (Figure 2.2k). Although patchy, DOC concentration had generally higher values in summer than in winter, which is explained by the production of DOC by phytoplankton in spring and summer and the subsequent slow degradation (Van Engeland et al., 2010). Chl-a concentration (Figure 2.2l) was highest during the spring phytoplankton bloom. Except for the spring plankton bloom, the Chl-a concentration at MOW1 was higher than in the offshore stations. This is probably due to the higher availability of nutrients, in spite of the lower water clarity. The winter Chl-a concentrations reached values of a few $\mu\text{g/l}$ in winter, and were thus of the same order of magnitude or even higher than the offshore concentrations in spring and summer. Pheophytin is one of the breakdown products of chlorophyll and is thus an index of decomposable organic matter (Fuchs et al., 2012). The Pheo-a concentration had an opposite, although weaker, seasonal pattern than the Chl-a concentration. Inorganic nutrient concentrations (for example total dissolved nitrogen, total dissolved phosphate and silicates, see tables in Appendix 1) showed the typical pattern of the North Sea with relatively high concentrations in winter and low concentrations in summer due to nutrient utilization by phytoplankton (Lancelot et al., 2005).

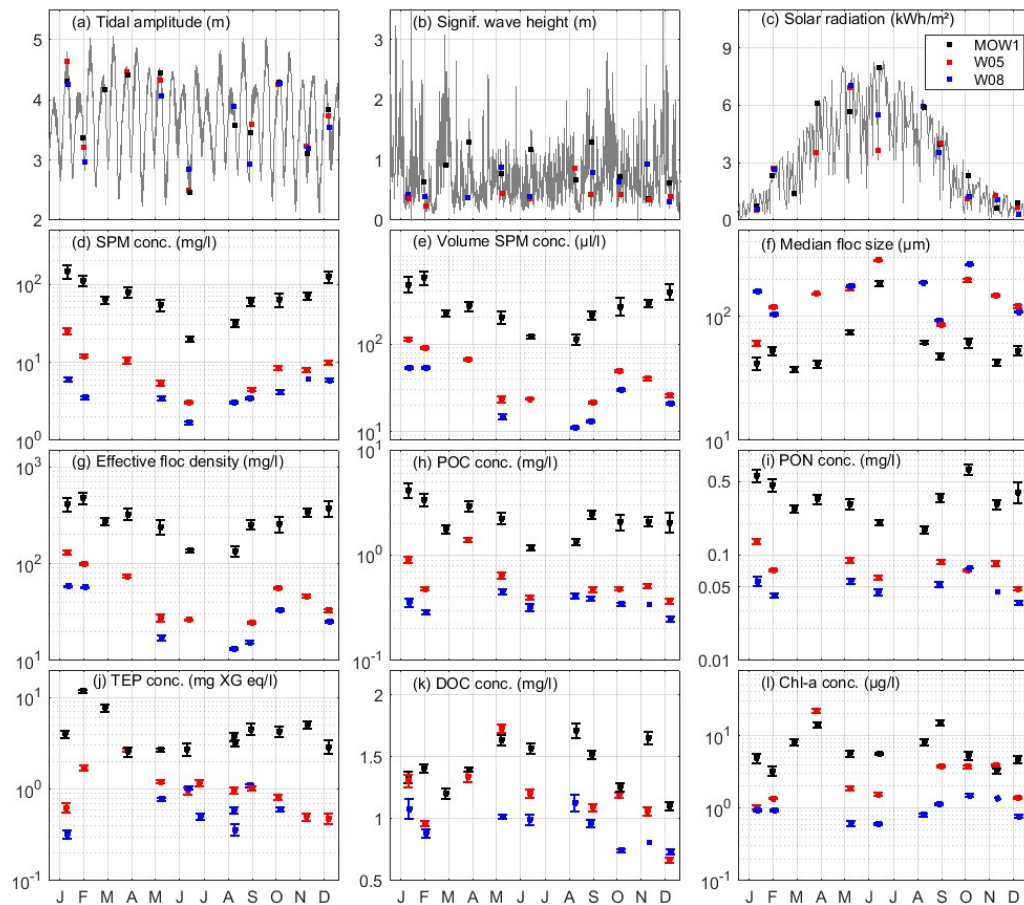


Figure 2.2: Physical (harmonic tidal amplitude, significant wave height, solar radiation) parameters and dissolved and particulate matter parameters from 2019 (TEP is from 2019 until August 2020) versus time (see § 2.1.1). For the latter, geometric means over the tidal sampling period are shown with their standard errors of the mean in the three sampling stations (MOW1: black, W05: red, W08: blue).

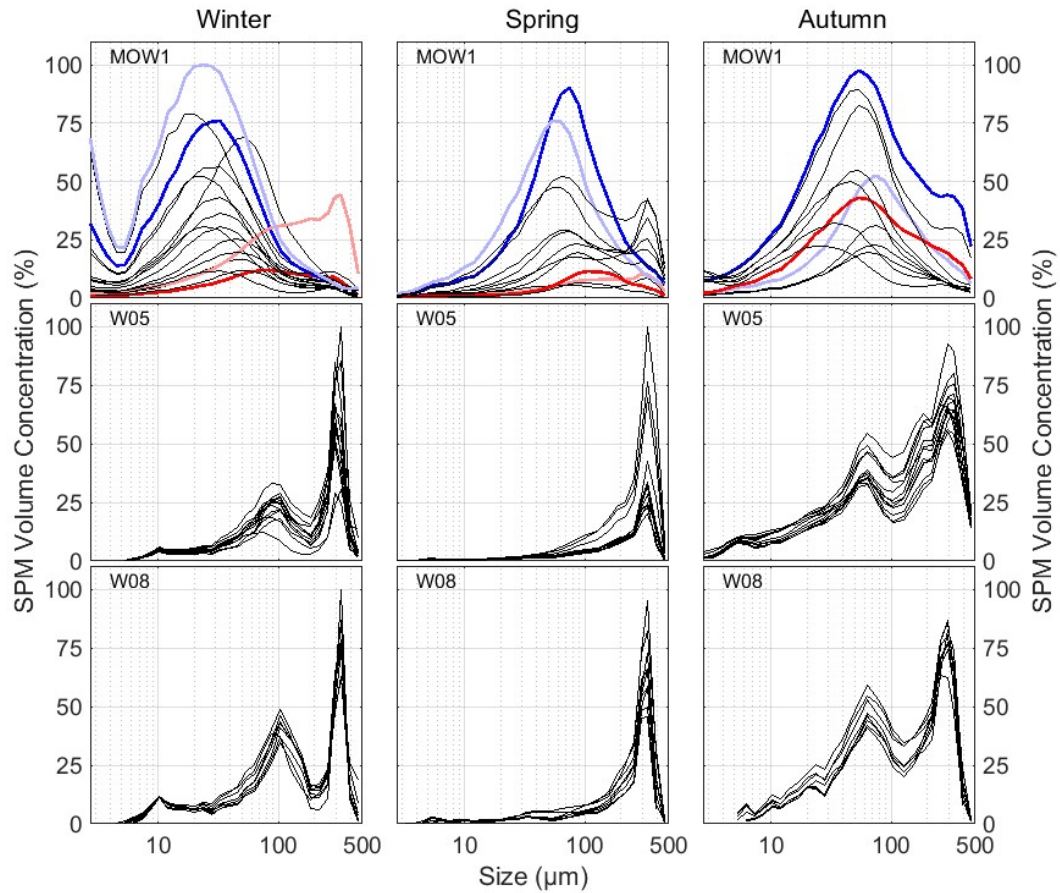


Figure 2.3: Hourly particle size distribution at about 2 m above the seabed during a tidal cycle at stations MOW1 (January, May, September), W05 (December, May, September) and W08 (December, May, September). The volume concentration is normalized by dividing all values with the largest one measured during the tidal cycle. FSD at MOW1 are highlighted around maximum flood currents (light blue), HW slack (light red), maximum ebb currents (blue) and LW slack (red).

2.4.2. Floc size

The hourly floc size distributions measured during a tidal cycle are shown in Figure 2.3 for the three stations for a winter, summer and autumn month. Common to all, are the tidal changes in volume concentration as a result of deposition, resuspension/erosion and advection. The FSDs at MOW1 were more variable during a tide than at W05 and W08, meaning that break-up and aggregation are dominating the FSD. At W05 and W08, the particles in suspension were not changing significantly in size. This points to strong aggregates and particles of biological origin that are not subject to turbulence-driven flocculation processes. In spring and, to some extent, in autumn, the FSD at MOW1 became bimodal, with a main peak around 60 μm and a second one around 300 μm . The latter is an indication of the occurrence of large biomineral flocs (Shen et al., 2018). The FSDs at W05 and W08 were unimodal in spring with a peak at 300 μm . In early autumn (September) and in winter they became bimodal, with a secondary peak at around 70 μm (winter) or 100 μm (early autumn). The winter FSD at W05 was more variable as it is located at the edge of the turbidity maximum zone. When the turbidity is higher, then the FSD resembles that of MOW1, in the opposite case it is similar to the offshore station W08 (the latter is shown in the figure). The low-pass filtered median floc sizes from the long-term LISST measurements (2016-2019) at MOW1 are shown in Figure 2.4. The median floc size is about 50 μm in winter and increases

up to 150 μm in summer. The four-class entropy analysis and the associated mean FSD show a mirrored evolution over the year as a function of seasonal changes. The FSD of class 1 ($D50 = 47 \mu\text{m}$) are most prominent between about 15 October and 15 March, those of class 2 ($D50 = 60 \mu\text{m}$) in the transitional periods characterized by an increase (15 March to 15 April) or decrease (15 September to 15 October) of biological activity. Class 3 ($D50 = 81 \mu\text{m}$) and 4 ($D50 = 116 \mu\text{m}$) prevail over spring and summer. The large biomineral flocs ($>200 \mu\text{m}$) are more frequent from late spring till early autumn during the decaying phytoplankton blooms, as indicated by the course in Chl-a.

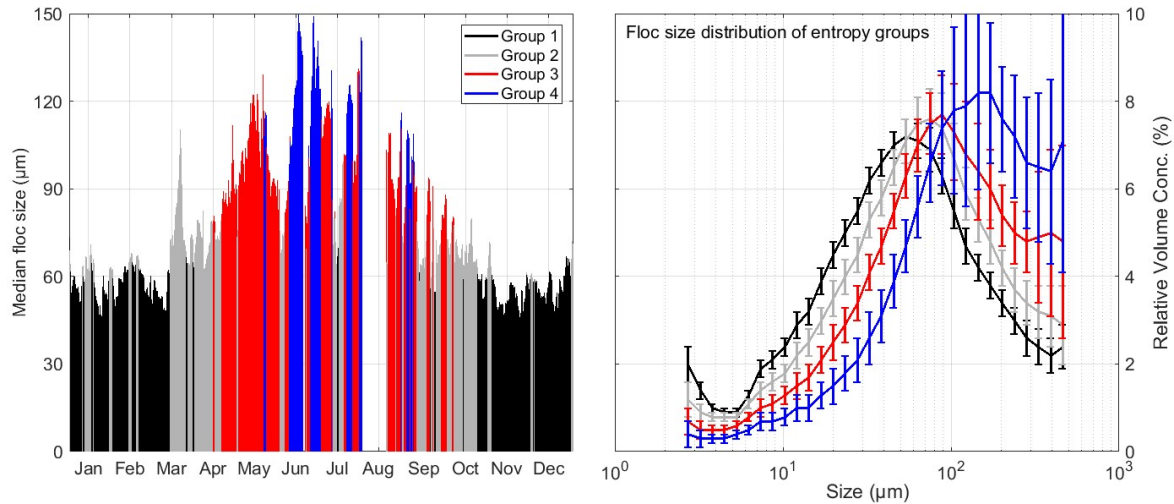


Figure 2.4: Mean of the low-pass filtered median floc sizes from the long-term LISST measurements (period 2007-2019) at MOW1 (left). The colors indicate the four entropy groups, the corresponding floc size distributions are shown in the right panel.

2.4.3. Particulate organic matter content of the SPM

The POC and PON fractions of SPM as a function of SPM concentration are shown in Figure 2.5. The graphs indicate an increase of the OM content with decreasing SPM concentration, which has been documented as a characteristic feature (e.g. Eisma & Kalf, 1987; Jago et al., 1994; Fettweis et al., 2006; Schartau et al., 2019). The POM content (measured as Loss-on-ignition, Lol) of the SPM (not shown) varies between about 10% to more than 90%. The fraction of POC incorporated in SPM varies between $\sim 2.5\%$ and 30% (POC), while the PON fraction is clearly lower, ranging between $\sim 0.35\%$ and 4%. Thus, the POC and PON content of SPM are about 4 and 28 times smaller than the POM content respectively. From about a 100 mg/l SPM concentration onward the POC and PON content reach an asymptotic value of about 2.5% and 0.35% respectively. The 10 to 15 time increase of the POC and PON content occurs over two orders of magnitude in SPM concentration and shows that SPM in the nearshore contains proportionally significantly less OM than in the offshore (see tables in Appendix 1 for the exact values). The best estimates of K_{POM} , f_1 and f_2 for annual (all year) representations of POC:SPM, PON:SPM and TEP:SPM are listed in Table 2.1 In all cases m_{POM} was taken as the best estimate for the POM model (eq. 4) for the Lol data set from the German Bight and amounts to 0.13 (see Schartau et al., 2019).

TEPs incorporate mainly organic carbon. Thus, measured TEP concentrations are not independent of the POC measurements, which is reflected in the significant ($p < 0.05$) correlation between POC and TEP in the data with an $R^2 = 0.59$. Accordingly, the dependency between TEP and SPM concentration (Figure 2.5c) is similar to those found for POC and PON (Figures 5a and 5b). Instead of a percentage fraction of SPM, the TEP:SPM ratio is given here in mass units (g XG eq.)/g (Figure 2.5c), because the concentration of the Alcian blue stained

microgels cannot be easily related to a mass concentration e.g. of organic carbon, in the presence of resuspended mineral particles. A derivation of a dependency between Alcian blue stained particles and their carbon content at different SPM concentrations is a relevant side aspect of our study (see Appendix 3). The TEP:SPM ratio is approximately 0.05 (g XG eq.)/g at SPM concentrations greater than 100 mg/l. With decreasing SPM concentrations, the ratio increases by one order of magnitude, to ~ 0.3 (g XG eq.)/g at SPM concentrations below 6 mg/l.

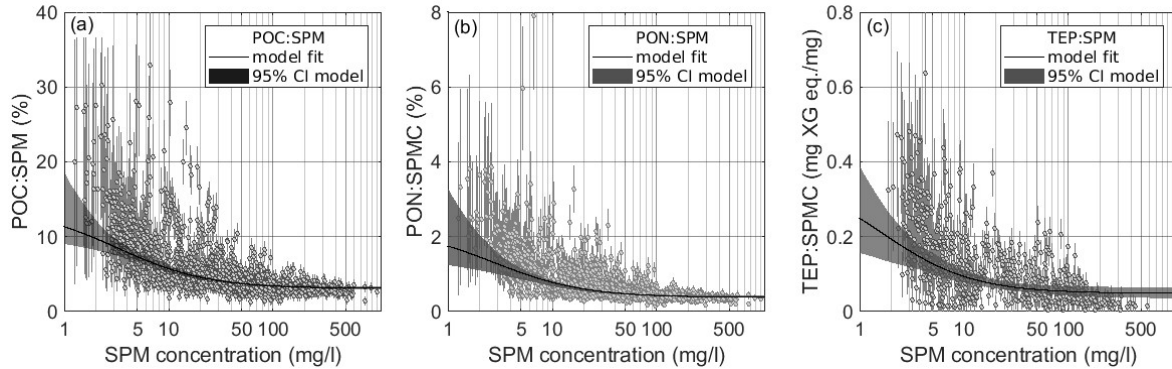


Figure 2.5: Model fit and 95% confidence intervals through all data for the POC content (left), PON content (middle) and the TEP content (right) as a function of the SPM concentration. The error bars represent the uncertainties of the measurements (see § 2.2.1). The shaded area is the 95% confidence interval of an ensemble of individual model fits, based on 100 optimizations with different, randomly sampled, data subsets.

2.4.4. Model estimates of the seasonally sorted data of POC, PON and TEP

The annual composite data of POC:SPM, PON:SPM and TEP:SPM, as depicted in Figure 2.5, exhibit extensive variability. For the most part, this variability can be attributed to seasonal changes. The fits of the models to annual composite data resolve and explain only differences between the different observational types. Seasonal variations have been further resolved by fitting the models to seasonally sorted data. Table 2.1 includes estimates of K_{POM} , f_1 and f_2 all four seasons separately. A higher resolution of temporal changes of parameter values was derived for model fits to TEP:SPM data, with monthly parameter estimates (see Table in appendix 2). In general, the non-linear dependency of the POC and PON content of SPM (Figure 2.6) varies in a similar way as the TEP:SPM ratio (Figure 2.7), with clearly altered seasonal signals.

At high SPM concentrations, greater than 100 mg/l, the variability remains small and temporal differences between the model solutions are indistinguishable for POC:SPM and PON:SPM. A large spread in the seasonally resolved model solutions were obtained for TEP:SPM ratio at SPM > 100 mg/l (Figure 2.7). The only noticeable difference is the lower estimate of f_2 obtained for modelling the TEP:SPM ratio at high SPM concentrations in winter. Whether this estimate is actually associated with a clear difference in the mineral-associated fraction of TEP in winter is unclear. Apart from this, the overall spread does not follow any seasonal pattern and must be attributed to larger uncertainties in the model fits of the TEP:SPM ratio. Overall, seasonal variations in the mineral-associated fractions of POC, PON, and TEP in SPM could not be identified and appear to be negligible. The small changes may rather be associated with variations in sediment types that contain variable constituents and fractions of minerals.

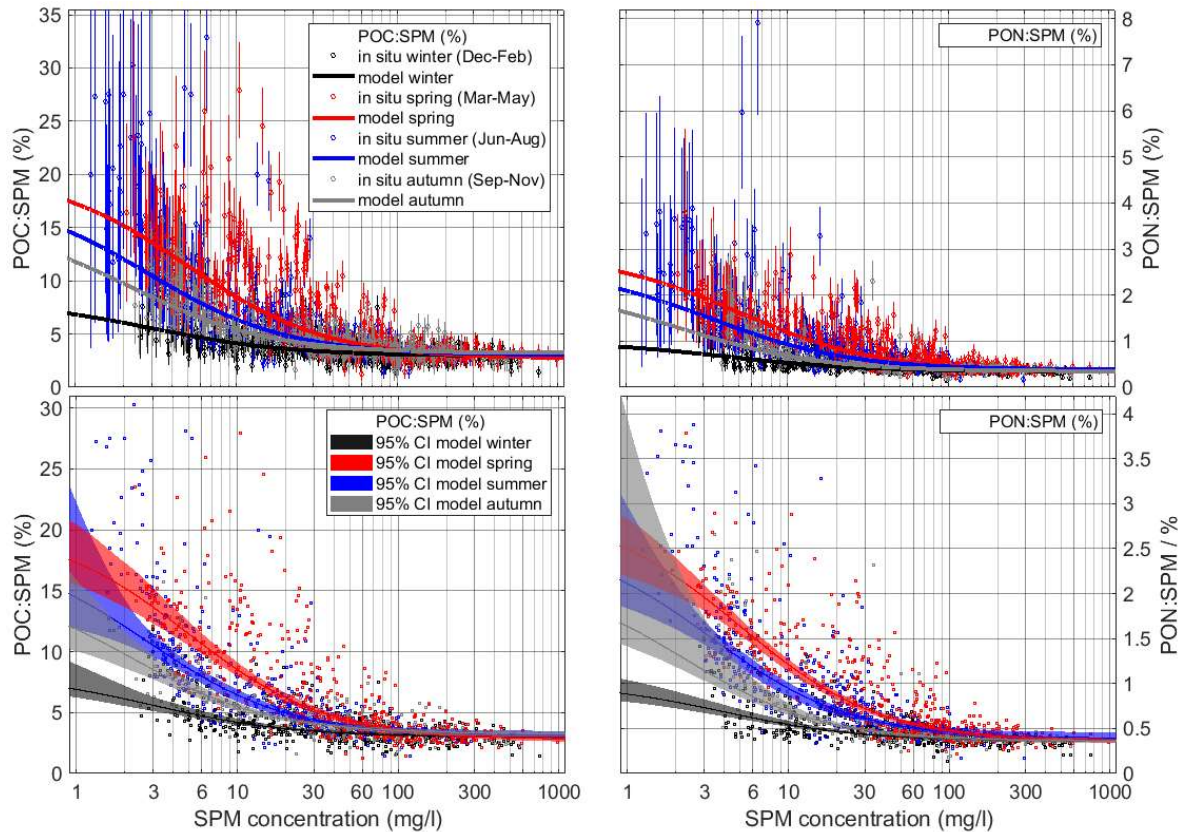


Figure 2.6: POC and PON content (in %) as a function of SPM concentration (data from 2004-2020). Top panels show the uncertainties of the data as described in §2.2.1 and model estimates for the different seasons. Bottom panels show the 95% confidence interval of an ensemble of individual model fits, based on 100 optimizations with different, randomly sampled, data subsets.

For SPM concentrations below ~ 100 mg/l, we identified clear and distinctive seasonal patterns. Our results show a correlation with season (and thus with primary production), which is most pronounced in the low-turbid data. In all cases, the seasonal changes could be well resolved (Figures 6 and 7). During the winter season the variations of the SPM's content of POC, PON, and TEP remain small for a large range of SPM concentrations, with only a small increase of respective fractions at low SPM concentrations. The general picture changes drastically for the spring period when phytoplankton blooms induce a substantial increase in the POC and PON content of the SPM, and also the TEP:SPM ratios follow this signal. At SPM concentrations of 1 mg/l, the lower end of the sample values, the POC and PON fractions of SPM are $\sim 17\%$ and $\sim 2.5\%$, and for TEP ~ 0.4 (g XG eq.)/g. During spring the measured POC and PON contents of the SPM feature some high values at SPM concentration between 10 to 50 mg/l, which are not captured by the model solution and are likely caused by the high spatio-temporal variability of patches with elevated phytoplankton biomass concentrations. Still, the model's optimized solutions for spring yield highest in the production of fresh POC, PON, and TEP in this range of SPM concentrations. According to the optimized model solutions, the elevated spring values gradually decrease during summer and autumn, a trend that can hardly be recognized on the basis of the highly scattered sample data alone. The differences between the summer and autumn signals are somewhat less distinctive than their differences to spring conditions. This is because transitional

months like September may include a prolonged bloom signal from summer or involve secondary bloom events due to the recurrence of elevated nutrient concentrations. The transitions from autumn to winter conditions are again well pronounced.

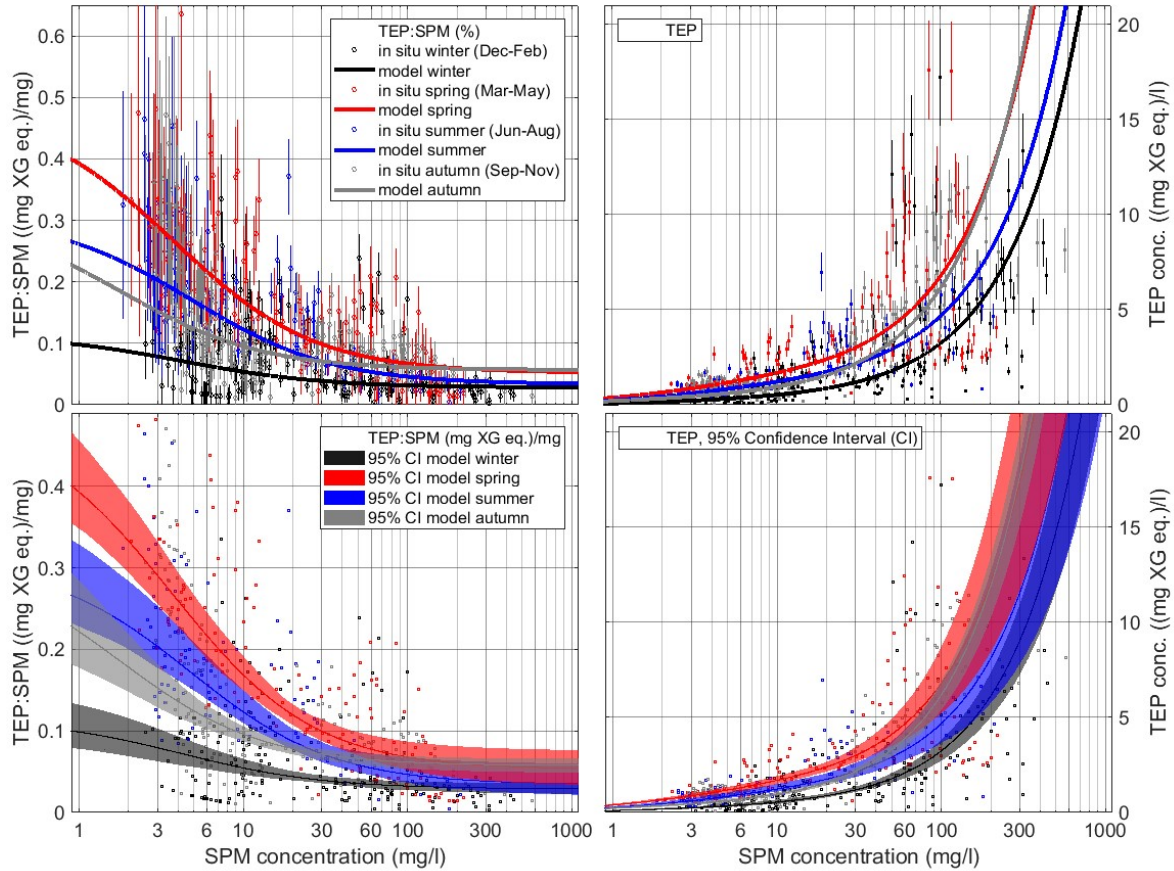


Figure 2.7: TEP content (left) and TEP concentration (right) as a function of SPM concentration. The lines are the result of the TEP-SPM model for the different seasons. The error bars represent the uncertainties of the TEP measurements, see § 2.2.1. Bottom panels show the 95% confidence interval of an ensemble of individual model fits, based on 100 optimizations with different, randomly sampled, data subsets.

The ratio $(f_{1,POC}):(f_{1,PON}) = (POC_f:PON_f)/(PON_f:PON_f)$ is indicative for the C:N ratio of the estimated fresh POM ($POC_f:PON_f$), while the same ratio for the f_2 parameter represents the C:N ratio of the estimated mineral-associated POM ($POC_m:PON_m$), see Table 2.2 and Figure 2.8. Both ratios have a seasonal variability, the $POC_f:PON_f$ ratio compares well with the $POC:PON$ ratio from the observations, which confirms the credibility of our parameter estimates. The winter and autumn values of the fresh $POC_f:PON_f$ and of the $POC_{obs}:PON_{obs}$ are above the Redfield ratio ($6.62 \text{ molN molC}^{-1}$) and the summer-spring values below it, but all values agree within the levels of uncertainty. The mineral-associated ratio $POC_m:PON_m$ is always above the Redfield ratio well beyond the lower 95% confidence limits (except summer), implying that the mineral-associated POM is more enriched in C than the fresh POM.

Table 2.1: Model parameters for POC, PON and TEP for all data (year) and for the four seasons. The units for K_{POM} are mg/l (same unit as SPM concentration) and for f_1 and f_2 [g/(g POM)] for POC and PON and in [g XG eq./(g POM)] for TEP.

$m_{POM}=0.13$	K_{POM} CI 95% [lower, upper]	f_1 CI 95% [lower, upper]	f_2 CI 95% [lower, upper]
Year			
POC	3.25 [0.24, 5.53]	0.122 [0.065, 0.981]	0.268 [0.248, 0.291]
PON	2.73 [0.13, 5.75]	0.021 [0.006, 0.203]	0.033 [0.031, 0.036]
TEP	1.61 [0.20, 4.36]	0.367 [0.100, 1.200]	0.422 [0.285, 0.583]
Winter			
POC	3.02 [1.34, 4.49]	0.058 [0.038, 0.112]	0.260 [0.248, 0.273]
PON	3.20 [2.16, 4.22]	0.008 [0.007, 0.011]	0.032 [0.030, 0.033]
TEP	4.25 [2.68, 6.00]	0.097 [0.058, 0.152]	0.251 [0.185, 0.318]
Spring			
POC	4.92 [3.11, 6.70]	0.197 [0.158, 0.261]	0.239 [0.216, 0.258]
PON	4.31 [2.95, 5.61]	0.032 [0.027, 0.038]	0.031 [0.028, 0.034]
TEP	3.67 [2.12, 4.83]	0.489 [0.386, 0.641]	0.457 [0.265, 0.677]
Summer			
POC	2.79 [0.28, 5.40]	0.173 [0.105, 0.993]	0.267 [0.237, 0.306]
PON	2.82 [1.34, 4.05]	0.028 [0.022, 0.043]	0.034 [0.031, 0.039]
TEP	3.27 [1.63, 4.62]	0.379 [0.281, 0.567]	0.456 [0.296, 0.601]
Autumn			
POC	2.18 [0.63, 3.62]	0.141 [0.085, 0.350]	0.282 [0.255, 0.304]
PON	0.90 [0.08, 8.00]	0.033 [0.009, 0.106]	0.031 [0.028, 0.033]
TEP	1.46 [0.10, 10.00]	0.267 [0.020, 1.200]	0.514 [0.392, 0.647]

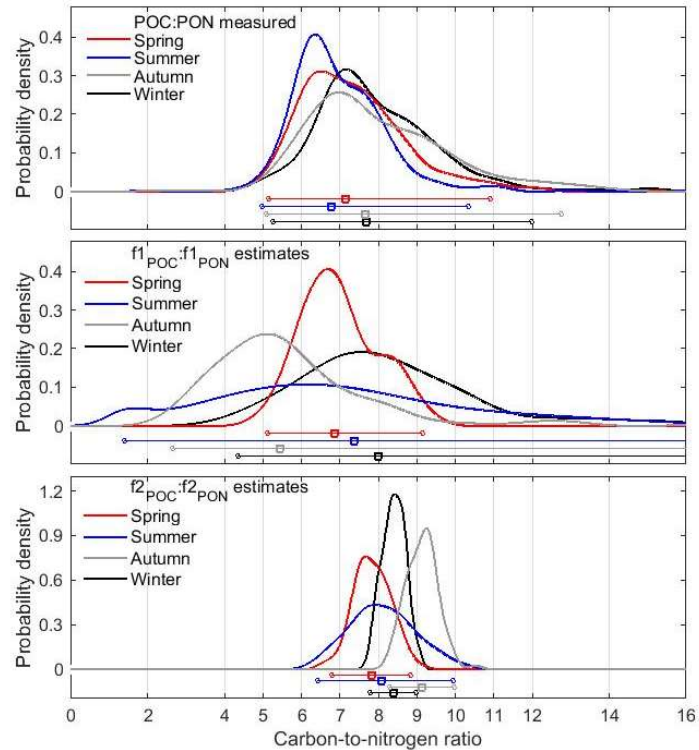


Figure 2.8: Probability density distribution of the POC:PON ratio from in situ measurements and of the Carbon to Nitrogen ratios of the model parameters $f_1(POC):f_1(PON)$ and $f_2(POC):f_2(PON)$. The horizontal bars are the 95% CI.

Table 2.2: C/N ratios of the model parameters $f_1(\text{POC}):f_1(\text{PON})$ and $f_2(\text{POC}):f_2(\text{PON})$ and of the ratio $\text{POC}_{\text{obs}}:\text{PON}_{\text{obs}}$ from in situ measurements.

	$f_{1,\text{POC}}:f_{1,\text{PON}}$ CI 95% [lower, upper]	$f_{2,\text{POC}}:f_{2,\text{PON}}$ CI 95% [lower, upper]	$\text{POC}_{\text{obs}}:\text{PON}_{\text{obs}}$ CI 95% [lower, upper]
Winter	7.99 [4.35, 16.15]	8.39 [7.78, 8.98]	7.67 [5.27, 11.99]
Spring	6.85 [5.12, 9.14]	7.81 [6.80, 8.83]	7.13 [5.14, 10.19]
Summer	7.37 [1.41, >20]	8.06 [6.43, 9.95]	6.76 [4.99, 10.33]
Autumn	5.42 [2.66, >20]	9.12 [8.31, 9.96]	7.64 [5.11, 12.76]

2.5. Discussion

The main objective of the study is to investigate to what extent a model-based separation of the organic particulate matter into fresh and mineral-associated, i.e. fresh and labile versus more recalcitrant fractions, may unravel a signal that relates to the seasonal buildup and breakdown of flocs in coastal oceans. In principle, flocculation is depending on a number of local environmental conditions, e.g. turbulence, cation concentration, SPM concentration as a proxy particle number density, mineral composition, POM concentration and composition (e.g. TEP) and microorganism (Dyer, 1989; Mietta et al., 2009; Keyvani & Strom, 2014; Lai et al., 2018; Zhang et al., 2021). The bulk mineralogical composition of the SPM in the study area is relatively constant and consists of 32-39% clays, 25-33% carbonates, 12-18% quartz, 11-15% amorphous silicates and 5-8% feldspars and accessory minerals (Adriaens et al., 2019). The cation concentrations are high and well above the threshold for salinity induced flocculation so that flocculation in the study area is above all controlled by the POM composition of the SPM, the SPM concentration and the hydrodynamic conditions. The effect of turbulence and SPM concentration on flocculation in the study area has been described in previous studies (Fettweis et al., 2006; Fettweis et al., 2014; Fettweis & Baeye, 2015). They reported that maximum floc size was mainly controlled by turbulence intensity (tides and waves), which is higher in the nearshore area than offshore, but does not exhibit a pronounced seasonal signal. Our LISST data (Figure 2.3) confirm that the size of the largest flocs is similar during all seasons, but their abundance is higher in spring and summer, because they seem to be more tightly bound and resist better shear-induced breakup.

The seasonal dependence of SPM concentration with lowest values in summer (Figure 2.2d) contrasts with the inverse dependence of the median floc sizes which are highest in summer (Figure 2.4, left panel). Thus, SPM concentration in itself can be ruled out to explain flocculation and the qualitative properties of SPM may provide a much better clue. Given the large variability in SPM concentration within the nearshore areas and along their transition to the offshore waters, their variation may unravel predominant variations of the processes involved. In the following discussion we will show how the modified application of the POM-SPM model of Schartau et al. (2019) to the POC, PON and TEP sample data turned out to be beneficial. With the aid of the calibrated model solutions we could estimate how the relative fractions of freshly produced labile and semi-labile OM (of POC, PON, and TEP) along with the rather recalcitrant mineral-associated OM content of the SPM change with SPM concentration. A starting point of this approach is the obvious concurrence of seasonal rises and declines in median floc size (Figures 2.3 and 2.4) with the model parameter K_{POM} , which numerates the seasonal built up of fresh organic material and its components (Figures 2.5-2.7 and Table 2.1). Our synthesis between model application and in situ measurements delivers important insight into the complex process of flocculation in a region of great variability. Based on results of our analyses we can expand the scope of discussion on how

the fresh and the mineral-associated OM fractions of the SPM affect the process of biophysical flocculation.

2.5.1. Spatio-temporal variations of floc characteristics

Flocs in the nearshore high turbid station MOW1 were subject to extensive temporal variations in volume concentration, density and size during a tidal cycle (Figures 2.2 and 2.3). The FSDs were skewed towards smaller sizes around peak flow (blue in Figure 2.3) and developed a peak in the larger size classes around slack water (red in Figure 2.3). Lee et al. (2012) have shown that the flocs at MOW1 are characterized by a multimodal size distribution that consists of small particles, flocculi, microflocs, and macroflocs. The smallest particles likely consist of clay-sized particles of various mineral composition, the flocculi are breakage-resistant aggregates of clay minerals, microflocs can be attributed to the medium size aggregates, whereas macroflocs can be identified as the large aggregates with diameters up to a few hundred micrometers. Tran and Strom (2017) have shown in a laboratory experiment that silt and clay combine into flocs. In some contrast to this, we observe (Figure 2.3 and 2.4) that the FSDs at MOW1 all had well pronounced modes within the smallest size classes in winter. This mode diminished towards summer. This indicates that in winter abundant fine-grained mineral particles do not aggregate into flocs. They settle slowly and remain in suspension longer, resulting in a background turbidity that is higher than in summer. In general, lower turbulence intensities before slack water promote the aggregation of the more mineral (i.e. with a POC content of about 3%) flocculi and microflocs into larger macroflocs. In winter these macroflocs have similar characteristics than the microflocs, i.e. they are mineral enriched (Tang & Maggi, 2016). In summer, according to Fettweis and Baeye (2015), the small particles, flocculi and microflocs also coagulate with freshly produced OM to form quite stable aggregates that are enriched with biogenic substances, including phytoplankton cells and detrital substances. These spring and summer flocs have lower densities than the winter and autumn flocs (see Figure 2.2g and Tables in Appendix 1) but reach floc sizes that involve settling velocities that exceed those of the smaller winter flocs leading to their accumulation near the bed and the decrease of the average SPM concentrations in the water column.

In contrast, in the offshore stations W05 and W08, the seasonal variabilities in the concentration of SPM and the OM parameters were less pronounced and the FSD distribution rather constant over the tides (Figure 2.3), showing that here aggregation dominates disaggregation kinetics (Fettweis & Lee, 2017). The principal variations in these parameters occurred between seasons and not within tides. In winter and autumn, the FSDs were multimodal, with a first mode around 10 μm , a second one around 50-100 μm and a third one around 300 μm (Figure 2.3). The first mode could consist of flocculi, while the second mode could be formed by minerals from biogenic origin (carbonates, amorphous quartz). In spring, the 300 μm peak dominated the FSDs. In summer, the increase of the median floc size in these offshore stations (see Figure 2.2) indicates that the observed decrease of the lower modes is caused by the incorporation of these particles into the larger aggregates. These larger biological aggregates can be lighter and even settle slower than smaller biomineral aggregates found at MOW1 (Maggi & Tang, 2015).

2.5.2. TEP concentration and its relation to floc size

2.5.2.1. Seasonal variation in TEP concentration

A correlation of TEP concentrations with the rise and decline of phytoplankton blooms is reported from lab cultures (Fukao et al., 2010), estuarine and nearshore areas (Ramaiah et al., 2001; Bhaskar and Bhosle, 2006; Chowdhury et al., 2016), and from the open ocean (Mari et al. 2017). Others report temporary disconnection of TEP from Chl-a concentrations

(Ortega-Retuarta et al., 2017, Lee et al., 2020). Our data do not show a close relationship between Chl-a and TEP concentration (See Figure 2.2j and 2.2l). In the shallow nearshore station MOW1 a substantial fraction of TEP seems to be rather mineral-associated, entering the water column via resuspension of sediment particles. The TEP concentration followed the SPM concentration irrespective of the season and thus also during winter when primary production has largely ceased (Figure 2.2d, 2.2j and Figure 2.7, right panel). This general dependency is modulated by a seasonal signal, depending on the amount of POC and PON being built up via primary production. Our seasonal pattern is in line with findings from the turbidity maximum of the Seine estuary (Morelle et al., 2018). There, the highest TEP concentrations coincide with the lowest EPS and DOC concentration in winter and vice versa in summer. In contrast, the more offshore stations, where SPM concentration remained most of the time below 10 mg/l, had TEP and POC concentrations that were generally higher in spring and summer than in winter. The offshore environments with low turbid conditions agree with the correlation found by Mari and Burd (1998) between DOC and TEP concentrations suggesting that TEP are formed by coagulation of the dissolved EPS (Mari & Burd, 1998). These results indicate the occurrence of two types of TEP, presumably having different chemical characteristics with respect to their stickiness and their potential to promote the formation of flocs of large size.

An immediate dependency between the total abundance of TEP and floc size cannot be inferred from our data. The interpretation of the results for the station MOW1 is complicated by the fact that similar TEP concentrations resulted in different floc sizes in winter and summer (see Figure 2f and 2j). Morelle et al. (2018) have explained the higher TEP concentration in winter by deposition and resuspension processes. This would mean that due to the larger flocs in spring and summer, a large part of the TEP is found in the benthic boundary layer or on the bed, while in winter it is resuspended. However, this interpretation does not explain why floc sizes were smaller in winter and is not supported by studies relating floc size to TEP concentration (e.g. Passow, 2002; Verney et al., 2009; Deng et al., 2019) and by our data that show larger floc sizes in spring and summer. Our analysis suggests that biophysical flocculation in highly turbid areas is strongly affected by the occurrence of fresh OM rather than the total amount of OM. TEP production rapidly increased when the maximum capacity for the build-up of fresh POC and PON was reached (Figure 2.9). This occurs when phytoplankton approaches nutrient limited growth conditions (Engel et al., 2004; Schartau et al., 2007). Part of the fresh OM consists of EPS and will partly be transformed into TEP. We could not explicitly resolve the process of TEP formation from dissolved precursors, but found generally higher DOC concentration in spring and summer. Figure 2.2k shows that DOC concentration, which contains EPS, has a maximum in late spring and summer, as in the Seine estuary (Morelle et al., 2018).

In order to assess the relationship between the time evolution of SPM and TEP in their quantities and qualities, Figure 2.10 shows the low-pass filtered median floc size data at the high turbid station MOW1 (as in Figure 2.4) together with the low-pass filtered long-term SPM concentration time series (upper panel), as well as the seasonal evolution of fresh and total TEP concentration (lower panel) derived from calibrated results of the TEP-SPM model based on monthly model parameter estimates of K_{POM} , f_1 and f_2 (see Table in Appendix 2). When fresh TEP is produced (from half February onward), the median floc size increases (in particular from March on, when the proportion of fresh TEP to total TEP ratio increases) and SPM concentration decreases. Although fresh TEP concentration is at its maximum in early spring, the increase in median floc size, the changes in floc size distribution (Figure 2.4) and the decrease in SPM concentration occur more gradually. The progressive raise in floc size follows the increase and the decrease of the fresh TEP fraction ($TEP_{fresh}:TEP_{total}$). This ratio

is low during winter (about 2%) and starts to increase from the beginning of February to about 15% in March and then more quickly to reach a maximum around 60% in May-June. The peaks in floc sizes as well as the lowest SPM concentrations were observed during this period.

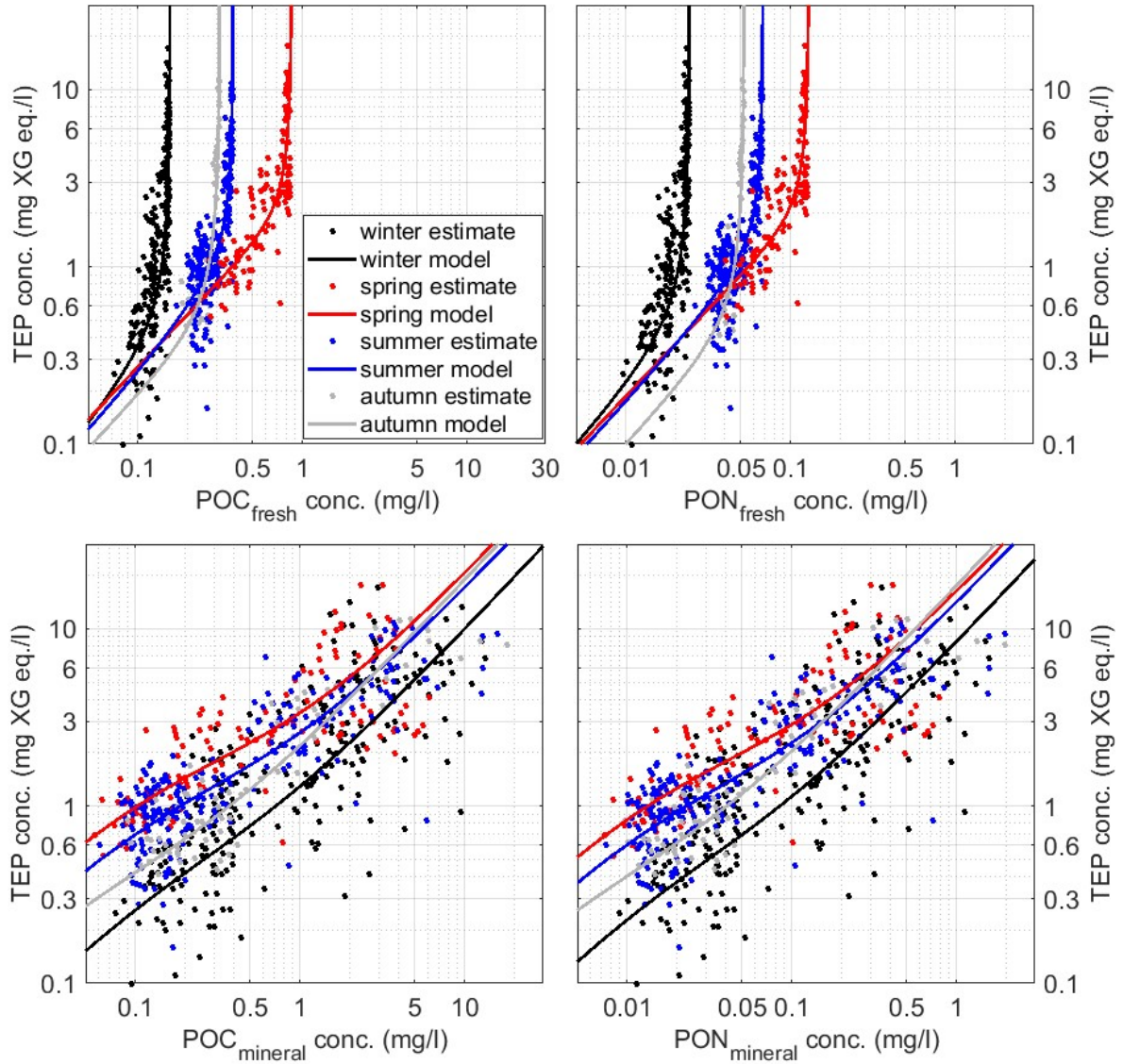


Figure 2.9: The observed total TEP concentration versus the model derived fresh (upper panel) and mineral-associated (lower panel) POC and PON concentration. The lines are the estimated total TEP concentration as a function of POC and PON concentration derived from the POM-SPM model.

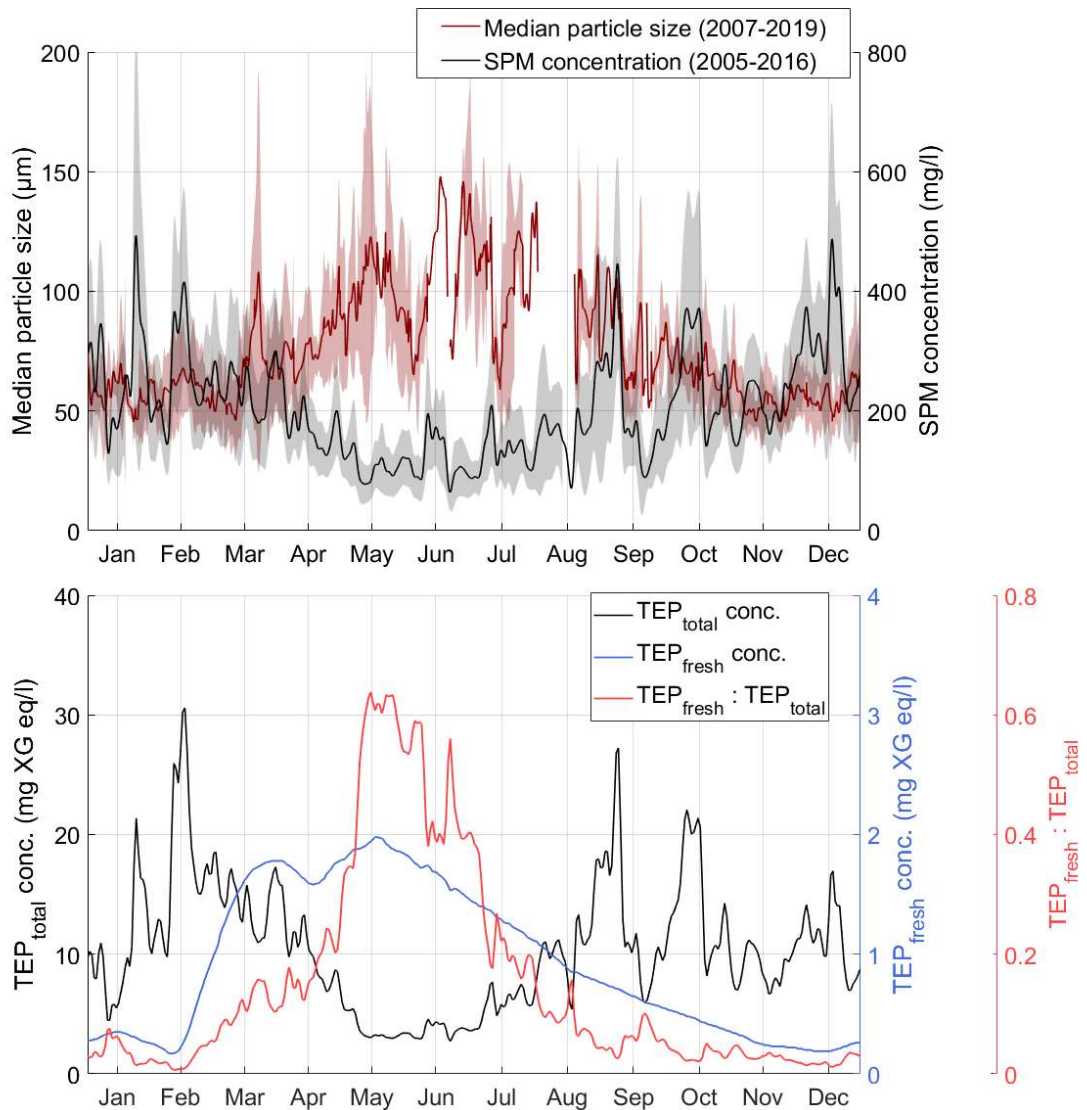


Figure 2.10: (a) Long-term and low-pass SPM concentration (2005-2016) and median floc size (2007-2019) at 2 m above bed. The shaded area is the standard deviation if more than 2 data points are available. (b) The model estimates of total (black) and fresh (blue) TEP concentration calculated from the long-term SPM concentration time series. The red line is the fraction of fresh TEP in the total TEP. All data are from the near shore station MOW1.

The decrease of the fresh TEP concentration after its quick accumulation in spring occurs gradually over a period of about 6 months (May-November) and can be due to hydrolyzation, consumption and/or deposition. This is in contrast with the early spring period, where most of the fresh TEP accumulation occurs within about one month (February-March), before reaching a maximum in early May. The production of fresh TEP correlates with the first increase in Chl a concentration in February in 2019 and the first decrease of SPM concentration from beginning of March onward (Figure 2.11). These findings support the hypothesis that in early spring in the turbid nearshore, when light conditions are still depleted, light adapted phytoplankton species initiate the spring bloom and also induce the formation of fresh TEP. In contrast to the mineral-associated TEP, it is this initial occurrence of fresh TEP that eventually promotes aggregation and the formation of larger flocs with higher settling rates. This in turn lowers SPM concentration and reduces light attenuation, which paves the way for species with higher light requirements in the phytoplankton seasonal succession.

Altogether, the results underline that the different components of the SPM (i.e., mineral, organic matter and living particles) form an integrated dynamic system with direct interactions and feedback controls.

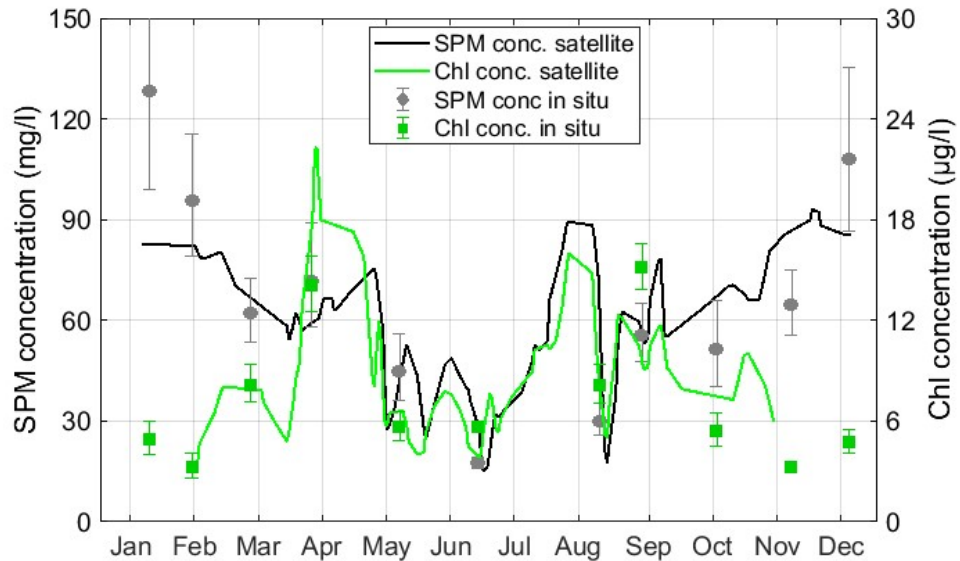


Figure 2.11: Time series of surface SPM and Chl-a concentration in 2019 derived from remote sensing (Sentinel-3/OLCI) and in situ observations at station MOW1 (nearshore). The in-situ data are mean values over a tidal cycle, the error bars are the standard error of the mean.

2.5.2.2. TEP in autumn and winter

What are the quantitative and qualitative characteristics of TEP outside the growth season? The presence of high concentrations of TEP in autumn and winter above all in the turbid nearshore (Figure 2.2k) raises questions on the characteristics of this organic matter. Mari et al. (2007) mention that the efficiency of the transformation of EPS into TEP and the TEP reactivity decrease with time. This would mean that the TEP stickiness varies as a function of the degradation stage and age. Winter TEP would then be smaller in size and less sticky, while in spring and summer it would consist of larger and more sticky particles that become actively involved in flocculation dynamics (Engel et al., 2020). The biomineral flocs resist better to shear-induced break-up in spring and summer due to availability of more reactive TEP and of the inclusion of free-floating bacteria and other microorganisms into the flocs that produces themselves exopolymers (Fettweis et al., 2014; Jachlewski et al., 2015; Shen et al., 2019). The bacteria associated with TEP contribute to the hydrolysis of the OM and thus foster the gradual decay and disaggregation of the biomineral flocs in autumn (Smith et al., 1992; Alldredge et al., 1993; Passow & Alldredge, 1994), which is reflected in the observed decrease in floc size in our data. As the transition from summer to winter is gradual, one would expect that TEP concentration decreases through microbial respiration until a minimum is reached just before the onset of the algae bloom in early spring. The latter is observed in the low turbid offshore stations W05 and W08, but not in the turbid MOW1 station, see Figure 2.2j. Other studies highlight the relationship between OM content and mineral surface area (Keil et al., 1994; Mayer, 1994). This means that with increasing SPM concentration, the OM concentration and thus also TEP concentration increases, while the POM content of the SPM decreases until reaching an asymptotic value at high SPM concentrations (>100 mg/l) of about 3% POC, 0.4% PON, and 0.04 (mg XG eq.)/mg TEP (Figures 2.5-2.7). At high SPM concentrations the fresh OM represents only a small part of the total OM and is hardly detectable due to the high variability of the measurements. Both the fresh and

recalcitrant OM can be associated to the mineral surfaces, being protected from microbial respiration (Keil et al., 1994; Kalbitz et al., 2005; Hemingway et al., 2019; Chen et al., 2021). The protected mineral-associated OM explains the high TEP concentrations in winter in high turbid areas such as the Belgian nearshore, Chesapeake Bay (Malpezzi et al., 2013) or the Seine estuary (Morelle et al., 2018).

The mineral-associated POC over TEP ratio is about 1 in winter and between 0.52 and 0.59 (mean 0.56) during the other seasons (see Appendix 3). The higher ratio in winter is the result of the optimal estimation of the POC and TEP content in the SPM based on our data. The model estimates a lower value of the TEP content in the SPM in winter at high SPM concentrations than for the other seasons (Figure 2.6). Such distinction could be explained by a lower amount of mineral-associated TEP in winter and by the occurrence of two different mineral-associated TEP fractions. One is more recalcitrant and remains, while the other one is still subject to gradual but slow degradation and eventually disappears in winter. The first one could consist of the TEP that occurs in between the layers of the clay crystal structures (Mayer, 1994; Blattmann et al., 2019). The second one could consist of a semi-labile biofilm on the surface of the mineral particles (Decho & Gutierrez, 2017). Anyway, the mineral-associated POC over TEP ratios indicates that the recalcitrant mineral-associated TEP makes up a great portion of the mineral-associated POC.

To conclude, while also present during autumn and winter, fresh TEP occurs at much lower concentration then. It could originate from winter biological activity, from bacteria or phytoplankton (Chl-a concentration in winter is on average between 1.1 $\mu\text{g/l}$ at W08 and 3.5 $\mu\text{g/l}$ at MOW1, see Appendix 1). The flocs in autumn and winter can thus be considered as biophysical in nature as few fresh TEP is available to aggregate cohesive particles (such as clay minerals) with non-cohesive ones (such as carbonates) into larger floc. The rising tails in the winter FSD at MOW1 (Figures 2.3 and 2.4) point to the occurrence of particles smaller than the measuring range of the LISST (i.e. 2.72 μm) and indicate that the efficiency of biophysical aggregation in winter is, however, much lower than in spring and summer in the high turbid nearshore.

2.5.3. Spatial variation in SPM composition

2.5.3.1. Asymptotic decrease of OM content with increasing SPM concentration

The surface sediments at W05 and W08 consist of medium sand with small amounts of fines (a few %) and POC contents in the fraction $<63 \mu\text{m}$ of about 1.8% and 1.1% respectively. These values are lower by a factor of 4 and 8, respectively, than the mean POC content of the SPM in these stations (see Tables A.2 and A.3 in Appendix 1). In these stations the SPM concentration was generally below 10 mg/l. This is a clear indication that the suspended material can only to a minor part originate from the sea bed. This illustrates nicely the increasing decoupling of near bed and water column processes with water depth and distance from the coastline. In the nearshore station MOW1, the amount of the fraction $<63 \mu\text{m}$ in the sediments is about 50% (Fettweis and Van den Eynde, 2003), the POC content of the surface sediments (fraction $<63 \mu\text{m}$) is only lower by a factor of 1.5 than of the SPM at high concentrations (2% versus 3%) and indicates that the surface layer of the seabed is actively involved in the tidally induced resuspension and deposition of the particulate material (Table A.1 in Appendix 1). The asymptotic value of 3% POC at high SPM concentration shows that the minerals are saturated and that no long-term accumulation of OM occurs in the nearshore station MOW1. The fresh OM that is not associated with the mineral surfaces will thus quickly be consumed in the food web. Similar values of the POC contents of the SPM have been found in the turbidity maxima of the Seine and Loire estuary (Etcheber et al., 2007), lower ones in the Gironde estuary (Etcheber et al., 2007) and higher ones in the

Yangtze (Milliman et al., 1984) and Congo river (Bouillon et al., 2012). It is remarkable that these variations in POC content between different areas are relatively small (2%-5%), which points to a similar composition of the SPM in many turbid aquatic ecosystems over the world. The small differences are probably caused by methodological differences, measuring uncertainties and by different mineral-associations of the SPM, as the preservation of OM is controlled mainly by its clay mineralogy (Blattmann et al., 2019).

2.5.3.2. Nearshore to offshore gradient in fresh and mineral-associated OM

We used the Sentinel-3/OLCI satellite images of SPM concentration to extract the cross-shore variation of mineral-associated and fresh components of POM, POC, PON and TEP at the water surface. Taking the model parameters for f_1 , f_2 , K_{POM} and m_{POM} (see Table 2.1), we applied the model pixelwise to the remote sensing data. In this way we generated eight further secondary satellite products purely based on SPM surface concentration. For the purpose of this study we discuss these data for all seasons along a transect that connects the three measuring stations from the coast (MOW1) with SPM concentration $\cong 80$ mg/l via W05 to the offshore (W08) with $\cong 2$ mg/l (see Figure 2.12).

The mineral-associated part (middle) follows to a large part the SPM concentration and has the same strong decrease with increasing distance from the coast. The fresh POM (left) in contrast, nearly keeps his level along the whole transect. The major seasonal formation of fresh POM thus occurs not only within the shallow coastal regions but extends along the whole area. These patterns are similar for all components of the POM and TEP and for all seasons. For the mineral-associated parts, winter has the highest and summer the lowest values except for TEP where the highest values are during the periods of spring and autumn blooms. The fresh parts are always highest in spring and lowest in winter. The ratios of fresh to mineral-associated POC, PON and TEP (right) show that there is a zone somewhere around station W05, where both fractions are about equal (ratio = 1). This may be identified as a transition zone where, seen from the land, the near coast conditions with particle dominance from the sea bed turn into open sea conditions with particles who are of pelagic origin. This transition zone is located in between MOW1 and W05 in spring and summer at a water depth around 10 to 15 m and corresponds with a surface SPM concentration of about 40 mg/l in spring and about 20 mg/l in summer. It is located more offshore in autumn where it occurs around W05 (water depth around 20 m) with about 8 mg/l SPM concentration and close to W08 in winter.

2.5.4. Consequences for modelling and monitoring of coastal ecosystems

Changes in coastal ecosystems are often correlated with changes in water clarity or SPM concentration and thus with the POM content of the SPM (e.g. May et al., 2003; Capuzzo et al., 2015). The composition of SPM is the result of multiple natural processes that reflect the continuous mixing of marine and terrestrial particles of various ages and origins over geological time scales (Adriaens et al., 2018). Also, human activities have impacted the SPM concentration and composition. While the strongest anthropogenic changes in the study area occurred during the last decades, human occupation and landscape development date back to the last two millennia. They inevitably have had an impact on SPM composition and concentration (Baeteman et al., 2002). In the last decades, the North Sea has been subject to changes in SPM concentration and biological activities amongst which are the decrease in phytoplankton production and changes in community structures (Capuzzo et al., 2018; Nohe et al., 2020); the shift in chlorophyll a phenology (Desmit et al., 2020); the imbalance in the biogeochemical cycles of nutrients (Rousseau et al., 2006, Desmit et al., 2018); and the increase of the SPM concentration due to major construction works (Van Maren et al., 2015).

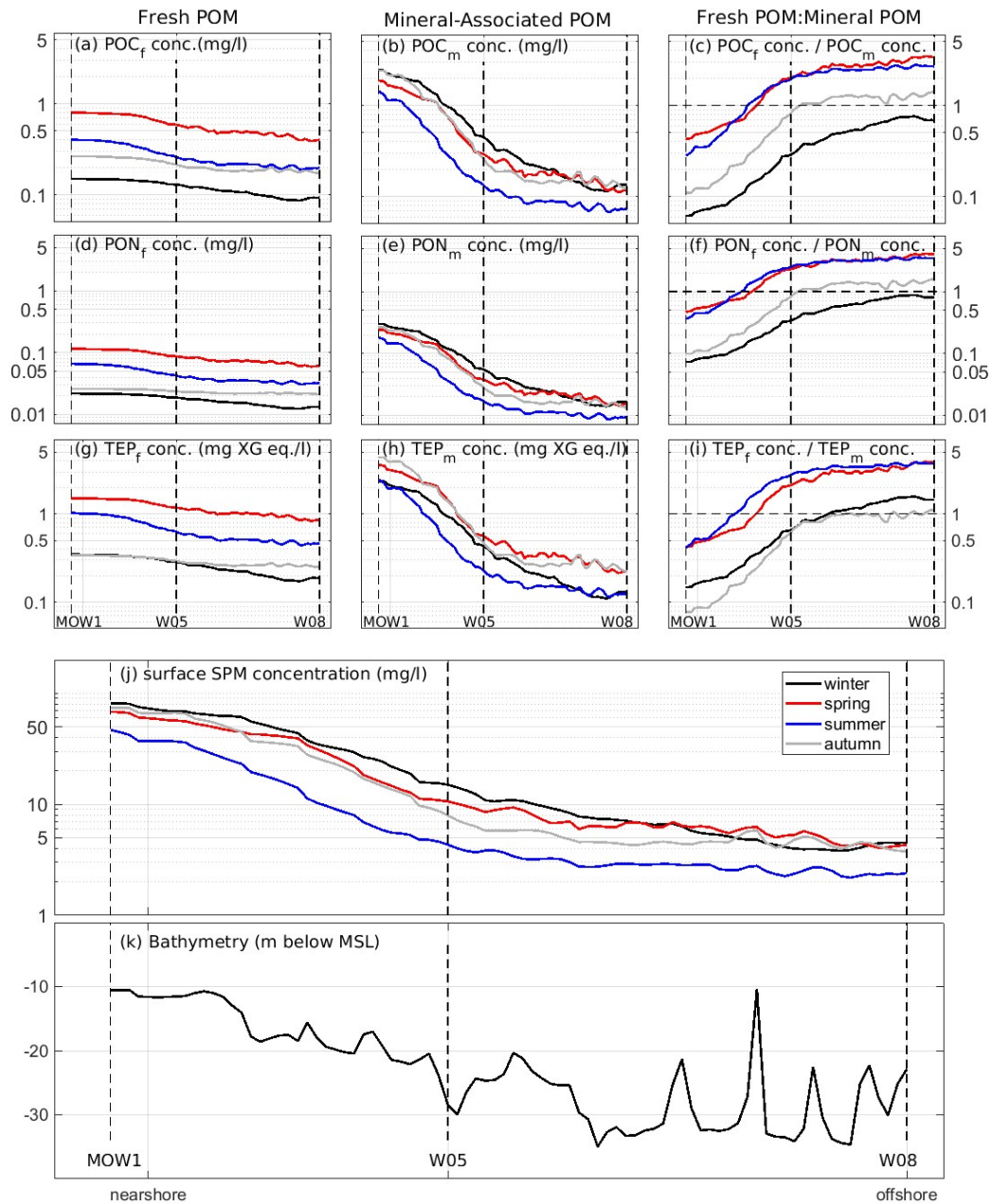


Figure 2.12: Model estimates of the nearshore (MOW1) to offshore (W08) fresh (left column) and mineral-associated (middle column) POC (a-b), PON (d-e) and TEP (g-h) concentrations calculated from the Sentinel-3/OLC derived surface SPM concentrations (j) using the model parameters of Table 2.1. The right column shows the ratios of fresh to mineral POC (c), PON (f) and TEP (i) concentration. Values above 1 have a fresh POC, PON or TEP concentration that exceed the mineral-associated one. The lower panel (k) shows the bathymetry (m below mean sea level) along the transect. The large changes in bathymetry between W05 and W08 are from sandbanks.

The area where the concentration of fresh and mineral-associated POM is about equal is of particular interest (Schartau et al., 2019). For the German Bight, this transition zone is typically found at water depths of approximately 15 to 20 m along cross-shore transects and is characterized by a maximum of the settling velocities (Maerz et al., 2016). Human activities, e.g. dredging and dumping operations in the turbid nearshore, wind farms in the

low turbid offshore areas or the effect of global warming (Fettweis et al., 2012; Jaiser et al., 2012; Baeye et al., 2015; Høyer & Karagali, 2016) might influence the localization of this transition zone and could make it a key element in monitoring programs such as the EU Marine Strategy Framework Directive. With our data-model syntheses we could consolidate a relationship that can be applied to SPM concentrations derived from other sources, e.g. from in situ long-term observations using optical and acoustic sensors or from remote sensing. A good example for such an application was documented by Schartau et al. (2019) for resolving spatio-temporal variations in fresh and mineral-associated fractions of POM in the German Bight. Though still imperfect, the application of the refined model to satellite SPM concentration products or high-resolution in-situ time series of calibrated optical or acoustical instruments will yield spatio-temporal compositional changes of the SPM, with respect to POC, PON, and TEP, both on large scales and for anomalous events. This greatly facilitates the monitoring of water quality parameters along the gradient from a domination of mineral-associated OM towards a domination of fresh OM, as documented in Figures 2.10 and 2.12, and enhances its information content without the increase of resources.

Many oceanographic quantities are often inaccessible to direct observation, due to the high cost of in situ sampling, the limitation of the standard water quality parameters and the low spatial and time resolution. Proxies, based on automated, highly resolving instruments are valuable as they help to extend undersampled or unobserved parameters. In this regard, SPM concentration as a proxy for POM, POC, PON, and TEP concentrations seems to be a key ingredient for the assessment and calibration of numerical models of coastal waters, ranging from SPM transport and deposition to key ecosystem processes.

Specifically, we have shown that the floc size distribution depends on the SPM concentration and on the availability of fresh TEP. In areas where the fresh over mineral-associated TEP is about unity and the SPM concentration low, flocculation occurs on a seasonal time scale rather than a tidal one (Figure 2.3). In high turbid environments flocculation occurs on both a tidal and seasonal time scale (Figure 2.3, 2.4 and 2.10). Our model-based differentiation between fresh and mineral-associated POC, PON, and TEP shows, that SPM concentration can be used as a proxy of the flocculation kinetic model parameters (i.e., break-up and aggregation) adopted in numerical SPM transport models.

2.6. Conclusions

The relevant processes and the critical parameters that drive the mutual interactions between sediment and biological dynamics occur on a wide range of spatial and temporal scales. The OM content of the SPM is highly variable due to physical processes, such as tides and waves, varies with season due to biological activities and with the SPM concentration. There is a distinct difference between the offshore, more open ocean, and the turbid nearshore conditions. In the turbid nearshore areas where SPM concentration often exceeds 100 mg/l the OM fraction in association with the mineral particles is dominant, masking the smaller signal of fresh OM produced by primary production. In contrast, in the offshore stations the fresh OM components prevail and therefore explain most of the variability seen in the SPM concentration. POC and PON measurements represent bulk properties of the OM in suspension, combining compounds of various types from labile, semi-labile, to refractory OM as well as specific components such as TEPs and pigments. Our data demonstrate that biophysical flocculation cannot be explained by these bulk observables. However, a model-based separation between a more reactive labile and a less reactive mineral-associated fraction of POC, PON and specifically TEP is a productive approach to make the impact of OM on the flocculation process detectable under long-time field observations. From our data-model synthesis we learned that the median floc size increases only when fresh TEP becomes a substantial fraction of the SPM. With our study we could resolve the contradiction

that similar TEP concentrations result in different floc sizes in winter and summer. Our results document that fresh TEP is one of the important controls of particles settling in coastal waters.

POM is associated with the mineral fraction and primarily with phyllosilicates (clays). It is therefore no surprise that the POM concentration increases with SPM concentration in coastal waters where due to water depths below 20 m and changing turbulence levels from tidal currents and waves, significant exchanges between pelagic and sea bed material exist. The fresh POM, and more specifically the presence of fresh TEP in spring and summer is not associated with these minerals but rather with the phytoplankton activity. This fresh TEP is responsible for the formation of larger biophysical flocs in spring and summer in the high turbid areas rather than the total TEP concentration. The nearly absence of fresh TEP in winter as a glue after particle collisions limits the floc sizes. Our results underline that the different components of the SPM, which are mineral, organic matter and living particles, form an integrated dynamic system with direct interactions and feedback controls.

Collecting data, such as SPM, POC, PON and TEP concentrations, from samples in the oceans or coastal seas, is expensive and often biased towards moderate weather conditions. Especially, anomalous, short-term events can often not be captured as shipping schedules are planned long in advance. SPM concentration, however, as a key proxy, can be measured either by remote sensing or automated in-situ systems. Samples then are only needed for better calibrations of these instruments. We have shown that these standard water quality measurements can be used to provide mathematical descriptions of additional complementary information, such as fresh and mineral-associated POM. The models can be applied to measurements from optical or acoustical sensors or satellites to generate further secondary data products. Our approach could change the scope of in situ observations from merely the collection of data towards the improvement and validation of models that describe fundamental aspects of SPM composition in coastal seas. The availability of proxies could have important implications for future monitoring programs, as they may fill the lack of continuous long-term data of POM properties and as such could help to improve the efficiency of our monitoring systems by identifying more efficient locations for water sampling or for the deployment of observational instruments.

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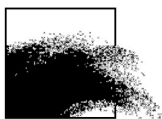
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BEHEERSEENHEID VAN HET
MATHEMATISCH MODEL VAN DE NOORDZEE



APPENDIX 1: Tables with mean values

APPENDIX 2: Monthly model parameters for TEP:SPM model

Table B.1: Monthly model parameters for TEP. The units for K_{POM} are mg/l (POC, PON) and mg XG eq./l (TEP) and for f_1 and f_2 [g/(g POM)] for POC and PON and in [g XG eq./g POM] for TEP. For the monthly fits three months are combined, centered around the month of interest.

$m_{POM}=0.13$	K_{POM} CI 95% [lower, upper]	f_1 CI 95% [lower, upper]	f_2 CI 95% [lower, upper]
January	4.25 [2.68, 6.00]	0.098 [0.059, 0.153]	0.251 [0.186, 0.319]
February	2.37 [1.66, 3.61]	0.078 [0.006, 0.198]	0.656 [0.465, 0.845]
March	1.91 [1.82, 1.99]	0.971 [0.583, 1.200]	0.444 [0.173, 0.793]
April	3.67 [2.12, 4.83]	0.489 [0.386, 0.641]	0.457 [0.265, 0.677]
May	4.96 [2.24, 7.11]	0.476 [0.386, 0.722]	0.090 [0.022, 0.154]
June	4.69 [2.58, 6.54]	0.412 [0.305, 0.576]	0.136 [0.065, 0.235]
July	4.78 [3.11, 6.80]	0.312 [0.233, 0.426]	0.297 [0.150, 0.531]
August	2.68 [1.03, 4.32]	0.371 [0.226, 0.714]	0.540 [0.392, 0.695]
September	1.91 [1.73, 2.10]	0.387 [0.285, 0.400]	0.526 [0.414, 0.653]
October	1.77 [1.56, 1.95]	0.291 [0.183, 0.435]	0.499 [0.406, 0.518]
November	1.99 [1.90, 2.13]	0.138 [0.058, 0.235]	0.346 [0.263, 0.441]
December	2.50 [1.46, 3.67]	0.081 [0.027, 0.147]	0.314 0.251, 0.383[]

APPENDIX 3: Carbon content of the TEP

Engel and Passow (2001) have reported that the carbon concentration of the TEP (mg/l) is linearly correlated with the TEP concentration (in (mg XG eq.)/l). The conversion factor between both depends on the chemical composition of the TEP and ranges from about 0.51 to 0.88 (mg/ (mg XG eq.)). The slope of this regression line can be estimated by the POC:TEP ratio. The ratio derived from the measured POC and TEP concentrations is about 1 for all data, lower values are found in summer (0.64) and autumn (0.80) and higher ones in spring (2.08) and winter (1.28). Clearly, only the summer and autumn values are realistic and within the range reported by Engel and Passow (2001). The ratios derived from the POM:SPM model have a lower variability than those from the measurements. The fresh POC over fresh TEP ratio is approaching a constant value at SPM concentration above about 50 mg/l, whereas the ratio POC:TEP for the mineral-associated fraction (also derived from the POM:SPM model) is constant. The ratio for the fresh POC and fresh TEP is on average about 0.50 (spring), 0.38 (summer), 0.87 (autumn) and 0.45 (winter), corresponding with an overall slope factor of 0.55 ± 0.22 . Similarly, the mineral-associated POC over TEP ratio for spring is 0.52, for summer 0.63, for autumn 0.54 and for winter 1.04 (on average 0.68 ± 0.24). If all the POC is TEP, then these ratios provide an upper limit of the C content of fresh TEP. It is remarkable that the differences between fresh and mineral-associated ratios are small and that, notwithstanding the large uncertainties associated with the ratios (see Figures 5-7), the values of the slope factor derived from the model agree with the estimates from Engel and Passow (2001). The overall conversion of TEP concentration into carbon TEP concentration based on the model estimates is: $C\text{-TEP (mg/l)} = 0.57 \pm 0.21 \text{ TEP (mg XG eq./l)}$.

Engel, A., & Passow, U. (2001). Carbon and nitrogen content of transparent exopolymer particles (TEP) in relation to their Alcian Blue adsorption. *Marine Ecology Progress Series*, 219, 1-10. doi:10.3354/meps219001